

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231639223>

Surface-Enhanced Raman Scattering and Density Functional Theoretical Study of Anthranil Adsorbed on Colloidal Silver Particles

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · OCTOBER 2004

Impact Factor: 3.3 · DOI: 10.1021/jp047899h

CITATIONS

27

READS

24

4 AUTHORS:



M. Baia

Babeş-Bolyai University

49 PUBLICATIONS 805 CITATIONS

SEE PROFILE



Lucian Baia

Babeş-Bolyai University

99 PUBLICATIONS 1,296 CITATIONS

SEE PROFILE



Wolfgang Kiefer

University of Wuerzburg

881 PUBLICATIONS 9,877 CITATIONS

SEE PROFILE



Juergen Popp

Friedrich Schiller University Jena

408 PUBLICATIONS 6,077 CITATIONS

SEE PROFILE

Surface-Enhanced Raman Scattering and Density Functional Theoretical Study of Anthranil Adsorbed on Colloidal Silver Particles

M. Baia,[‡] L. Baia,[‡] W. Kiefer,[§] and J. Popp^{*,†}

Physics Department, Babes-Bolyai University, 400084 Cluj-Napoca, Romania, Institut für Physikalische Chemie, Universität Würzburg, D-97074 Würzburg, Germany, and Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena, D-07743 Jena, Germany

Received: May 17, 2004; In Final Form: July 27, 2004

Surface-enhanced Raman spectrum of anthranil (2,1-benzisoxazole) in activated silver colloid was recorded and compared with the conventional Raman spectrum. The experimentally observed Raman bands along with their corresponding infrared bands were assigned based on the results of density functional theory (DFT) calculations. The significant changes evidenced between the SER and normal Raman spectra combined with the theoretical data obtained for Ag–anthranil model systems demonstrated that this molecule is adsorbed on the colloidal silver particles through the lone pair electrons of the nitrogen atom. The contribution of the chemical mechanism to the SERS enhancement was proved by the behavior of the electronic absorption spectrum of the mixture of activated silver colloid and anthranil solution. The orientation of the adsorbed species with respect to the metal surface was also predicted.

Introduction

During the past two decades, surface-enhanced Raman spectroscopy (SERS) has become a convenient technique for analyzing the adsorption of molecules on metallic surfaces.¹ It has been proven to be a very sensitive method that is able to detect molecules at trace concentration levels (ca. 10^{-12} mol dm⁻³) and to quench the fluorescence background by radiationless energy transfer to the metal surface from adsorbed species.^{1–3} Recently, semiquantitative and quantitative analysis based on SERS has been described,^{4,5} and therefore SERS has received considerable attention in the chemical, environmental, and biomedical fields, and also in the biological sciences.

To induce the SERS effect, molecules are required to be in close proximity to a suitable roughened surface of certain metals, such as silver, copper, and gold. However, not all molecules exhibit SERS spectra; usually those having a heteroatom such as nitrogen, sulfur, or oxygen, or some functional groups such as CN, SO₃, SH, and COOH, which can interact with metal surfaces,^{6,7} show SERS phenomenon governed by physical–chemical adsorption.⁸

The main mechanisms proposed to account for the SERS effect are physical (electromagnetic) enhancement⁹ and chemical (charge-transfer) enhancement.^{10,11} In the former, the enhancement of the electromagnetic field near the metal surface is supposed to arise from plasmon resonances.⁹ According to this mechanism, the magnitude of enhancement is very sensitive to the physical nature of the metal surface, for example, the surface roughness of electrodes and the shape of particles for colloidal suspensions. In the chemical mechanism, the interaction between a specific group of the molecules and the metal atoms is responsible for the appearance of SERS.^{10,11} This interaction leads to a change in the molecular polarizability as a result of

the charge transfer between the molecule and metal through σ or π bonds or other weak interactions.

Anthranil (2,1-benzisoxazole), whose infrared and Raman spectra have been reported,¹² and its derivatives are well known due to their extensive applications in pharmacology and analytical chemistry.^{13–17} While the topical anthranil treatment was suggested for possible use in the bioassay of tumor promoters¹³ and some anthranil derivatives have shown cytotoxic and mutagenic activity,¹⁴ other anthranil derivatives proved to possess a protective antiulcer effect and sedative activity.^{15,16} It was also shown¹⁸ that anthranil is the key intermediate in the decomposition process of nitroaromatic explosives.

