Study of the Adsorption of 1,2,3-Triazole on Silver and Gold Colloidal Nanoparticles by Means of Surface Enhanced Raman Scattering

Barbara Pergolese,*,† Maurizio Muniz-Miranda,‡ and Adriano Bigotto†

Department of Chemical Sciences, University of Trieste, Via L. Giorgieri 1, I-34127 Trieste, Italy, and Department of Chemistry, University of Firenze, Via della Lastruccia 3, I-50019 Sesto Fiorentino, Italy

The adsorption of 1,2,3-triazole on silver and gold colloidal nanoparticles is studied by means of surface enhanced Raman scattering (SERS). Further information about the adsorption mechanism on silver is obtained by recording the normal Raman spectra of the Ag(I)/1,2,3-triazole coordination compound. SERS data are interpreted with the help of density functional theoretical calculations of models of the ligand bound to silver or gold surface adatoms. 1,2,3-Triazole interacts with both silver and gold substrates in its anionic form through the lone pairs of the N_1 and N_3 atoms with a tilted orientation with respect to the metal surface.

Introduction

Benzoazoles and their derivatives have widespread application in the field of anticorrosion protection of metals. Among these, benzotriazole is a highly effective corrosion inhibitor for several metals (copper, in particular) and their alloys,[1–9] and a large number of investigations were carried out in order to elucidate the interaction mechanism between this molecule and metal surfaces. Since surface enhanced Raman scattering (SERS) can give detailed information about the adsorption mechanism on metal surfaces,[10–13] SERS investigations of benzotriazole were performed.[14–16] It was found that benzotriazole interacted with copper, silver, and iron surfaces as a deprotonated form through the 1,2,3-triazole moiety, leading to the formation of a polymeric surface complex where N_1 and N_3 were the interacting molecular sites. Thus, an investigation of the adsorption mechanism of the molecular fragment of benzotriazole directly involved in the interaction with metal surfaces (i.e., 1,2,3-triazole moiety) is worthwhile. To this aim a SERS study of 1,2,3-triazole (hereafter TZ3) adsorbed onto silver and gold colloidal nanoparticles has been here performed. Two different metal substrates have been taken into account, in order to check if the adsorption could be affected by the nature of metal. Further information about the adsorption mechanism on silver can be obtained by comparison between the SERS spectra of 1,2,3-triazole adsorbed on silver and the vibrational spectra of the Ag(I)/TZ3 coordination compound. Density functional theoretical (DFT) calculations have been useful for a detailed interpretation of the SERS spectra in both Ag and Au hydrosols, by considering various models of surface complexes where the ligand is bound to metal atoms or ions.

Experimental Section

TZ3 (97%) was obtained from Aldrich. Silver colloids were prepared following Creighton's procedure,[17] by adding silver nitrate (Aldrich, purity 99.998%) to an aqueous solution of excess sodium borohydride (Aldrich, purity 99%) as reducing agent. Gold colloids were prepared by reduction of tetrachloroauric acid (Aldrich, purity 99.9%) with excess sodium citrate (Aldrich, purity 99%) according to Turkevich's procedure.[18] TZ3 was added to the metal colloidal suspensions in order to obtain 10^{-4} M concentrations. The sols, before and after addition of TZ3, were monitored by UV–visible absorption spectra obtained with a UNICAM Helios spectrophotometer. Ag(I)/TZ3 coordination compound was prepared according to the procedure suggested by Nomiya et al.[19] The product was repeatedly washed with water and ethanol and dried on magnesium perchlorate. The elemental analysis (found: C, 13.7; H, 1.9; N, 22.7; $(C_2H_2N_3)Ag_2$ requires C, 13.6; H, 1.2; N, 23.9) indicates the formation of the metal/ligand complex with 2:1 stoichiometric ratio. SERS spectra in gold colloids were obtained with a SPEX Ramalog instrument. An AT personal computer was used for data acquisition and monochromator control. Excitation was provided by the 647.1 nm line of a Spectra-Physics 165 krypton ion laser. SERS spectra in silver colloids were recorded using the 514.5 nm line of a coherent argon ion laser, a Jobin-Yvon HG2S monochromator equipped with a cooled RCA-C31034A photomultiplier and a data acquisition facility. Power density measurements were performed with a power meter instrument (Model 362, Scientech, Boulder, CO) giving ∼5% accuracy in the 300–1000 nm spectral range.

