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Surface enhanced Raman spectroscopic studies on 1H-1,2,4-triazole adsorbed on silver colloidal nanoparticles

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ABSTRACT

1H-1,2,4-triazole is a very effective corrosion inhibitor for copper. The adsorption of this compound on silver colloidal nanoparticles has been studied by means of surface enhanced Raman scattering (SERS). SERS data are interpreted with the help of DFT calculations of models of the surface complex formed by 1H-1,2,4-triazole on the silver colloidal nanoparticles surface. It was found that this compound is adsorbed on metal surface in its anionic form and that it interacts with silver through the N_1 and N_2 atoms. The molecular plane assumes a tilted orientation with respect to the silver surface.

1. Introduction

The azoles are extensively used in surface treatment of materials, in particular in the field of protection of metals from corrosion. Therefore, a large number of investigations were carried out in order to clarify the interaction mechanism between these substances and metal surfaces and, for this purpose, the SERS technique has proved very informative. 1H-1,2,4-triazole (TZ4) is a very effective corrosion inhibitor for copper [1]. Even if several spectroscopic investigations were carried out on this compound [2,3], studies of the adsorption behaviour of TZ4 on metals are scarce, despite its well-known corrosion inhibition efficiency. In particular, SERS investigations on TZ4 were performed only for the molecule adsorbed on microlithographically prepared copper surfaces [4]. In this study the authors found that TZ4 adsorbed on copper in its non-dissociatively form with a flat orientation, but no conclusions about the molecular sites of interaction with the metal were drawn.

In order to gain a better understanding of the adsorption behaviour of TZ4 on metal surface, we planned a SERS investigation of this compound on silver colloids. In fact, Ag, belonging to the same group of Cu, has similar chemical and physical properties to copper. Moreover, unlike Cu sols, Ag colloids offer the enormous advantage of stability and reproducibility. Finally, it is of note that the SERS enhancement factor of Ag is higher than that of Cu.

DFT calculations of the harmonic vibrational wavenumbers of surface complexes formed by TZ4 with silver adatoms have been also carried out. In fact, these kind of calculations are able to give useful information about the interaction between adsorbates and metal substrates; in particular, DFT calculations were previously employed successfully for other ligands [5–7]. The results of this combined SERS/DFT investigation of TZ4 are reported here.

2. Experimental procedure

TZ4 (98%) was obtained from Aldrich. Silver colloids were prepared following the Creighton's procedure [8], by adding silver nitrate (Aldrich, purity 99.998%) to an aqueous solution of excess sodium borohydride (Aldrich, purity 99%), as reducing agent. Milli-Q water was used in the preparation. All glassware was thoroughly cleaned with HNO_3 and washed with Milli-Q water in order to avoid impurities in the colloid preparation. TZ4 was added to the sol in order to obtain a final concentration of about 10^{-3} M. The sols, before and after addition of TZ4, were characterized using UV–vis absorption spectra obtained with a UNICAM Heλios spectrophotometer. Raman spectra were obtained with a SPEX Ramalog

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Table 1
Experimental, calculated data and assignment for TZ4A compared with the related SERS bands

$\tilde{\nu}^a$	$\tilde{\nu}_{calc}{}^b$	Symmetry species	PED[c]	$\tilde{\nu}_{SERS}$
1487	1508	A_1	$21r_{1,2}$, $12r_{4,5}$, $12r_{3,4}$, $11\alpha_{6,3,2}$,$11\alpha_{7,5,1}$, $10\alpha_{7,5,4}$,$10\alpha_{6,3,4}$	1500
1384	1364	A_1	$70r_{1,2}$, $10r_{4,5}$, $10r_{3,4}$	1340
1253	1194	A_1	$9r_{3,4}$, $9r_{4,5}$, $7r_{1,2}$, $19\alpha_{6,3,4}$,$19\alpha_{7,5,4}$, $9\alpha_{6,3,2}$, $9\alpha_{7,5,1}$	1283
1146	1197	B_2	$33r_{3,4}$, $33r_{4,5}$, $9\alpha_{2,3,4}$, $9\alpha_{1,5,4}$	1158
1063	1008	A_1	$22r_{1,5}$, $22r_{2,3}$, $23\alpha_{3,4,5}$,$7\alpha_{7,5,1}$, $7\alpha_{6,3,2}$, $5\alpha_{1,5,4}$, $5\alpha_{2,3,4}$	1056[d]
1025	980	B_2	$12r_{2,3}$, $12r_{1,5}$, $29\alpha_{2,1,5}$,$29\alpha_{1,2,3}$	1027[d]
971	949	A_1	$18r_{1,5}$, $18r_{2,3}$, $26\alpha_{3,4,5}$,$11\alpha_{1,5,4}$, $11\alpha_{2,3,4}$	984
–	–			669
–	–			610

[a] Normal Raman spectrum of TZ4 in alkaline solution.
[b] Calculated data for TZ4A.
[c] r: stretching; α: in-plane bending; γ: out-of-plane bending; τ: torsion; only contributions ≥5 are reported.
[d] Wavenumber values obtained by deconvolution of the SERS band at 1059 cm^{-1}.

instrument. An AT personal computer was used for data acquisition and monochromator control. Excitation was provided by 514.5 nm radiation from a Spectra-Physics 165 argon ion laser and the samples were contained in capillary cells. The treatment of the spectral data was performed using the PerkinElmer IRDM and the Galactic GRAMS386 software.