For understanding the action of potential drugs, such as anthranil, it is essential to find out if the structure of the adsorbed species is similar to that of the free molecule. In these investigations, a silver surface may serve as an analogue for an artificial biological interface and, after elucidating the adsorption mechanism of a molecule, the study can be expanded to the adsorption on membranes or other interesting biological surfaces for medical or therapeutic treatments.¹⁹

In the present study, SERS has been applied to the anthranil molecule to get insights about its adsorption behavior on the colloidal silver particles and to find out, from the enhancement of different Raman bands, the most probable orientation of the adsorbed species relative to the metal surface. Density functional theory (DFT) calculations have been also performed on different Ag–anthranil model complexes to provide valuable information concerning the interaction between the anthranil species and the silver surface.

Experimental Section

Materials and Spectroscopic Methods. Anthranil (2,1-benzisoxazole) of 99% purity was purchased from Lancaster, and all other materials involved in substrate and solutions preparation were purchased from Aldrich as analytical pure reagents.

* Corresponding author. E-mail: Juergen.Popp@uni-jena.de.

[‡] Babes-Bolyai University.

[§] Universität Würzburg.

[†] Universität Jena.

A stable sodium citrate silver colloid was prepared according to the standard procedure of Lee and Meisel²⁰ and employed as the SERS substrate. The resultant colloid was yellowish gray, with an absorption maximum at 412 nm. To 3 mL of silver colloid, small amounts of 10^{-1} M ethanol solution of anthranil were added dropwise using a micropipette. NaCl solution (10^{-2} M) was also added (10:1) to produce a stabilization of the colloidal dispersion that yields a considerable enhancement of the SER signal.²¹ The final concentration of the sample in the colloidal suspension was approximately 2.8×10^{-4} M.

UV–vis absorption spectra were recorded with a Perkin-Elmer Lambda 19 UV–vis–NIR spectrometer with a scan speed of 240 nm/min.

The FT-Raman spectrum of the sample was recorded using a Bruker IFS 120HR spectrometer with an integrated FRA 106 Raman module and a resolution of 2 cm^{-1} . Radiation (1064 nm) from a Nd:YAG laser was employed for excitation. The detection system consisted of a liquid-nitrogen-cooled Ge detector. The infrared spectrum was recorded with a Bruker IFS 25 spectrometer and a resolution of 2 cm^{-1} . The SER spectra of the sample on silver colloid, collected in backscattering geometry, were recorded on a Dilor Labram system equipped with an Olympus LMPlan FI 50 microscope objective, an 1800 lines/mm grating, and an external laser with an emission wavelength of 514 nm. In the recording of the SER spectra, a power of 150 mW incident on the sample was employed. The spectral resolution was about 2 cm^{-1} .

Computational Details. Theoretical calculations of the structure and vibrational wavenumbers of the investigated compound were performed using the Gaussian 98 program package.²² Density functional theory (DFT) calculations were carried out with Becke's 1988 exchange functional,²³ the Perdew–Wang 91 gradient corrected correlation functional (BPW91),²⁴ and Becke's three-parameter hybrid method using the Lee–Yang–Parr correlation functional (B3LYP).²⁵ The 6-31+G* Pople split-valence polarization basis set was used in the geometry optimization and normal modes calculations at all theoretical levels.

Theoretical calculations were also performed for Ag–anthranil model compounds to simulate the geometry and the vibrational modes of the most probable new-formed metal–molecule SERS complex. The calculations were done at the BPW91 theoretical level, having in view previous results²⁶ that claimed the inferiority of the B3LYP functional as compared to the BPW91 methods in calculating silver-containing molecules. In this case, “purposely tailored” basis sets have been employed, namely 6-31+G* for the N, C, O, and H atoms and LanL2DZ for the Ag atom, which may have some advantages, particularly as regards basis set completeness.²⁷

At the optimized structures of the examined species, no imaginary frequency modes were obtained, proving that a local minimum on the potential energy surface was found.