Theoretical Calculations

Calculations of models of surface complexes formed by the 1,2,3-triazolate anion (hereafter TZ3A) with silver and gold atoms or ions were performed using the GAUSSIAN 98 package.[20] Optimized geometries were obtained at the density functional level of theory with Becke's 1988 exchange functional in combination with the Perdew–Wang 91 gradient-corrected correlation functional (bpw91). The calculations with this functional provided a satisfactory agreement between calculated and experimental vibrational wavenumbers, without using scaling factors. The LANL2DZ basis set was used for all calculations. By allowing that all the parameters could relax, all calculations converged to optimized geometries, which corresponded to true energy minima, as revealed by the lack of imaginary values in the wavenumber calculations. The atomic numbering of the models of surface complexes adopted in the

---
* Corresponding author. Telephone: +390405583950. Fax: +390405583903. E-mail: pergoles@dsch.univ.trieste.it.
† University of Trieste.
‡ University of Firenze.

Adsorption of TZ3 on Ag and Au Nanoparticles

J. Phys. Chem. B, Vol. 108, No. 18, 2004 **5699**

TABLE 1: SERS Data, Calculated Frequencies, and Assignments for Ag$_2$/TZ3 Surface Complex

$\tilde{\nu}_{obs}$[a]	$\tilde{\nu}_{calc}$		PED[b]
	3282	A$_1$	50r$_{7,5}$, 50r$_{6,4}$
	3259	B$_2$	50r$_{7,5}$, 50r$_{6,4}$
1443	1441	A$_1$	53r$_{5,4}$, 11α$_{3,4,6}$, 11α$_{1,5,7}$, 5α$_{5,4,6}$
1405	1362	B$_2$	19r$_{1,5}$, 19r$_{3,4}$, 17α$_{6,4,5}$, 17α$_{7,5,4}$, 11α$_{7,5,1}$, 11α$_{3,4,6}$
1227	1195	A$_1$	35r$_{1,5}$, 35r$_{3,4}$, 12α$_{1,2,3}$
1163	1166	B$_2$	17r$_{1,5}$, 17r$_{3,4}$, 11r$_{2,3}$, 11r$_{1,2}$, 13α$_{3,4,6}$, 13α$_{1,5,7}$, 5α$_{5,4,6}$, 5α$_{4,5,7}$
1098	1119	A$_1$	28r$_{4,5}$, 8r$_{1,2}$, 8r$_{2,3}$, 13α$_{3,4,6}$, 12α$_{1,5,7}$, 11α$_{5,4,6}$, 11α$_{4,5,7}$
	1052	A$_1$	31r$_{2,3}$, 31r$_{1,2}$, 19α$_{1,2,3}$
987 (sh)	1015	B$_2$	29r$_{1,2}$, 29r$_{2,3}$, 7α$_{2,1,5}$, 7α$_{2,3,4}$
970	957	A$_1$	6r$_{1,5}$, 6r$_{3,4}$, 12α$_{5,4,6}$, 11α$_{4,5,7}$, 9α$_{1,2,3}$, 8α$_{2,1,5}$, 8α$_{2,3,4}$, 6α$_{3,4,6}$, 6α$_{2,5,7}$
911	950	B$_2$	11r$_{1,2}$, 11r$_{2,3}$, 23α$_{3,4,5}$, 23α$_{1,5,4}$, 6α$_{3,4,6}$, 6α$_{1,5,7}$
809	861	A$_2$	33γ$_{7,5}$, 33γ$_{6,4}$, 27τ$_{4,5}$
	782	B$_1$	41γ$_{7,5}$, 41γ$_{6,4}$, 9τ$_{3,4}$, 9τ$_{2,5}$
703	659	B$_1$	29γ$_{8,1}$, 29γ$_{9,3}$, 20τ$_{1,2}$, 20τ$_{2,3}$
	634	A$_2$	24γ$_{8,1}$, 24γ$_{9,3}$, 6γ$_{7,5}$, 6γ$_{6,4}$, 32τ$_{4,5}$
240	274	B$_2$	47r$_{1,8}$, 47r$_{3,9}$
204	188	A$_1$	42r$_{1,8}$, 42r$_{3,9}$
	171	B$_2$	26α$_{2,1,8}$, 26α$_{2,3,9}$, 23α$_{5,1,8}$, 23α$_{4,3,9}$
	141	A$_2$	30γ$_{8,1}$, 30γ$_{9,3}$, 11τ$_{3,4}$, 11τ$_{1,5}$, 9τ$_{1,2}$, 9τ$_{2,3}$
	87	B$_1$	30γ$_{8,1}$, 30γ$_{9,3}$, 11τ$_{3,4}$, 11τ$_{1,5}$, 9τ$_{1,2}$, 9τ$_{2,3}$
	62	A$_1$	25α$_{2,1,8}$, 25α$_{2,3,9}$, 23α$_{5,1,8}$, 23α$_{4,3,9}$

