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Surface Enhanced Raman Scattering and Normal Coordinate Analysis of 1,10-Phenanthroline Adsorbed on Silver Sols

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The surface enhanced Raman scattering of 1,10-phenanthroline adsorbed on silver sol has been obtained and analyzed by using normal mode calculations based on a valence force field suitably determined for this molecule. Evidence has been found for Ag−N bond formation with the silver surface, supporting the validity of a chemisorption process. The experimental and calculated data suggest an adsorbate−substrate interaction with perpendicular or tilted orientation of the molecule with respect to the colloidal surface. The halide anion effect on the SER spectrum improves a charge-transfer enhancement process involving adsorbate and metal electronic states. The results obtained on colloids agree with those detected by measurements performed on silver electrode. The similarity between SERS and normal Raman spectra of the corresponding 1:2 Ag(I)-phenanthroline complex indicates that the molecule is perturbed upon adsorption as well as upon coordination in the argentous complex.

Introduction

The surface enhanced Raman scattering represents a very useful tool to evaluate the adsorption of organic molecules onto metal surfaces by considering the relative intensities and the frequency shifts of the bands with respect to the corresponding Raman bands of the free molecule.

This study takes advantage of the normal coordinate analysis, as already tested in the case of benzo[*c*]cinnoline[1], 2,2′-bipyrimidine[2] and bipyrazine.[3] In the present work, the SER spectrum of 1,10-phenanthroline adsorbed on silver colloidal particles is analyzed by considering that the crystal and molecular structures of this molecule are known in the literature,[4,5] and the vibrational spectra were widely studied.[6,7] Moreover, 1,10-phenanthroline shows close similarity with other molecules already investigated by the SERS technique (Figure 1), especially with 2,2′-bipyrimidine. As for 2,2′-bipyrimidine, 1,10-phenanthroline is expected to adsorb on silver via the lone pairs of the nitrogen atoms of the molecule.

1,10-Phenanthroline was previously studied as adsorbed on silver electrode,[8,9] and the formation of Ag^+ complexes during the oxidation−reduction cycles was evidenced and related to the carbonization process onto the silver surface.[9] More recently, Moskovits and co-workers[10] studied the photochemical reaction of 1,10-phenanthroline adsorbed on aged silver colloids using a flow-cell method. In the present work, the adsorption mechanism of 1,10-phenanthroline in Ag hydrosols is investigated by means of both spectral measurements and normal mode calculations, in comparison with the SERS detected from spectroelectrochemical measurements and with the normal Raman scattering of the corresponding argentous complex.

Experimental Section

1,10-Phenanthroline monohydrate (purity 99%), supplied by Aldrich Co., was purified by sublimation under vacuum (mp 100−104 °C).

Stable silver colloids were prepared according to the method of Creighton et al.[11] by reduction of $AgNO_3$ with excess $NaBH_4$.

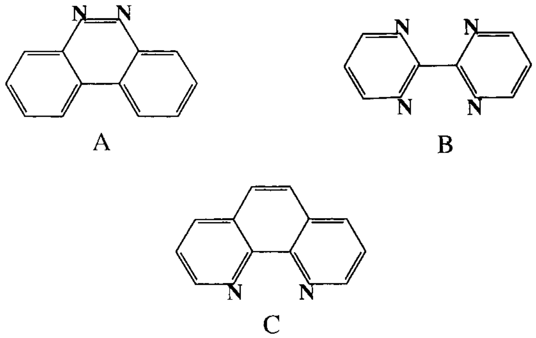

Figure 1. Molecular structures of benzo[*c*]cinnoline (A), 2,2′-bipyrimidine (B) and 1,10-phenanthroline (C).

1,10-Phenanthroline (10^{-4} M) was added after a week from the sol preparation to avoid reduction products.[12] Before the addition of the ligand, the UV−vis extinction spectrum exhibited only a strong plasmon band at about 390 nm. A rapid aggregation occurred by the addition of ligand, resulting in an additional broad band at about 600 nm. Also, aged Ag colloids were employed, after four months from the preparation; without ligand, they showed a pronounced plasmon band at about 700 nm in the visible extinction spectrum, due to aggregated silver particles.

Ag(I)-diphenanthroline-NO_3 was prepared as reported for the argentous complex of 2,2′-bipyrimidine.[2] Anal. Calcd for $Ag[C_{12}H_8N_2]_2NO_3 \cdot H_2O$: C, 52.57; H, 3.31; N, 12.77; Ag, 20.34. Found: C, 52.42; H, 3.08; N, 13.31; Ag, 20.36.

Raman spectra were recorded by using the 514.5 nm exciting line of an Ar^+ laser, a power of 50 mW on the sample, a Jobin−Yvon HG2S monochromator equipped with a cooled RCA-C31034A photomultiplier and a data acquisition facility. UV−vis extinction spectra were measured using a Cary 5 spectrophotometer.

Normal Mode Calculations

The SER spectroscopy provides useful information on the molecule−substrate interaction and the orientation geometry,

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by considering both wavenumbers and intensities of the observed bands. More quantitative details for interpreting the SERS data can be achieved by normal mode calculations, assuming a suitable molecule−substrate model. The organic ligand is supposed to maintain, unaltered, the molecular structure, thus a force field properly obtained for the free molecule can be employed. The metal substrate, in the simplest approach, is mimed by an isolated silver atom, which interacts with the molecule through force constants evaluated from the Ag-molecule stretching vibrations observed in the SERS. The position of the metal atom is estimated on the basis of structural parameters taken from the corresponding coordination compounds.

The theoretical justification of the static and dynamic characteristics assumed for this model is based on the following considerations: (1) a strong Raman enhancement of the ligand implies chemisorption, as shown also by the presence of Ag-molecule stretching bands in the low-frequency region; (2) chemisorption occurs at specific surface active sites, characterized by the presence of one (or more) metal atom, named "adatom",[13] that can be considered as isolated by the surrounding metal surface; (3) the close similarity between the SERS of the ligand and the normal Raman spectrum of the corresponding argentous complex allows the use of structural parameters transferred from the coordination compound. Hence, the interaction with the substrate represents a "perturbation" to the dynamic system of the free molecule, which can be satisfactorily described by Ag-molecule force constants. According to the normal coordinate calculations performed on both free and adsorbed molecules, it is possible to obtain frequency shifts to compare with those experimentally measured.