Results and Discussion

The overall planar anthranil molecule consists of two planar cycles, a phenyl and an isoxazole ring, and belongs to the C_s point group symmetry. The schematic structure of this molecule with the labeling of the atoms is given in Figure 1. Mille et al.¹² have recorded and assigned the infrared and Raman spectra of the 2,1-benzisoxazole molecule and compared them with those of the 1,2-benzisoxazole compound. In the present study, a more detailed assignment of the vibrational modes of the title compound based on the results of DFT calculations is provided. The infrared and Raman spectra of the anthranil molecule in

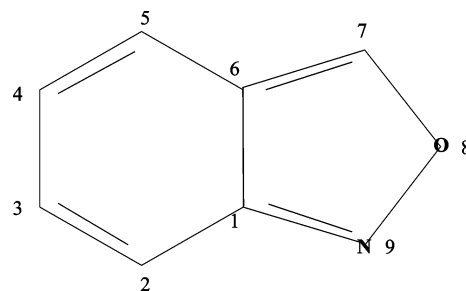


Figure 1. Schematic structure of the anthranil molecule with the labeling of the atoms.

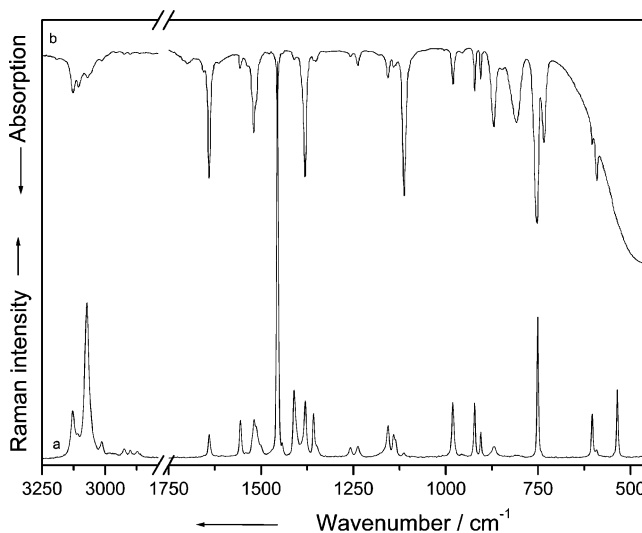


Figure 2. FT-Raman (a) and infrared (b) spectra of the anthranil molecule.

the spectral range between 450 and 3250 cm^{-1} are presented in Figure 2. The assignment of the observed bands, which is summarized in Table 1, was based on the visual inspection of normal mode displacement vectors by taking into account the vibrational bands' positions and intensities. The proposed assignment is in agreement with the previously reported data.¹²

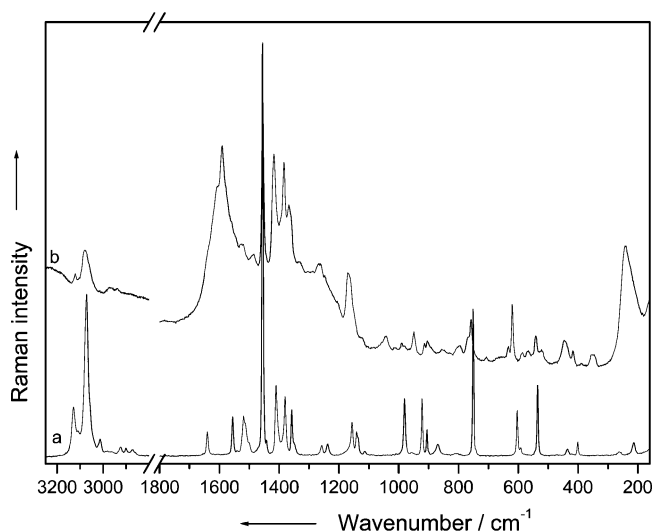
By comparing the calculated vibrational wavenumbers with the experimental results (see Table 1), one can observe that, similar to the results of previous studies,^{28,29} the computed data using the B3LYP method are larger than those calculated with the BPW91 method. The disagreement between the theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry.³⁰ It is also noteworthy to mention that the theoretical simulations were performed for the gas phase, while the experimental data were obtained for a liquid sample. However, as can be seen from Table 1, the predictions of the DFT methods for the vibrational frequencies are in consistently good agreement with the experimental values and allow for the complete assignment of the vibrational modes.