[a] SERS spectra of TZ3 in silver colloid. [b] r = stretching, α = in-plane bending, γ = out-of-plane bending, τ = torsion; only contributions ≥5 are reported.

TABLE 2: SERS Data, Calculated Frequencies, and Assignments for Au$_2$/TZ3 Surface Complex

$\tilde{\nu}_{obs}$[a]	$\tilde{\nu}_{calc}$		PED[b]
	3290	A$_1$	50r$_{7,5}$, 50r$_{6,4}$
	3269	B$_2$	50r$_{7,5}$, 50r$_{6,4}$
1433	1461	A$_1$	54r$_{5,4}$, 11α$_{3,4,6}$, 11α$_{1,5,7}$
1382	1362	B$_2$	19r$_{1,5}$, 19r$_{3,4}$, 16α$_{6,4,5}$, 16α$_{7,5,4}$, 11α$_{7,5,1}$, 11α$_{3,4,6}$
1291			
1233	1225	A$_1$	31r$_{1,5}$, 31r$_{3,4}$, 7r$_{1,8}$, 7r$_{3,9}$, 12α$_{1,2,3}$
1169	1183	B$_2$	16r$_{1,5}$, 16r$_{3,4}$, 12r$_{1,2}$, 12r$_{2,3}$, 13α$_{3,4,6}$, 13α$_{1,5,7}$
1099	1132	A$_1$	26r$_{4,5}$, 9r$_{1,2}$, 9r$_{2,3}$, 5r$_{1,5}$, 5r$_{3,4}$, 11α$_{3,4,6}$, 11α$_{1,5,7}$, 9α$_{5,4,6}$, 9α$_{4,5,7}$
	1046	B$_2$	23r$_{2,3}$, 23r$_{1,2}$, 7r$_{1,8}$, 7r$_{3,9}$, 8α$_{2,1,5}$, 8α$_{2,3,4}$
	1034	A$_1$	31r$_{1,2}$, 31r$_{2,3}$, 12α$_{1,2,3}$, 5α$_{5,4,6}$, 5α$_{4,5,7}$
986	969	A$_1$	10r$_{1,5}$, 10r$_{3,4}$, 5r$_{1,8}$, 5r$_{3,9}$, 12α$_{1,2,3}$, 10α$_{5,4,6}$, 10α$_{4,5,7}$, 8α$_{2,3,4}$, 8α$_{2,1,5}$, 5α$_{1,5,7}$, 5α$_{3,4,6}$
951	947	B$_2$	18r$_{1,2}$, 18r$_{2,3}$, 19α$_{3,4,5}$, 19α$_{1,5,4}$, 6α$_{3,4,6}$, 6α$_{1,5,7}$
	877	A$_2$	34γ$_{7,5}$, 34γ$_{6,4}$, 25τ$_{4,5}$
803	792	B$_1$	40γ$_{7,5}$, 40γ$_{6,4}$, 9τ$_{3,4}$, 9τ$_{1,5}$
694	641	B$_1$	33γ$_{8,1}$, 33γ$_{9,3}$, 16τ$_{1,2}$, 16τ$_{2,3}$
646	627	A$_2$	27γ$_{8,1}$, 27γ$_{9,3}$, 27τ$_{4,5}$, 5τ$_{1,5}$, 5τ$_{3,4}$
256	336	B$_2$	44r$_{1,8}$, 44r$_{3,9}$
	253	B$_2$	25α$_{2,1,8}$, 25α$_{2,3,9}$, 23α$_{5,1,8}$, 23α$_{4,3,9}$
	197	A$_2$	31γ$_{8,1}$, 31γ$_{9,3}$, 11τ$_{3,4}$, 11τ$_{1,5}$, 9τ$_{1,2}$, 9τ$_{2,3}$
225	192	A$_1$	37r$_{1,8}$, 37r$_{3,9}$, 5α$_{5,1,8}$, 5α$_{4,3,9}$
	110	B$_1$	29γ$_{8,1}$, 29γ$_{9,3}$, 10τ$_{1,2}$, 10τ$_{2,3}$, 10τ$_{1,5}$, 10τ$_{3,4}$
	76	A$_1$	23α$_{2,1,8}$, 23α$_{2,3,9}$, 21α$_{5,1,8}$, 21α$_{4,3,9}$