These calculations also allow distinction between totally symmetric modes, which provide a more efficient contribution to the enhancement on the basis of the charge-transfer mechanism. According to Lombardi et al.,[14] the totally symmetric vibrations involving large shifts of the equilibrium position in a corresponding excited state may have large intensity enhancements in near-resonance condition, as in the case of bulk Raman scattering. When the CT effect occurs, the equilibrium position of the CT excited state may definitely change along the direction normal to the surface; thus, the totally symmetric modes accompanied by large displacements of the nitrogen atoms bound to the silver substrate must exhibit strong SERS enhancements. Hence, taking the CT resonance into account, it is possible to explain the different behavior of a single mode among the same symmetry modes, whereas the surface selection rules[15] predict uniform enhancements of these vibrations on the basis of the electromagnetic effect.

Therefore, the present calculation requires a suitable description of the normal modes of both free molecule and adsorbate−substrate model system.

Normal Coordinate Analysis of the Free Molecule. The vibrational spectrum of 1,10-phenanthroline was first studied by Perkampus and Rother.[6] Then Altmann and Perkampus performed a normal coordinate analysis[16] of this molecule, on the basis of the force fields proposed by Schettino et al.[17] for the in-plane vibrations of phenanthrene and by Scully and Whiffen[18] for the out-of-plane modes of aromatic molecules. More recently, Thornton and Watkins[7] reinvestigated the vibrational spectrum of 1,10-phenanthroline and its perdeuterated analogue and proposed a complete reassignment of the observed bands. It partially differed from the previous assignment[16] for some in-plane bands, mainly in the spectral region of the ring stretching modes.

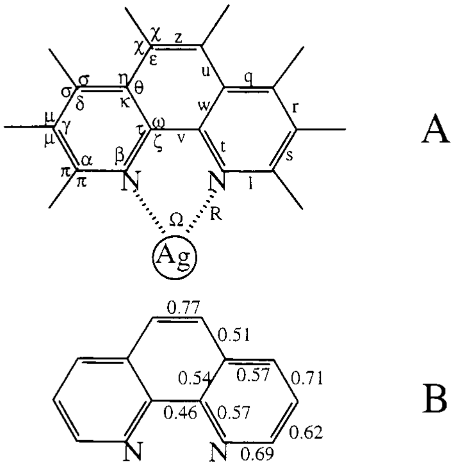

Figure 2. Internal coordinates of free and adsorbed 1,10-phenanthroline (A); π bond orders as evaluated by the Hückel method (B).

Therefore, a refinement of the previous force field is necessary in order to have intramolecular potentials at our disposal that are able to satisfactorily reproduce the fundamental vibrations of the free molecule. Hence, the SER spectrum of the molecule adsorbed on silver substrate can be interpreted in terms of calculated frequency shifts.

Only the in-plane force field has been refined because in the SERS of planar molecules such as 1,10-phenanthroline, the in-plane bands are generally more intense and determinant for understanding the type of metal−molecule interaction.[2] The molecular structure, considered in the present calculations, is that which was already used by Altmann and Perkampus,[16] with C_{2v} molecular symmetry.

The refined force field is reported in Table 1, in terms of internal coordinates as described in Figure 2A. The comparison between calculated and observed values is shown in Table 2. The main difference with the previous force field[16] involves the force constants of the ring stretching vibrations. In particular, the value of the K_z force constant increases from 7.000 to 8.339 mdyn/Å. Also, the force field of phenanthrene, as refined by Altmann and Perkampus[19] from that reported by Schettino *at al.*,[17] showed an identical behavior of the same force constant, increasing its value from 6.99 to 8.30 mdyn/Å. This variation is related to the "olefinic" character of the corresponding C−C bond, which presents a quite short distance, about 1.37 Å, for 1,10-phenanthroline[4] as well as for phenanthrene.[20]

The ring stretching force constants generally have values related to the corresponding bond distances and orders. For a double bond stretching, a reasonable force constant exhibits values between 8 and 9 mdyn/Å, for a single bond stretching between 4.5 and 5 mdyn/Å, and for an aromatic bond stretching between 6 and 7 mdyn/Å. A simple calculation based on the Hückel method allows us to draw an interesting correlation between stretching force constants and π bond orders (Figure 2B). The highest value of force constant, relative to the "z" bond stretching ($K_z = 8.339$ mdyn/Å), corresponds to the highest value of bond order, whereas the lowest value, relative to the "v" bond stretching ($K_v = 5.748$ mdyn/Å), corresponds to the lowest value of bond order. The force constants relative to the "u", "w", "q", "t", and "s" coordinates, as well as the corresponding π bond orders, have typical values of aromatic bonds. Finally, the "l" and "r" bonds also present some character of double bond, and the corresponding force constants have high values (7.537 mdyn/Å). As a further check on the confidence of the present force field, normal mode calculations have also been performed for perdeuterated 1,10-phenanthroline. The