The SER spectrum of the anthranil is illustrated in Figure 3 along with the conventional Raman spectrum. Similar to the case of the adsorbed isoxazole molecules³¹ that exhibit Raman signals only in the presence of chloride anions, SERS enhancements were obtained only for anthranil species adsorbed on activated silver colloids. After a close analysis of the spectra (Figure 3) and the data summarized in Table 2, one can note that the SERS bands are broader and their peak positions and relative intensities are changed relative to their corresponding Raman bands. These spectral features suggest the existence of

TABLE 1: Assignment of the Theoretical Wavenumber Values (cm^{-1}) to the Experimental Bands of the Anthranil Molecule

experimental		theoretical		vibrational assignment
IR	Raman	calc. ^b	calc. ^c	
	214 mw	206	212	ring 1 + 2 out-of-plane def
	264 w	244	253	
	401 mw	394	407	N ₉ C _{1,2} + C _{5,6,7} bend
	435 w	427	442	ring 1 out-of-plane def
	536 m	529	544	C _{1,2,3} + C _{4,5,6} bend
591 ms	592 sh	589	604	ring 2 out-of-plane def
604 m	603 m	596	613	N ₉ C _{1,6} + O ₈ C _{7,6} bend
734 m	741 sh	751	763	CH wag
752 s	751 ms	756	767	C _{1,2,3} + C _{4,5,6} + C ₇ O ₈ N ₉ bend
809 m	812 vw	826	857	CH twist (ring 1)
868 m	869 mw	863	902	N ₉ O ₈ stretch
906 m	905 m	887	918	C _{1,2,3} + C _{3,4,5} + C _{4,5,6} bend
921 m	922 m	906	932	C ₇ O ₈ N ₉ bend
956 w	957 vw	956	968	C ₇ H twist
981 m	980 m	993	1008	ring 1 breathing
1113 s	1114 vw	1116	1155	C ₇ H twist
1141 m	1140 m	1133	1166	CH bend (ring 1)
1157 m	1156 m	1157	1190	
1238 m	1237 m	1234	1267	C _{6,7} O ₈ stretch
1258 w	1258 m	1249	1292	CH rock (ring 1)
1352 m	1357 m	1348	1390	CH rock (ring 1) + C ₁ N ₉ stretch
1381 s	1380 m	1365	1419	C ₁ N ₉ + C _{6,7} stretch
1410 m	1409 m	1398	1436	C _{1,6} + C _{3,4} stretch
1456 m	1454 vs	1465	1503	C _{2,3} + C _{4,5} stretch
1513 sh	1513 sh	1518	1563	C _{1,2,3} sym. stretch
1520 m	1518 m			
1555 m	1555 m	1555	1600	C _{4,5,6} sym. stretch
1641 s	1640 m	1637	1689	C _{1,2,3} + C _{4,5,6} + C _{5,6,7} as. stretch
3013 m	3012 m	3123	3188	CH stretch (ring 1)
3068 m	3071 s	3133	3198	
3106 m	3108 sh	3147	3212	
3128 m	3128 m	3219	3285	C ₇ H stretch

^a Abbreviations: ring 1 = phenyl ring, ring 2 = isoxazole ring, w = weak, m = medium, s = strong, sh = shoulder, stretch = stretching, bend = bending, twist = twisting, wag = wagging, rock = rocking, sym. = symmetric, as. = asymmetric. ^b Calculated with BPW91/6-31+G*. ^c Calculated with B3LYP/6-31+G*.

**Figure 3.** FT-Raman (a) and SERS (b) spectra of the anthranil molecule.

a strong interaction between the anthranil molecules and the silver surface, unlike the isoxazole species that have shown weak interactions with the metal surface not involving charge-transfer mechanism.³¹

Inspection of the structure of the anthranil species suggests that it may bind to the silver surface either through the lone

TABLE 2: Assignment of the Normal Vibrational Modes of the Anthranil Molecule to the SERS Bands