[a] SERS spectra of TZ3 in gold colloid. [b] r = stretching, α = in-plane bending, γ = out-of-plane bending, τ = torsion; only contributions ≥5 are reported.

SCHEME 1: (a) Ag$_2$/TZ3A; (b) Au$_2$/TZ3A
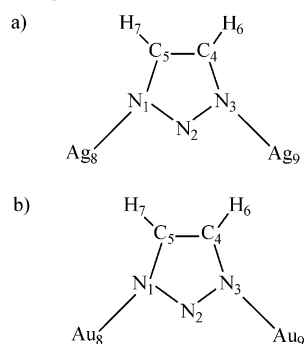
calculations (hereafter Ag$_2$/TZ3A and Au$_2$/TZ3A) is indicated in Scheme 1. The harmonic wavenumbers were calculated at the same level of approximation, using the parameters corresponding to the structure obtained from the optimization step.

Force constants in internal coordinates, which were calculated according to the procedure described elsewhere,[21] were used for a standard zero-order **GF**-matrix treatment from which vibrational wavenumbers and potential energy distributions (PEDs) were obtained. The theoretical results of the models of the surface complexes are reported in Tables 1 and 2, along with the SERS data.

Results and Discussion

SERS Spectra in Silver Hydrosols. A comparison between the SERS spectrum on Ag colloidal nanoparticles and the normal Raman (hereafter RS) spectrum of TZ3 in aqueous solution shows marked differences in both positions and intensities of several bands (Figure 1). On the contrary, even if a few bands are shifted due to the interaction of the molecule with the metal surface, SERS spectrum and RS spectrum in alkaline solution, where the substance is present in the dissociated form, are well
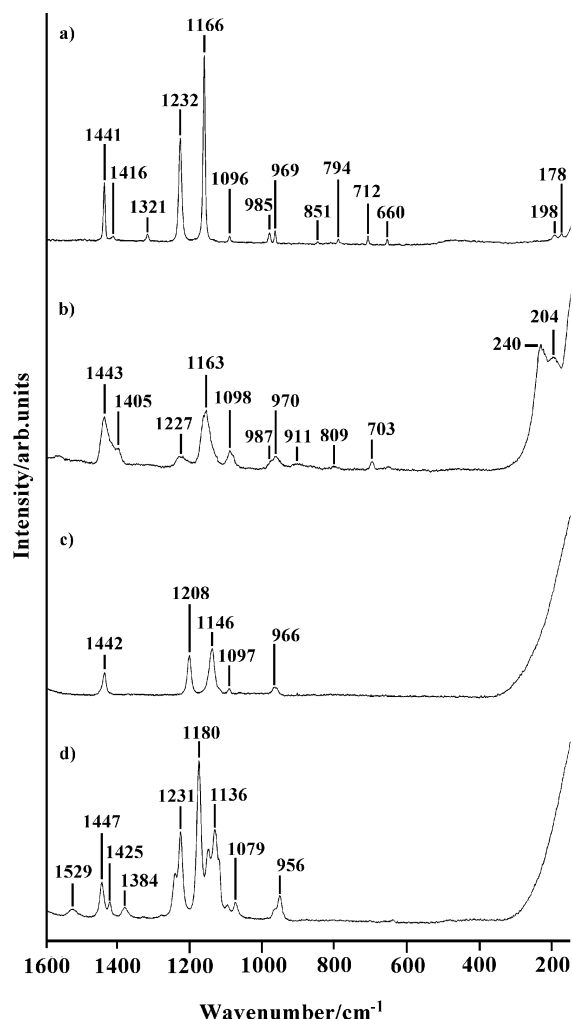
Figure 1. (a) RS spectrum of Ag(I)/TZ3 coordination compound; (b) SERS spectrum of TZ3 in silver colloid; (c) RS spectrum of TZ3 in alkaline aqueous solution; (d) RS spectrum of TZ3 in aqueous solution.

correlated. This evidence suggests that TZ3 interacts with the silver surface in the anionic form, as observed in the case of benzotriazole on silver, copper, and iron surfaces.[14−16] Moreover, the close similarity between the SERS spectrum of TZ3 in silver hydrosols and the RS spectrum of Ag(I)/TZ3 coordination compound (see Figure 1) indicates that the molecule is chemisorbed on silver hydrosol and that the binding arrangement to silver colloidal nanoparticles approaches that existing in the complex.