TABLE 1. Force Constants of Free and Adsorbed 1,10-phenanthroline

type	description	value	dispersion
free molecule			
C−H stretching	K_c	5.069	0.018
ring stretching	$K_t = K_w = K_s = K_q = K_u$	6.142	0.339
	$K_l = K_r$	7.537	0.551
	K_z	8.339	0.485
	K_v	5.748	0.484
ring bending	$H_\theta = H_\omega = H_\tau = H_k$	0.845	0.135
	$H_\alpha = H_\beta = H_\gamma = H_\delta = H_\epsilon$	1.147	0.211
	$H_\zeta = H_\eta$	0.763	0.201
CH bending	$H_\pi = H_\mu = H_\sigma$	0.466	0.010
	H_χ	0.539	0.037
ring stretch−	$F_{sr} = F_{sl} = F_{tl} = F_{qr} = F_{uz}$	0.538	0.148
ring stretch	$F_{wt} = F_{uq}$	0.301	0.213
interaction (ortho)	$F_{uw} = F_{wq} = F_{vt} = F_{wv}$	0.586	0.154
ring stretch−	$F_{st} = F_{qs} = F_{lr} = F_{tq} = F_{uu}$	−0.514	0.211
ring stretch	$F_{lw} = F_{wr} = F_{wz} = F_{lv}$	−0.077	0.239
interaction (meta)	$F_{ww} = F_{vu} = F_{qz} = F_{ru}$	−0.286	0.238
	$F_{qv} = F_{tw} = F_{tu} = F_{tt}$	0.161	0.160
ring stretch−	$F_{lq} = F_{tr}$	0.056	0.227
ring stretch	$F_{uw} = F_{sw} = F_{vz} = F_{qw} = F_{tu} = F_{tq} = F_{qu} = F_{lw}$	−0.088	0.118
interaction (para)	$F_{su} = F_{sv} = F_{rv} = F_{rz} = F_{tz} = F_{lt} = F_{lu}$	−0.103	0.130
ring strech−	$F_{s\alpha} = F_{s\gamma} = F_{r\gamma} = F_{r\delta} = F_{l\alpha} = F_{l\beta} = F_{z\epsilon}$	0.311	0.205
ring bend interaction	$F_{t\beta} = F_{t\tau} = F_{t\zeta} = F_{q\delta} = F_{q\kappa} = F_{v\zeta} = F_{q\eta} = F_{u\eta} = F_{u\theta} = F_{u\epsilon} = F_{w\kappa} = F_{w\tau} = F_{w\theta} = F_{w\omega} = F_{v\omega}$	0.414	0.108
ring stretch− CH bend	$F_{l\kappa} = F_{s\pi} = F_{s\mu} = F_{r\mu} = F_{r\sigma} = F_{q\sigma} = F_{u\chi} = F_{z\chi}$	0.308	0.047
interaction			
ring bend−ring bend	$F_{\gamma\alpha} = F_{\gamma\delta} = F_{\alpha\beta} = F_{\delta\kappa} = F_{\tau\beta} = F_{\epsilon\epsilon} = F_{\epsilon\theta}$	0.024	0.023
interaction	$F_{\tau\kappa} = F_{\theta\omega} = F_{\tau\theta} = F_{\omega\omega} = F_{\zeta\zeta} = F_{\omega\zeta} = F_{\omega\kappa} = F_{\zeta\beta}$	0.160	0.194
CH bend−CH bend interaction	F_{cc}	0.085	0.016
Ag/molecule complex			
Ag−N stretching	K_R	2.000 [a]	
N−Ag−N bending	H_Ω	0.500 [a]	
Ag−N stretch/Ag−N stretch	F_{RR}	−0.300 [a]	
Ag−N stretch/N−C stretch interaction	$F_{Rl} = F_{Rt}$	0.259	
Ag−N stretch/C−N−C bend interaction	$F_{R\beta}$	−0.491	

[a] Transferred from ref 2 without refinement. Stretching constants in units of mdyn Å^{-1}, bending constants in units of mdyn Å rad^{-2}, stretching−bending interaction in units of mdyn rad^{-1}.

TABLE 2. Observed and Calculated In-Plane Frequencies of 1,10-Phenanthroline

	1,10-phenantroline-h_{10}		4,5-phenantrene-d_{1o}	1,10-phenantroline-d_8.	
species	observed [6]	calculated this work	observed [20]	observed [6]	calculated this work
A_1	302	210	231	229	200
	403	401	392	385	383
	552	557	532	536	541
	710	707	667	675	682
	854	853	772	788	800
	1037	1041	813?	815	816
	1094	1104	(833)	833	835
	1142	1157	860	852	874
	1186	1189	897	883	911
	1217	1217	1118	1117	1111
	1295	1293	1205	1206	1209
	1345	1343	1304	1294	1275
	1414	1412	1372	1378	1379
	1446	1442	1392	1412	1421
	1502	1504	1475	1464	1483
	1599	1591	1563	1552	1561
	1616	1616	1597	1590	1601
	3032	3021	2252	2251	2251
	3058	3056	2277	2274	2274
	3066	3082	2290	2291	2297
	3082	3092	2312?	2312	2300
B_2	427	431	414	399	411
	499	490	473?	480	462
	623	617	597	607	605
	724	738	677	694	704
	896	889	830	808	804
	985	986	849	842	819
	1079	1067	863	855	834
	1137	1141	948	934	943
	1206	1195	971	974	954
	1253	1237	1022?	1034	1029
	1313	1326	1270	1255	1233
	1405	1389	1326	1334	1304
	1421	1426	1352	1384	1390
	1492	1504	1432	1427	1460
	1561	1560	1528	1542	1537
	1586	1591	1589	1577	1577
	3008	3021	2230?	2240	2250
	3032	3031	? 2265	2251	2257
	3059	3056	2273	2269	2274
	3115	3092	2286	2291	2299

calculated frequencies, reported in Table 2, suggest a reassignment for a few bands, as observed by Thornton and Watkins,[7] the results of which are in close analogy with that reported by Bree et al.[21] for perdeuterated phenanthrene.

Normal Coordinate Analysis of the Ag/Molecule Complex. In Table 1, we also report the values of the force constants that are able to describe the interaction between 1,10-phenanthroline and a silver atom of the colloidal surface. This atom is considered to be bound to the molecule via the lone-pairs of the two nitrogen atoms, as well as in the case of 2,2′-bipyrimidine adsorbed on silver sols.[2] We have assumed a geometry for the Ag-molecule interaction that is very close to that proposed for 2,2′-bipyrimidine, with an N−Ag−N "bite" angle of 71° and an Ag−N distance of 2.318 Å. Small variations in both the angle and the distance, with a relative error up to 2%, do not imply significant variations in the calculated frequencies.