experimental		theoretical	
Raman	SERS	calc. ^b	vibrational assignment
214 mw	216 sh	208	ring 1 + 2 out-of-plane def
	237 s	217	Ag–N stretch +
264 w	270 sh	257	ring 1 + 2 out-of-plane def
401 mw	417 m	398	N ₉ C _{1,2} + C _{5,6,7} bend
435 w	446 m	426	ring 1 out-of-plane def
536 m	522 m	526	C _{1,2,3} + C _{4,5,6} bend
592 sh	620 m	581	ring 2 out-of-plane def
603 m	632 w	599	N ₉ C _{1,6} + O ₈ C _{7,6} bend
741 sh	758 m	741	CH wag
751 ms	768 sh	752	C _{1,2,3} + C _{4,5,6} + C ₇ O ₈ N ₉ bend
812 vw	794 mw	831	CH twist (ring 1)
869 mw	856 w	864	N ₉ O ₈ stretch
905 m	904 w	888	C _{1,2,3} + C _{3,4,5} + C _{4,5,6} bend
922 m	913 w	912	C ₇ O ₈ N ₉ bend
957 vw	949 m	956	C ₇ H twist
980 m	990 w	1000	ring 1 breathing
1114 vw	1120 w	1131	C ₇ H twist
1140 m	1162 sh	1136	CH bend (ring 1)
1156 m	1170 m	1161	
1237 m	1244 sh	1239	C _{6,7} O ₈ stretch
1258 m	1265 m	1254	CH rock (ring 1)
1348 sh	1335 m	1345	CH rock (ring 1) + C ₁ N ₉ stretch
1357 m	1367 ms		
1380 m	1384 s	1377	C _{1,6} + C _{3,4} stretch
1409 m	1417 s	1403	C _{1,6} + C _{3,4} stretch
1454 vs	1454 vs	1462	C _{2,3} + C _{4,5} stretch
1513 sh	1518 m	1523	C _{1,2,3} sym. stretch
1518 m	1524 m		
1555 m	1589 s	1563	C _{4,5,6} sym. stretch
1640 m	1640 sh	1639	C _{1,2,3} + C _{4,5,6} + C _{5,6,7} as. stretch
3071 s	3078 ms	3130	CH stretch (ring 1)
3128 m	3120 w	3226	C ₇ H stretch

^a Abbreviations: ring 1 = phenyl ring, ring 2 = isoxazole ring, w = weak, m = medium, s = strong, sh = shoulder, stretch = stretching, bend = bending, twist = twisting, wag = wagging, rock = rocking, sym. = symmetric, as. = asymmetric. ^b Calculated on the complex 1 with BPW91/6-31+G* for the N, C, O, and H atoms and LanL2DZ for the Ag atom.

pair electrons of the nitrogen or oxygen atoms or through the π electron system of the aromatic ring. To determine from a theoretical point of view the most probable binding possibility, DFT calculations have been performed on model compounds having a silver atom bound respectively to the nitrogen and oxygen atoms, and to the phenyl ring. It was found that the geometry of the compound with an Ag–O bond is not stable, and thus the existence of a molecule–metal interaction through the oxygen atom was theoretically excluded. Moreover, the total atomic charges of the nitrogen and oxygen atoms of the free anthranil molecule have been compared, and it was found that at the BPW91 theoretical level their values are $-0.307\ 177$ for the nitrogen atom and $0.246\ 744$ for the oxygen atom, respectively. Considering the fact that an increased negative charge on an atom increases the atom's probability to act as an adsorptive site,³² it becomes obvious that the anthranil molecules would bind the colloidal silver particles via the nitrogen atoms. One should also mention that the Ag–anthranil model complex with the Ag–N bond provides two possible configurations, one with the silver atom below the molecular plane and another one with the silver atom above this plane. According to the results obtained from DFT calculations concerning the total energy of both conformers, the latter isomer is the most stable one and will be further denoted as the Ag–anthranil model complex with an Ag–N bond. The optimized geometry of this compound, labeled as complex 1, is illustrated in Figure 4.

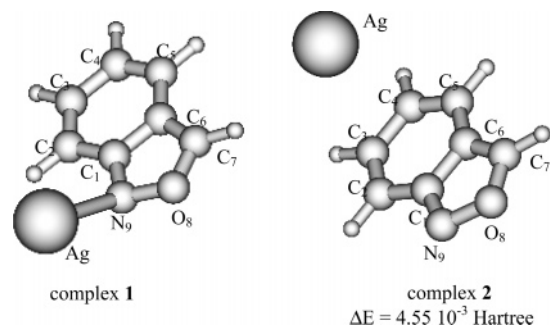


Figure 4. Optimized geometries of the most probable Ag-anthranil SERS complexes. The energy difference between both complexes is indicated in parentheses.