3. Computational procedure

Calculations on the 1,2,4-triazolate anion (hereafter TZ4A) and on its complexes with silver adatoms were carried out using the GAUSSIAN 03 package [9]. Optimized geometries were obtained at the density functional level of theory with the Becke 3-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP). The 6-311++G(d,p) was used for the calculations of TZ4A, whereas, in the case of the TZ4A/Ag complexes, a mixed basis set (6-311++G(d,p) for all atoms except silver, LANL2DZ for silver) was used. By allowing that all the parameters could relax, all the calculations converged to optimized geometries, which corresponded to true energy minima, as revealed by the lack of imaginary values in the wavenumber calculation. Harmonic vibrational 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 [10], were used for a standard zero-order GF-matrix treatment from which vibrational wavenumbers and potential energy distributions (PEDs) were obtained.

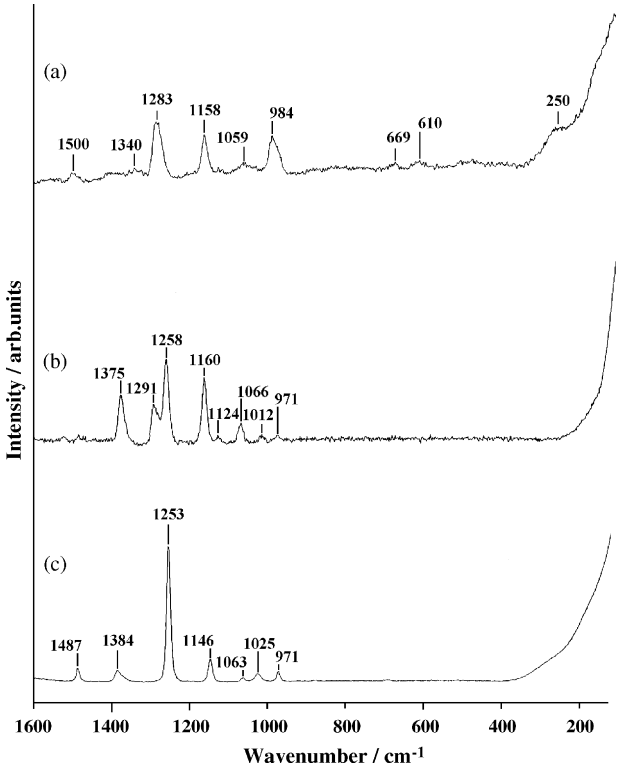

Fig. 1. (a) SERS spectrum of TZ4 in silver colloid; (b) Raman spectrum in aqueous solution; (c) Raman spectrum of TZ4 in alkaline solution. Excitation: 514.5 nm.

A satisfactory agreement between calculated and experimental vibrational wavenumbers was obtained without using scaling factors. Calculated data for TZ4A compared with normal Raman and the related SERS wavenumbers are reported in Table 1. The theoretical results of the models of the surface complexes are reported in Table 2, along with the SERS data.

4. Results and discussion

The Raman spectra obtained, both normal and surface-enhanced, are reported in Fig. 1. From the comparison between the SERS spectrum in Ag colloid and the normal Raman (hereafter RS) spectrum of TZ4 in aqueous and alkaline solution, it can be evinced that TZ4 interacts with the silver surface in the anionic form.

It can be observed that some bands undergo wavenumber-shifts upon going from the RS to the SERS spectrum. Moreover the SERS band at 250 cm^{-1} can be confidently attributed to the

Table 2
SERS wavenumbers compared with the calculated data obtained adopting models A, B, C, D

$\tilde{\nu}_{SERS}$	$\tilde{\nu}_{calc}$ model A	$\tilde{\nu}_{calc}$ model B	Symm. species[a]	$\tilde{\nu}_{calc}$ model C	$\tilde{\nu}_{calc}$ model D	Symm. species[b]
1500	1498	1518	A_1	1518	1518	A′
1340	1304	1305	A_1	1305	1305	A′
1283	1137	1211	A_1	1211	1211	A′
1158	1228	1215	B_2	1215	1215	A′
1056	1030	1097	A_1	1097	1097	A′
1027	915	1038	B_2	1038	1038	A′
984	983	943	A_1	943	943	A′
669	690	676	A_2	676	676	A″
610	652	652	B_1	652	652	A″
250	248	252	A_1	252	252	A′

[a] Symmetry of normal modes calculated for models A and B.
[b] Symmetry of normal modes calculated for models C and D.