The force constants used for adsorbed 2,2′-bipyrimidine[2] have been introduced in the present calculation in addition to the force field refined for free 1,10-phenanthroline. To measure the experimental shifts between the observed frequencies of free and adsorbed 1,10-phenanthroline, we have obtained the Raman spectra in water and in chloroform solution, which are reported in Figure 3 together with the solid Raman spectrum. Figure 4 shows the SER spectrum of 10^{-4} M 1,10-phenanthroline adsorbed on freshly prepared silver sol (see the Experimental

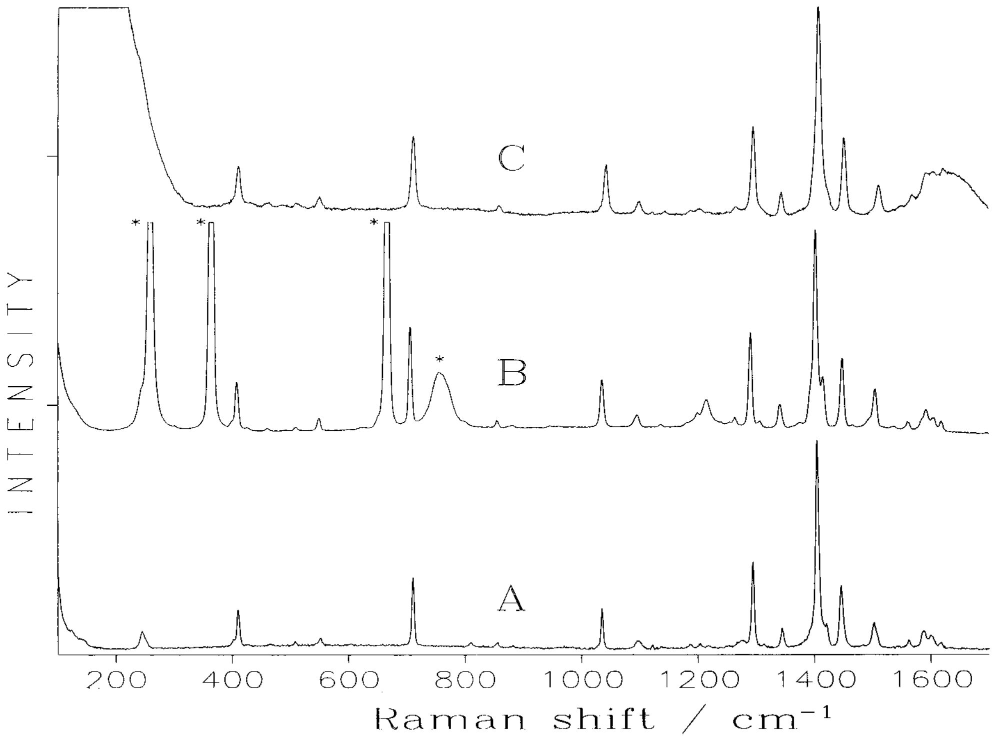

Figure 3. Normal Raman spectra of 1,10-phenanthroline: solid sample (A); chloroform solution (B); aqueous solution (C). Dots mark $CHCl_3$ bands.

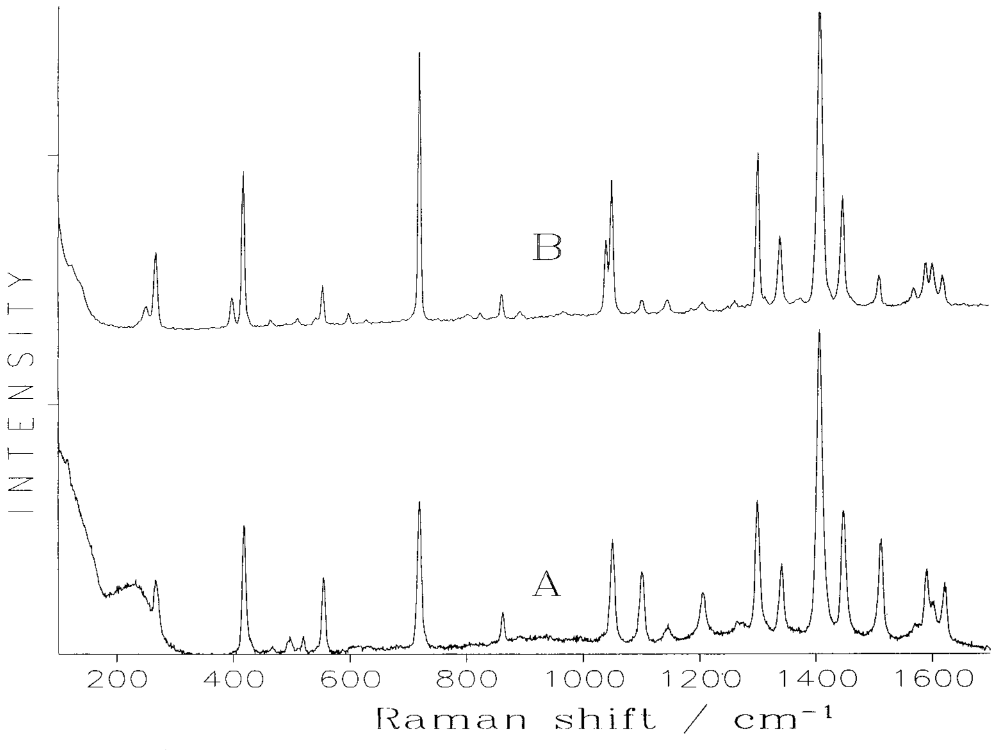

Figure 4. A: SER spectrum of 10^{-4} M 1,10-phenanthroline in freshly prepared Ag hydrosol, without halide ions; B: normal Raman spectrum of 1:2 Ag(I)-phenanthroline complex, solid sample.

Section), in comparison with the normal Raman scattering of the corresponding argentous complex.

Surface Enhanced Raman Scattering

The SER spectrum of the ligand is very intense, with an apparent enhancement factor of about four orders with respect to the normal Raman spectrum of the aqueous solution. The band at 419 cm^{-1} can be related to the A_2 Raman band observed at 410 cm^{-1} in the bulk, but the A_1 vibration observed in solution as a weak shoulder at 402 cm^{-1} contributes to its intensity. The SERS band at 1408 cm^{-1} is assigned to the B_2 species, despite a possible contribution of the A_1 vibration observed in the crystal spectrum and in chloroform solution as a weak Raman band at about 1414 cm^{-1}. The SERS band at 1146 cm^{-1}, corresponding to the A_1 Raman band observed at 1144 cm^{-1}, can gain intensity also from the B_2 vibration observed in the crystal Raman spectrum at 1137 cm^{-1}.