TABLE 3: Selected Theoretical Structural Parameters of Two Ag-Anthranil Model Complexes Compared with Those of the Free Anthranil Molecule

	complex 1 ^b	complex 2 ^b	anthranil ^c
bond lengths (pm)			
(CC _{Ph}) _{average}	141.655	141.958	141.828
C ₁ C ₂	142.583	143.000	142.978
C ₂ C ₃	138.194	138.056	138.144
C ₃ C ₄	143.644	144.540	143.900
C ₄ C ₅	138.060	138.577	138.172
C ₅ C ₆	142.686	142.521	142.797
C ₁ C ₆	144.767	145.055	144.979
C ₆ C ₇	138.478	138.488	138.526
C ₇ O ₈	134.747	134.839	134.988
O ₈ N ₉	141.030	140.757	140.825
N ₉ C ₁	134.786	134.074	134.196
bond angles (degree)			
C ₁ N ₉ O ₈	104.756	104.132	104.205
N ₉ O ₈ C ₇	110.289	110.908	110.842
O ₈ C ₇ C ₆	110.101	109.793	109.743
C ₂ C ₁ N ₉	127.893	127.199	127.287
C ₅ C ₆ C ₇	136.192	136.528	136.557
dihedral angle	179.513	179.655	180.0

^a Abbreviations: complex 1 = Ag-anthranil model complex having an Ag-N bond, complex 2 = Ag-anthranil model complex having an Ag atom bound to the phenyl group. ^b Calculated with BPW91/6-31+G* for the N, C, O, and H atoms and LanL2DZ for the Ag atom. ^c Calculated with BPW91/6-31+G*.

The other adsorption possibility of the anthranil species on the metal surface through the π electron system of the phenyl ring has been also theoretically tested. Thus, calculations on two model complexes, the first one having a silver atom bound to the benzene ring and the second one consisting of two silver atoms, one bound to the phenyl ring and another one bound to the nitrogen atom of the anthranil molecule, have been carried out. The calculations revealed that the geometry of the latter model compound is not stable and, thus, this adsorption possibility was excluded. The optimized geometry of the model compound having a silver atom bound to the benzene ring, denoted as complex 2, is shown in Figure 4.

The total energies, including zero point energy (ZPE) corrections, of all model complexes that were proved to be possible from a theoretical point of view, have been further compared, and it was found that the Ag-anthranil compound having an Ag-N bond (complex 1) is the most stable one. The calculated wavenumber values of this compound are given in Table 2 and were used for the assignment of the experimentally observed SERS bands.

As was already mentioned, the optimized geometries of the theoretically most probable SERS complexes are shown in Figure 4, while their structural parameters are listed in Table 3 together with those of the free anthranil molecule. As can be

seen from Table 3, the CC bond lengths of the most stable Ag-anthranil complex are shorter than those of the free anthranil molecule, while the NO and NC bond lengths of the isoxazole group are longer. On the contrary, a lengthening of the CC bonds can be observed for the other model SERS complex, while the NO and NC bond lengths of the isoxazole ring are shorter. According to the geometry optimization calculations, the anthranil unit is planar, while a slight deviation from the planarity of this unit was observed for both SERS complexes. The calculated dihedral angles between the benzene and isoxazole rings of both compounds were found to be 0.487 and 0.345°, respectively. These changes of the structural parameters of the SERS complexes relative to those of the free anthranil molecule should be mirrored in their vibrational spectra.

The SER spectrum of anthranil (Figure 3) presents an intense band at 237 cm⁻¹, which is characteristic for the SER spectra of N-adsorbed species and is ascribed to the Ag-N stretching vibration.³³ The existence of this band can be regarded as evidence of the anthranil species bonding to the silver surface through the lone pair electrons of the nitrogen atom, even if out-of-plane deformation vibrations of both benzene and isoxazole rings give rise to bands in approximately the same spectral region.