According to the literature,[19] TZ3A is coordinated to two silver ions via the N_1 and N_3 atoms in this complex. Thus, it seems reasonable that this type of interaction is also present in the surface complex formed by TZ3A adsorbed on the silver colloidal surface. Further support of this hypothesis is provided by the observation of two distinct peaks in the 200−250 cm⁻¹ region of the SERS spectra, which have no counterpart in the RS spectrum of TZ3A and are attributable to Ag−N stretching fundamentals.

On this basis, in order to confirm the interpretation of the SERS bands, calculations of three different models of TZ3A interacting via the N_1 and N_3 atoms with two Ag surface adatoms have been carried out. In these models TZ3A is bound to two Ag(I) (model A), one Ag(I) and one Ag(0) (model B), and two Ag(0) (model C). The best agreement between experimental and calculated wavenumbers is provided by model A, where TZ3A is bound to two silver ions, as well as in the

coordination compound. Therefore, the results obtained from these latter calculations have been taken into account for the assignment of SERS spectra on silver colloidal nanoparticles. It is of note that TZ3A has a C_{2v} symmetry and, upon adsorption on the metal surface via the N_1 and N_3 molecular sites, the symmetry group of the surface complex can be assumed to remain the same.

It is to be stressed that, even if the electromagnetic effect is generally the main mechanism of the SERS enhancement, also the "chemical effect" should be taken into account, when a molecule is chemisorbed, as pointed out in other cases.[10,22−24] The chemical effect is important in the SERS spectra of compounds adsorbed on metal colloids activated by coadsorption of halide anions, because these latter are able to promote an efficient charge-transfer effect between the adsorbate and the metal.[25] However, in our case these anions are not present. Thus, the electromagnetic enhancement effect should be considered as predominant and it is reasonable to apply the surface selection rules,[26] based on electromagnetic theory, to get information about the molecular orientation adopted by TZ3 on the metal surface.