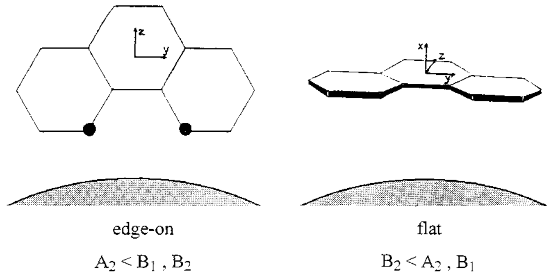

Figure 5. Two possible orientations of 1,10-phenanthroline adsorbed on silver surface. Relative band intensities predicted by the surface selection rules.

TABLE 3. Raman Bands of 1,10-phenanthroline

species	solid	solution| $CHCl_3$	solution H_2O	Ag colloid[a]	Ag(I) complex[b]
lattice modes	30 m/s				
	55 m				
	86 vvs				58 vs
B_1	123 vw				122 vw
A_2	144 sh				140 sh
Ag−N mode				230 s, broad	
B_1	245 m/s	247 sh	244 sh		254 w
A_2	253 sh			267 m	268 m
A_1	402 w/m	401 sh	402 sh		400 m
A_2	411 s	408 m	411 m	419 s	419 s
B_2	427 vw	426 vw	430 vvw		
B_1	466 w	461 vw	462 vw	468 w	466 w
B_2	495 vvw			498 w	490 vw
B_1	508 w	510 w	510 w	519 w	512 w
A_1	552 w/m	549 w/m	551 w/m	554 m/s	554 m
A_2	605 w	600 vvw	605 vvw	616 vvw	600 w
B_2	622 vw	622 vvw			630 vw
A_1	711 vs	706 s	710 s	720 vs	721 vs
A_2	810 m			810 w	806 vw
A_1	855 w	856 w	859 w/m	861 w/m	862 w/m
B_2	882 vvw	882 vw		888vw	
		948 vw			
A_2	960 vvw	962 vw			962 w/m
				988 vw	989 vw
NO_3 mode					1042 m
A_1	1035 s	1035 m	1042 m	1047 s	1050 m/s
A_1	1097 w/m	1095 w/m	1099 w/m	1099 m	1102 w
	1121 vvw				1123 vw
B_2	1136 w	1137 w	1144 w	1146 w	1146 w
A_1	1142 vw				
A_1	1187 w	1185 sh	1187 vw	1189 w	1188 w
B_2	1204 w	1200 w	1204 w	1205 w/m	1207 w
A_1	1218 w	1215 w/m	1218 w	1216 sh	1221 vw
B_2	1253 w	1256 vw			1252 w
	1263 vvw	1264 w	1265 vw	1267 w	1264 vw
	1274 w		1280 sh		1282 vw
A_1	1294 vs	1291 s	1297 s	1298 s	1302 s
B_2	1314 vw	1307 w			1317 vw
A_1	1345 m/s	1341 w/m	1343 w/m	1342 m/s	1341 m
		1376 w			1372 vw
B_2	1405 vs	1402 vs	1408 vs	1407 vvs	1410 vvs
A_1	1414 m	1415 w			
B_2	1420 m		1420 sh		1424 sh
A_1	1446 s	1448 m/s	1451 m/s	1447 s	1448 m/s
		1460			
B_2	1492 vvw	1496 sh			
A_1	1502 m	1505 w/m	1512 w/m	1509 m/s	1511 w/m
	1541 vvw	1538 vw			
B_2	1562 w	1561 w	1569 sh	1569 sh	1570 w
B_2	1588 m/w	1592 w/m	1591 w	1590 w/m	1591 w/m
A_1	1601 w	1605 w	1603 vw	1601 w	1604 w/m
A_1	1617 vw	1619 w	1622 w	1621 w/m	1622 w
A_1	3035 vw				3048 sh
A_1	3058 sh			3056 sh	3060 w
A_1	3065 w			3074 sh	3075 w
A_1	3080 sh			3081 w	

[a] Freshly prepared Ag colloid, without halide anions. [b] Solid sample.

By considering the relative intensities of the SERS bands, information can be obtained about the orientation of the adsorbed molecule onto the silver substrate. According to the Creighton's surface selection rules,[15] as shown in Figure 5, for "edge-on" adsorption the A_2 vibrations, spanning in the xy plane, parallel to the metal surface, should be the least enhanced. For "flat" adsorption the B_2 vibrations should be the least enhanced. As shown in Table 3, the most intense SERS bands belong to A_1 or B_2 symmetry species. In particular, all the B_2 bands observed in aqueous solution find corresponding SERS bands. Moreover, two new B_2 bands are observed at 498 and 888 cm^{-1}, only in the SERS, whereas the B_2 SERS bands at 1204 and 1591 cm^{-1} are largely enhanced with respect to the corresponding normal Raman bands. These spectral observations lead to the conclusion that a "flat" orientation, involving the π electrons of the aromatic rings, can be ruled out. Hence, an "edge-on" orientation can be proposed, also by observing between 200 and 250 cm^{-1} a strong and broad band, which suggests the presence of two Ag−N bonds. The present investigation closely agrees with the SERS experiments performed in freshly prepared Ag colloid by Moskovits and co-workers,[10] who proposed a bidentate chelation of 1,10-phenathroline with respect to the metal surface.

But the occurrence of intense A_2 species bands at 267 and 419 cm^{-1} also suggests the possibility of a "tilted" orientation of the molecule with respect to the silver substrate. In such a way, the A_2 vibrations can also undergo significant Raman enhancement. The deviation from the perpendicular orientation becomes more evident for cases in which the ligand is adsorbed on Ag colloid strongly aggregated by long aging (see experimental), as shown by the further intensification of the A_2 bands (Figure 6A). Nevertheless, the occurrence of the Ag−N stretching band suggests π electrons be not involved in the interaction with the substrate.