As one can see from Figure 3 and Table 2, the experimental SERS bands at 417, 632, and 768 cm⁻¹ attributed to the in-plane deformation vibration of both rings are shifted to higher wavenumbers up to 20 cm⁻¹ relative to their corresponding Raman bands. The band at 990 cm⁻¹ due to the breathing vibration of the benzene ring is also blue shifted in the SER spectrum by 10 cm⁻¹. The SERS band at 856 cm⁻¹ given by the NO stretching vibration is shifted to lower wavenumbers by 13 cm⁻¹ in comparison with its analogue Raman band. As revealed by theoretical calculations, the NO bond length of the most stable SERS complex is longer than that of the free molecule. The behavior of the NO stretching band in the SER spectrum supports the theoretical predictions that the Ag-anthranil complex with an Ag-N bond is the most probable one, otherwise a shift to higher wavenumber values of this band should have been observed in the SER spectrum. From Figure 3 and Table 2, one can also remark that most of the SERS bands present in the spectral range between 1400 and 1600 cm⁻¹, which are attributed to CC stretching vibrations, are shifted toward higher wavenumbers relative to their analogous Raman bands. This behavior agrees with the geometrical changes evidenced from the comparison of the CC bond lengths of the most stable SERS complex with those of the free anthranil molecule and confirms again that the model complex having an Ag-N bond is the most probable one. Thus, by taking into account the predictions of DFT calculations carried out on different SERS model complexes and from the comparison of the corresponding SERS and Raman bands, one can conclude that the anthranil molecules are adsorbed on the colloidal silver particles through the nonbonding electrons of the nitrogen atoms.

For a better understanding of the adsorption behavior of the anthranil species on the metal surface, the electronic absorption spectra of pure silver sol and the mixture of activated silver colloid and anthranil solution have been recorded and are presented in Figure 5. The spectrum of pure silver colloid (Figure 5a) shows a single absorption maximum at 412 nm due to small particle plasma resonance. The addition of anthranil to the activated sol (Figure 5b) causes a significant decrease and a shift of this absorption band toward longer wavelengths by 6 nm, while a new broad absorption signal appears at longer

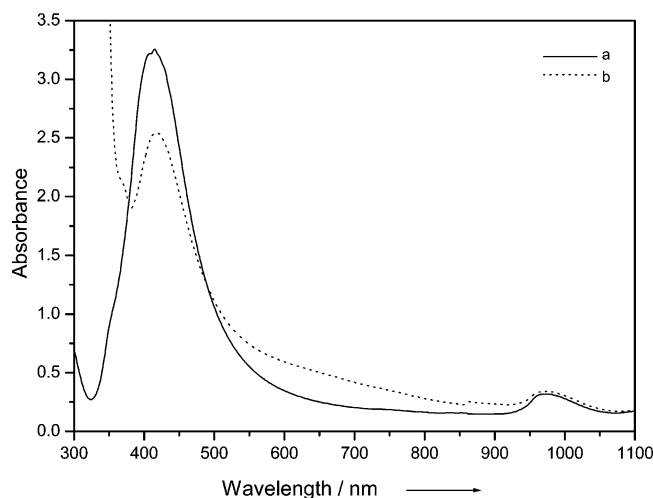


Figure 5. Absorption spectra of pure silver colloid (a) and with 10^{-1} M anthranil and 10^{-2} M NaCl (b).

wavelength values (around 700 nm). It is known that³¹ when two metallic spheres approach each other the band given by the small particle plasma resonance approximately remains at the original single sphere's wavelength, while a new band occurs at longer wavelengths. The latter absorption peak is known to arise from the aggregates of colloid particles formed upon addition of the adsorbed molecules.³⁴ However, this band has been reported to be due to a charge transfer between the metal and the adsorbate.³⁵ Unlike the isoxazole molecules, whose heteroatoms strongly impair the π electron delocalization and are considered to be physisorbed on the silver surface,³¹ the major changes evidenced between the Raman and SER spectra of anthranil corroborated with DFT calculations data obtained from different Ag–anthranil model complexes, and the features of the absorption spectrum of activated silver sol with added adsorbents allow us to conclude the chemisorption of the anthranil species on the colloidal silver particles and the contribution of the charge-transfer effect to the overall SERS enhancement.