The enhancement factors of the SERS bands have been estimated with reference to the band at 1443 cm⁻¹, which closely corresponds to the RS band of the triazolate anion at 1442 cm⁻¹. The SERS spectrum shows the occurrence of bands (at 1405, 911, 809, and 703 cm⁻¹) that have no counterpart in the RS spectrum. These are the most enhanced bands in the SERS spectrum. The two peaks at 1405 and 911 cm⁻¹ are related to two normal modes of B_2 symmetry, calculated at 1362 and 950 cm⁻¹, respectively (see Table 1 for further details). The band observed at 809 cm⁻¹ corresponds to the calculated normal mode at 861 cm⁻¹ of A_2 symmetry, while the band detected at 703 cm⁻¹ is assigned to the calculated normal mode at 659 cm⁻¹ of B_1 symmetry. By considering the molecule lying in the yz plane, where z corresponds to the molecular C_2 axis, the A_2, B_1, and B_2 normal modes scatter as α_{xy}, α_{zx}, and α_{yz} polarizability components, respectively. On the basis of the surface selection rules related to the electromagnetic SERS effect,[26] the occurrence of enhanced bands corresponding to A_2 and B_2 vibrational modes is diagnostic of a molecular orientation that is not normal nor parallel with respect to the metal surface, but is inclined on it. In fact, in an edge-on adsorption, the SERS bands corresponding to A_2 normal modes, which span in a plane (xy) parallel to the metal surface, should result in the least enhanced ones; in a flat-on adsorption, the B_2 normal modes, spanning in a plane (yz) parallel to the metal surface, should give rise to the least enhanced SERS bands.

SERS Spectra in Gold Hydrosols. Also in the case of gold colloids the SERS bands are better correlated to the Raman bands of TZ3A than to those of the neutral molecule in aqueous solution. Therefore, it can be deduced that TZ3 also adsorbs on gold colloidal nanoparticles in the anionic form. Unfortunately, the corresponding gold complex could not be obtained and the conclusions about the type of bonding are drawn by analogy with the SERS spectra on silver. Hence, it can be deduced that, also in the case of gold colloid, TZ3A interacts with the metal surface through the lone pairs of N_1 and N_3 atoms. A support to this hypothesis is provided by the occurrence of a broad and asymmetric SERS band at 256 cm⁻¹ with a shoulder on the Rayleigh wing at about 225 cm⁻¹ (Figure 2). These bands have no counterpart in the RS spectrum of TZ3A and are attributable to two Au−N stretching fundamentals. Since in the 200−250 cm⁻¹ region no peaks are observed in the spectrum of the pure gold colloid, the appearance of a
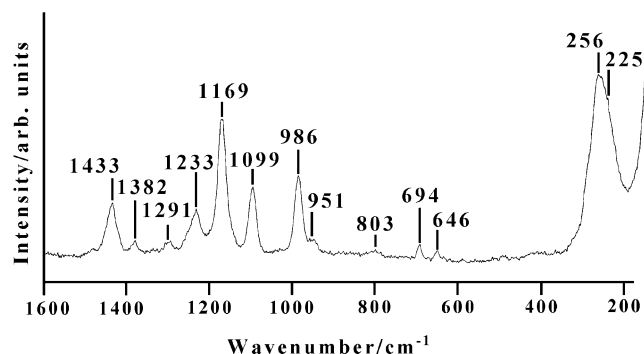
Adsorption of TZ3 on Ag and Au Nanoparticles

J. Phys. Chem. B, Vol. 108, No. 18, 2004 **5701**

Figure 2. SERS spectrum of TZ3 adsorbed on gold colloid.