Also, the SERS data obtained from aged silver colloids are in agreement with the results by Moskovits and co-workers,[10] who observed a tendency toward a "flat" orientation when the surface defects decreased with the colloidal aging. In addition, they observed photoreaction by using aged colloids with little aggregation in a flow-cell. In the present SERS experiments, instead, no photoproduct is detected, also by long laser irradiation: here, the catalytic active sites, responsible for the photoreaction effect, are probably involved in the colloidal particle aggregation.

For several SERS bands, marked upshifts occur with respect to the corresponding Raman bands of the free molecule, especially in the low-frequency spectral region. On the contrary, some bands, mainly those corresponding to ring stretching modes in the 1300−1600 cm^{-1} region, exhibit small downshifts. This evidence was previously observed in the case of benzo[*c*]cinnoline[1] adsorbed on Ag colloid and related to a decreasing of the ring bond strength due to the chemical interaction with the silver surface. In the present investigation, the SERS frequencies closely agree with those detected when 1,10-phenanthroline was adsorbed on Ag electrode[8,9] and with the Raman frequencies of the 1:2 Ag(I)-phenanthroline complex (Figure 4B), listed in Table 3.

To reproduce the observed frequency shifts, normal mode calculations have been performed by transferring the Ag/molecule potentials of the 2,2′-bipyrimidine/Ag complex.[2] But this calculation produces some upshifts significantly higher than those observed, especially for the A_1 band at 720 cm^{-1}.

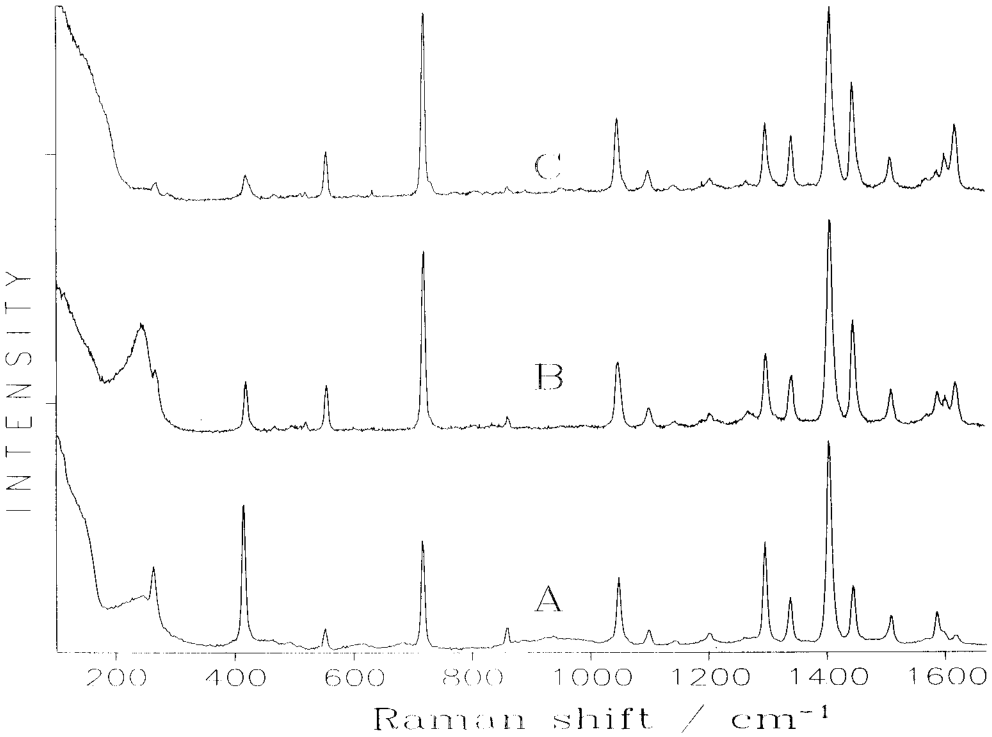

Figure 6. SER spectra of 10^{-4} M 1,10-phenanthroline: in aged Ag hydrosol, without halide ions (A); adsorbed on Ag colloid with addition of NaCl (B); adsorbed on Ag colloid with addition of NaBr (C).

Therefore, two new interaction force constants, between the Ag−N stretching modes and the vicinal C−N stretching and C−N−C bending modes, have to be introduced in the calculation. Also for adsorbed 2,2′-bipyrimidine, other interaction force constants should be necessary to improve the agreement between experimental and calculated frequencies.[2] Hence, in the present calculation (Table 4) most experimental shifts are satisfactorily reproduced.

The Ag-molecule force constants introduce constraints in the vibrational motion of the ligand, resulting in a general upshift of the molecular vibrations, mainly in the low-frequency region for ring bending deformations, as shown by the potential energy distribution of Table 4. The downshifts of the ring stretching modes, observed in the 1300−1600 cm^{-1} region, are instead predicted by introducing in the calculation the interaction force constants between Ag−N stretchings and "internal" coordinates of the molecule. Hence, this force field refinement, producing weakening of the ring bond strength, accounts for the chemisorption process, which can be regarded as forming coordination bonds between an electron-donor ligand and an electron-acceptor metal. This adsorption model becomes then more efficient when the ligand is adsorbed on Ag colloid in the presence of halide anions, which are able to induce positive charges onto the silver surface.[22]

Halide Anion Effect

The presence, in fresh as well as in aged Ag hydrosols, of halide anions like chloride or bromide, strongly adsorbed onto the metal surface, produces modifications in the SERS of 1,10-phenanthroline. No appreciable frequency shift is detected by addition of these anions, but a marked decrease in the enhancement of the SERS bands corresponding to out-of-plane vibrations is observed (Figure 6), mainly for the A_2 bands at 267, 419 and 811 cm^{-1}. This evidence indicates that, on the basis of the surface selection rules (Figure 5), the ligand here assumes a more strictly perpendicular orientation with respect to the substrate. Moreover, a change in the relative intensities of some A_1 species bands is also observed; for example, the SERS band at 720 cm^{-1} becomes as strong as the most intense band at 1408 cm^{-1}. This effect depends on the halide coadsorption because it is more evident in the presence of bromide anions, which exhibit stronger affinity to the silver. Actually, the adsorption of these anions is able to induce the formation of charge-transfer complexes between ligand and surface active sites, where there are positively charged Ag atoms.[22] Hence, the intensity changes can be explained by considering that, according to the charge-transfer enhancement mechanism,[14] totally symmetric bands showing large shift of the equilibrium positions along the direction of the charge-transfer exhibit strong SERS intensities. The SERS band observed at 720 cm^{-1} corresponds to a normal mode calculated at 719 cm^{-1}, which exhibits the largest Cartesian displacements of the nitrogen atoms, involved in the bonding with the silver substrate, along the direction toward the metal surface, as shown in Figure 7. The same figure shows the description of the observed C−H stretching modes of the ligand in Ag hydrosol. The highest band observed in the SERS at 3081 cm^{-1}, showing large Cartesian displacements along a direction parallel to the surface plane, is expected to present lower Raman enhancement when the charge-transfer mechanism is activated by coadsorbed halide anions, as experimentally observed (Figure 8). On the contrary, the CT mechanism plays a determinant role for the other C−H stretching bands at 3074 and 3056 cm^{-1}, which exhibit Cartesian displacements normal to the surface plane. Finally, the Ag−N stretching vibrations, which give rise to a strong and broad band between 200 and 250 cm^{-1} in the salt-free Ag colloid, are practically absent in the SERS with added bromide anions (Figure 6). As already discussed in the case of adsorbed 2,2′-bipyrimidine[2], the Ag−N vibrations are not enhanced by the charge-transfer mechanism because they are to be described as translations of the ligand and Ag atom in opposite directions.

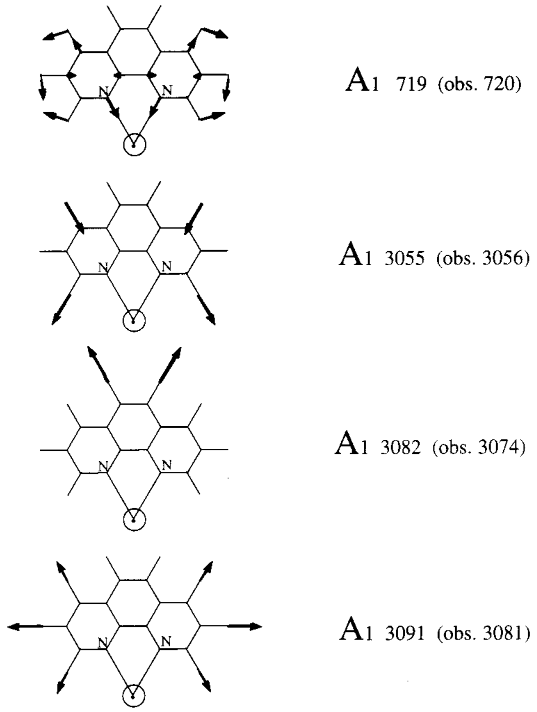

Figure 7. Cartesian displacements for some normal modes of the 1,10-phenanthroline/Ag complex corresponding to A_1 molecular modes (Å × 10 per change in the 719-cm^{-1} normal coordinate, Å × 3 per change in the other normal coordinates).

Discussion and Conclusion

The normal mode calculations, performed on the basis of a model of ligand interacting with a single silver atom through the lone-pair electrons of the nitrogen atoms, correctly describe the observed frequency shifts between SERS and normal Raman spectrum. This approach is justified by the spectral evidence of Ag−N stretching bands due to chemisorption of the ligand onto the metal surface and agrees with the enhancement mechanism based on the chemical interaction of the molecule with an atomic-scale active-site or “adatom”.[13]

On the basis of the surface selection rules, a perpendicular or a tilted orientation of the adsorbate with respect to the colloidal surface is proposed, whereas a flat adsorption via π electrons is ruled out. The tendency toward a nonperpendicular orientation is increased in aged Ag hydrosols. No evidence of photochemical reaction is detected in fresh or aged colloids.

Coadsorbed halide anions produce no frequency shift of the SERS bands, but a marked effect on the relative intensities. This effect is exhaustively explained in terms of the charge-transfer mechanism by considering the Cartesian displacements of the vibrations as resulting from the normal coordinate analysis. Moreover, the presence of halide anions induces a more perpendicular orientation of the ligand with respect to the metal substrate.

Apart from the possibility of explaining frequency shifts and relative intensities of the SERS bands on the basis of normal mode calculations, it is interesting to compare the results of this study with the experimental data of 1,10-phenanthroline adsorbed on Ag electrode. In the present experiments, the frequency shifts are generally comparable with those observed by spectroelectrochemical measurements.[9] No evidence of carbonization is detected in the salt-free colloid as well as in the presence of coadsorbed halide anions, as otherwise evident from electrode measurements.[8,9] Photographitization was detected by Cooney et al.[8] by laser irradiation, whereas El Hajbi et al.[9] attributed carbonization mainly to the Ag^+-Ag^o oxidation−reduction processes at the silver electrode. In colloidal suspensions, instead, the absence of OR cycles as well as the Brownian motion of the metal particles prevent the damage of the ligand.

Finally, no significant wavenumber difference occurs between the SERS bands of 1,10-phenanthroline adsorbed on silver sol and the corresponding Raman bands of the Ag(I)-diphenan-