TABLE 3: Wavenumber Shifts for the Most Intense Bands of the SERS Spectra in Ag and Au Colloids

Raman water soln with KOH	SERS Ag colloid	$\Delta\nu$	SERS Au colloid	$\Delta\nu$
1442	1443	+1	1433	−9
1208	1227	+19	1233	+25
1146	1163	+17	1169	+23
1097	1098	+1	1099	+2

peak attributable to Au−Cl stretching mode, due to the use of gold tetrachloroauric acid in the preparation of the colloid, can be ruled out.

The interpretation of the SERS spectra has been helped by DFT calculations of various models of surface complexes, where TZ3A is bound to two gold atoms or ions. Also in this case the C_{2v} symmetry is assumed in all calculations of the Au$_2$/TZ3A complexes. The best agreement between experimental and calculated wavenumbers was provided by the model in which TZ3A is bound to two Au(I) ions. Thus, the results obtained from these latter calculations were taken into account for the assignment of the SERS spectra of TZ3 in gold hydrosols.

The enhancement factors of the SERS bands have been estimated with reference to the SERS peak at 1433 cm^{-1}, corresponding to the band located in the RS spectrum of TZ3A at 1442 cm^{-1}. The SERS spectrum shows a strong intensity enhancement of the band at 986 cm^{-1}, which is related to the RS peak at 966 cm^{-1}, belonging to A$_1$ symmetry species. The relative intensity of this mode, upon adsorption on gold, varies in the ratio 1:5. The SERS band located at 694 cm^{-1}, with no counterpart in the RS spectrum, is assigned to the B$_1$ normal mode calculated at 641 cm^{-1}. The SERS band observed at 646 cm^{-1} also displays a strong Raman enhancement, since no band is observed in the RS spectrum of TZ3A below 800 cm^{-1}. It is assigned to the A$_2$ normal mode of the surface complex calculated at 627 cm^{-1}. As well as for the surface complex bound to silver, the A$_2$ and B$_1$ normal modes scatter as α_{xy} and α_{zx} polarizability components, respectively. Due to the intensity enhancement of A$_2$ and B$_1$ bands, a purely edge-on orientation on gold surface can be excluded. On the other hand, from the analogy between the SERS spectra profiles in silver and gold colloids, an inclined orientation of TZ3 can be suggested also on the gold surface.

Finally, comparing the adsorbate−metal stretching vibrations in silver and gold hydrosols, it can be observed that Au−N stretching modes occur at higher wavenumbers (225/256 cm^{-1}) than those assigned to Ag−N stretching modes (205/239 cm^{-1}). This could suggest that a stronger force constant is related to the bond between gold and nitrogen, and consequently, larger wavenumber shifts with respect to the RS bands of TZ3A are expected in the case of TZ3 adsorbed on gold colloid. This conclusion agrees with the experimental data reported in Table

3, where the largest wavenumber shifts correspond to ring vibrations, which are the most sensitive to the strength of the adsorbate/metal interaction.

Conclusion

The adsorption of 1,2,3-triazole on silver and gold colloidal nanoparticles has been studied by means of SERS spectroscopy. From the comparison of the SERS spectrum with the normal Raman spectra of TZ3 in neutral and alkaline aqueous solutions, it can be deduced that the molecule interacts in the ionized form with both metal surfaces. The close similarity between the SERS spectrum of TZ3 adsorbed on silver sol and the normal Raman spectrum of the Ag(I)/TZ3 coordination compound implies that the molecule is chemisorbed on silver colloidal nanoparticles and that the binding arrangement adopted by the adsorbate approaches that existing in the silver complex. Thus, the molecular interaction on silver takes place via the lone pairs of N$_1$ and N$_3$ atoms. The similarity between the SERS spectra obtained in silver and gold hydrosols suggests that, also in the case of gold nanoparticles, N$_1$ and N$_3$ represent the molecular sites involved in the interaction with the metal substrate. In order to give a more accurate interpretation of the SERS spectra, DFT calculations of different models of surface complexes, Ag$_2$/TZ3A and Au$_2$/TZ3A, have been performed. By considering the surface selection rules applied to the most enhanced SERS bands, it is deduced that the molecule interacts with both silver and gold nanoparticles with a tilted orientation with respect to the metal surfaces.