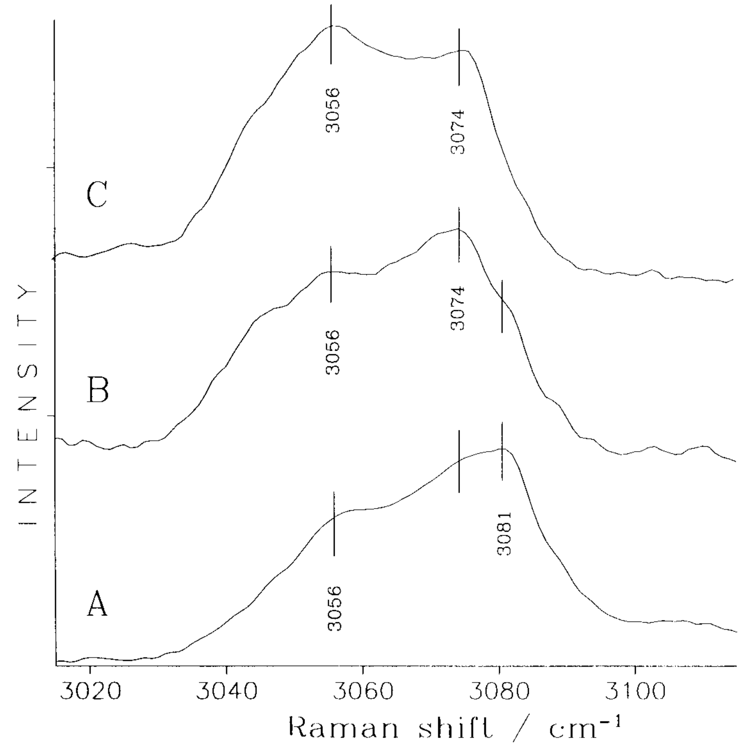

Figure 8. C−H stretching region in the SER spectra of 10^{-4} M 1,10-phenanthroline adsorbed on Ag colloids: without halide ions (A); with NaCl (B); with NaBr (C).

TABLE 4. Observed and Calculated Shifts between the Most Intense Raman Bands of free and adsorbed 1,10-phenanthroline

species	freq obs[a]	freq		shift obs	shift calc	potential energy distribution[d]
		calc[b]	calc[c]			
B_2	230	213	230			R (69), α (20), T (10)
A_1	230	236	245			R (47), α (41), T (10)
A_1	419	425	419	+17	+18	α (46), T (32), R (20)
A_1	554	562	558	+3	+2	α (67), T (24), β (7)
A_1	720	750	719	+10	+12	T (49), α (30), R (16)
A_1	861	869	852	+2	0	α (63), T (21), β (12), R (5)
A_1	1047	1045	1044	+5	+3	T (67), β (26), α (5)
B_2	1146	1144	1142	+2	+1	β (83), T (11), α (6)
B_2	1205	1200	1194	+1	0	β (66), T (18), α (13)
A_1	1298	1297	1288	+1	−4	β (52), T (34), α (12)
A_1	1342	1344	1343	−1	0	T (56), β (39), α (4)
B_2	1407	1394	1387	−1	−2	β (44), T (43), α (13)
A_1	1447	1446	1439	−4	−3	T (75), β (12), α (10)
A_1	1509	1504	1500	−3	−4	T (78), α (11), β (10)
B_2	1590	1591	1589	−1	−1	T (70), α (19), β (7)
A_1	1621	1617	1615	−1	−1	T (76), α (14), β (10)

[a] SERS bands of 1,10-phenanthroline adsorbed on Ag colloid. [b] Force costants transferred from ref 2 for the interaction between molecule and Ag atom. [c] Refined force field for the interaction between molecule and Ag atom. [d] T = ring stretch.; α = ring bend.; β = C−H bend.; R = Ag−N stretch. Observed shifts in the SERS refer to normal Raman spectrum in aqueous solution; calculated shifts and potential energy distribution refer to refined force field.

throline-NO_3 complex, as otherwise observed by El Hajbi et al.[9] Therefore, the molecule is perturbed by the interaction with the silver colloidal surface as well as ligand in the argentous coordination compound.

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References and Notes

(1) Neto, N.; Nocentini, M.; Muniz-Miranda, M.; Sbrana, G. *J. Mol. Struct.* **1990**, *218*, 423.

(2) Sbrana, G.; Neto, N.; Muniz-Miranda, M.; Nocentini, M. *J. Phys. Chem.* **1990**, *94*, 3706.

(3) Neto, N.; Muniz-Miranda, M.; Sbrana, G. *J. Phys. Chem.* **1996**, *100*, 9911.

(4) Nishigaki, S.; Yoshioka, H.; Nakatsu, K. *Acta Crystallogr. B* **1978**, *34*, 875.

(5) Ng, S. W. *Z. Kristallogr. (New Cryst. Struct.)* **1997**, *212*, 283.

(6) Perkampus, H.-H.; Rother, W. *Spectrochim. Acta* **1974**, *30A*, 597.

(7) Thornton, D. A.; Watkins, G. M. *Spectrochim. Acta* **1991**, *47A*, 1085.

(8) Cooney, R. P.; Howard, M. W.; Mahoney, M. R.; Mernagh, T. P. *Chem. Phys. Lett.* **1981**, *79*, 459.

(9) El Hajbi, A.; Alonso Vante, N.; Chartier, P.; Goetz-Grandmont, G.; Heimburger, R.; Leroy, M. J. F. *J. Electroanal. Chem.* **1986**, *207*, 127.

(10) Jang, N. H.; Suh, J. S.; Moskovits, M. *J. Phys. Chem. B* **1997**, *101*, 8279.

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

(12) Muniz-Miranda, M.; Neto, N.; Sbrana, G. *J. Phys. Chem.* **1988**, *92*, 954.

(13) Otto, A. *Light Scattering in Solids*; Cardona, M., Güntherodt, G., Eds.; Springer: Berlin, 1984; Vol. IV.

(14) Lombardi, J. R.; Birke, R. L.; Lu, T.; Xu, J. *J. Chem. Phys.* **1986**, *84*, 4174.

(15) Creighton, J. A. *Surf. Sci.* **1983**, *124*, 209.

(16) Altmann, W.; Perkampus, H.-H. *Spectrochim. Acta* **1979**, *35A*, 253.

(17) Schettino, V.; Neto, N.; Califano, S. *J. Chem. Phys.* **1966**, *44*, 2724.

(18) Scully, D. B.; Whiffen, D. H. *J. Mol. Spectrosc.* **1957**, *1*, 257.

(19) Altmann, W.; Perkampus, H.-H. *J. Mol. Spectrosc.* **1979**, *78*, 156.

(20) Trotter, J. *Acta Crystallogr.* **1963**, *16*, 605.

(21) Bree, A.; Solven, F. G.; Vilkos, V. V. B. *J. Mol. Spectrosc.* **1972**, *44*, 298.

(22) Muniz-Miranda, M.; Sbrana, G. *J. Raman Spectrosc.* **1996**, *27*, 105.