Since no significant difference in the spectral behavior displayed by TZ3 adsorbed on silver and gold colloidal nanoparticles can be observed, the different nature of the metal surface plays very likely a negligible role on the adsorption of TZ3 on metal surfaces.

References and Notes

(1) Wamhoff, H. 1,2,3-Triazoles and their Benzo Derivatives. In *Comprehensive Heterocyclic Chemistry*; Katrizky, A. R., Rees, C. W., Potts, K. T., Eds.; Pergamon Press: Oxford, 1984; Vol. 5, pp 669−732.

(2) Cotton, J. B.; Scholes, I. R. *Br. Corros. J.* **1967**, *2*, 1.

(3) Poling, G. W. *Corros. Sci.* **1970**, *10*, 359.

(4) Mansfeld, F.; Smith, T.; Parry, E. P. *Corrosion* **1971**, *27*, 289.

(5) Walker, R. *Corrosion* **1973**, *29*, 290.

(6) Walker, R. *Met. Finish.* **1973**, *71*, 63.

(7) Chin, R. J.; Altura, D.; Nobe, K. *Corrosion* **1973**, *29*, 185.

(8) Mansfeld, F.; Smith, T. *Corrosion* **1973**, *29*, 105.

(9) Walker, R. *J. Chem. Educ.* **1980**, *57*, 789.

(10) Bigotto, A.; Pergolese, B. *J. Raman Spectrosc.* **2001**, *32*, 953.

(11) Pergolese, B.; Bigotto, A. *J. Raman Spectrosc.* **2002**, *33*, 646.

(12) Cardini, G.; Muniz-Miranda, M. *J. Phys. Chem. B* **2002**, *106*, 6875.

(13) Muniz-Miranda, M. *Vib. Spectrosc.* **2002**, *29*, 229.

(14) Rubim, J.; Gutz, I. G. R.; Sala, O.; Orville-Thomas, W. J. *J. Mol. Struct.* **1983**, *101*, 1.

(15) Rubim, J.; Gutz, I. G. R.; Sala, O.; Orville-Thomas, W. J. *J. Mol. Struct.* **1983**, *100*, 571.

(16) Yao, J. L.; Ren, B.; Huang, Z. F.; Cao, P. G.; Gu, R. A.; Zhong-Qun, T. *Electrochim. Acta* **2003**, *48*, 1263.

(17) Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 790.

(18) Turkevich, J.; Stevenson, P. C.; Hillier, J. *Discuss. Faraday Soc.* **1951**, *11*, 55.

(19) Nomiya, K.; Tsuda, K.; Kasuga, N. C. *J. Chem. Soc., Dalton Trans.* **1998**, *10*, 1653.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick,

D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, revision A.6.; Gaussian Inc.: Pittsburgh, PA, 1998.

(21) Pergolese, B.; Bigotto, A. *Spectrochim. Acta A* **2001**, *57*, 1191.

(22) Aroca, R. F.; Clavijo, R. E.; Halls, M. D.; Schlegel, H. B. *J. Phys. Chem. A* **2000**, *104*, 9500.

(23) Muniz-Miranda, M. *J. Phys. Chem. A* **2000**, *104*, 7803.

(24) Srnová-Sloufová, I.; Vlcková, B.; Snoeck, T. L.; Stufkens, D. J.; Matejka, P. *Inorg. Chem.* **2000**, *39*, 3551.

(25) (25) Hildebrandt, P.; Keller, S.; Hoffmann, A.; Vanhecke, F.; Schrader, B. *J. Raman Spectrosc.* **1993**, *24*, 791.

(26) Moskovitz, M.; Suh, J. S. *J. Phys. Chem.* **1984**, *88*, 5526.