By inspection of specific enhanced bands in the SER spectrum in agreement with the surface selection rules,^{36–38} the orientation of the adsorbed species relative to the metal surface can be determined. According to these rules, the vibrational modes that involve a large change of the polarizability perpendicular to the metal surface are the most enhanced. By comparing the SER and Raman spectra of the anthranil molecule, obviously the bands attributed to out-of-plane vibrations are mainly enhanced. Thus, the SERS bands at 446 and 620 cm^{-1} assigned to the out-of-plane deformation vibrations of the phenyl and isoxazole rings are enhanced in comparison with their corresponding Raman bands, while the bands given by the in-plane ring deformation vibrations present in the SER spectrum at 632 and 768 cm^{-1} are only weakly enhanced. The bands evidenced at 758, 794, 949, and 1120 cm^{-1} in the SER spectrum and assigned to the out-of-plane deformation vibrations of the CH groups of both rings (see Table 2) are also enhanced compared to their analogous Raman bands. However, in the high wavenumber region of the SER spectrum one can observe the enhancement of the bands at 3078 and 3120 cm^{-1} , which were clearly attributed to the CH stretching vibrations. Moreover, the band at 990 cm^{-1} assigned to the breathing vibration of the phenyl ring, together with the bands due to the CC stretching vibrations of both rings situated in the spectral range between 1400 and 1600 cm^{-1} , are also enhanced in the SER spectrum. Having in view all of these features of the SER spectrum, we predict

that the adsorbed anthranil molecules adopt a tilted orientation relative to the silver surface. By assuming that the silver atom of the most stable Ag–anthranil model complex approximates the metallic surface and applying the surface selection rules to this compound, the band enhancement evidenced in the experimental SER spectrum should appear. Therefore, we can affirm that the orientation of the adsorbed species determined by following the enhancement of the experimental SERS bands according to the surface selection rules consistently agrees with that of the Ag–anthranil model complex. The theoretical value of the dihedral angle formed by the silver atom and the isoxazole plane of the molecule was found to be 137.882°.

Conclusion

The Raman and infrared spectra of the anthranil molecule have been recorded, and the assignment of the vibrational modes has been performed on the basis of the results of density functional theory calculations. The SER spectrum of the molecule in colloidal silver suspension has been also recorded and analyzed. By correlating the spectroscopic changes evidenced between the Raman and SER spectra and the results of DFT calculations performed on different Ag–anthranil model complexes, it was concluded that the anthranil molecule is adsorbed on the colloidal silver surface through the lone pair electrons of the nitrogen atom. The contribution of the charge-transfer effect to the overall SERS enhancement has been confirmed by the spectral modifications of the electronic absorption spectrum of activated silver sol with added adsorbent. By following the enhancement of the SERS bands according to the surface selection rules, a tilted orientation of the adsorbed anthranil species relative to the metal surface has been predicted.

Acknowledgment. The authors thank the German Science Foundation (DFG, Sonderforschungsbereich 630 Project No. C1) for financial support.

References and Notes

- (1) Chang, R. K.; Furtak, T. E. *Surface Enhanced Raman Scattering*; Plenum Press: New York, 1982.
- (2) Van Duyne, R. P. *Chemical and Biochemical Application of Lasers*; Moore, C. B., Ed.; Academic Press: New York, 1978; Vol. 4, Chapter 5.
- (3) Campion, A.; Kambhampati, P. *Chem. Soc. Rev.* **1998**, 27, 241.
- (4) Jones, J. C.; McLaughlin, C.; Littlejohn, D.; Sadler, D. A.; Graham, D.; Smith, W. E. *Anal. Chem.* **1999**, 71, 596.
- (5) Kneipp, K.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Chem. Rev.* **1999**, 99(10), 2957.
- (6) Otto, C.; Van der Tweel, T. J.; de Mul, F. F.; Greve, J. J. *Raman Spectrosc.* **1986**, 17, 289.
- (7) Suh, J. S.; Moskovits, M. *J. Am. Chem. Soc.* **1986**, 108, 4711.
- (8) Loury, R. B. *J. Raman Spectrosc.* **1991**, 22, 805.
- (9) Moskovits, M. *Rev. Mod. Phys.* **1985**, 57, 783.
- (10) Lombardi, J. R.; Birke, R. L.; Lu, T.; Xu, J. *J. Chem. Phys.* **1986**, 84, 4174.
- (11) Creighton, J. A. *Surf. Sci.* **1983**, 124, 208.
- (12) Mille, G.; Guiliano, M.; Angelelli, J. M.; Chouteau, J. *J. Raman Spectrosc.* **1980**, 9, 339.
- (13) Armuth, V.; Berenblum, I. *Cancer Lett.* **1982**, 15(30), 343.
- (14) Sokovikov, Ya. V.; Sokovikova, I. N.; Kotov, A. D.; Orlov, V. Yu. *Toksikologicheskii Vestnik* **2002**, 2, 29.
- (15) Manolov, P.; Todorov, S. *Eksp. Med. Morfol.* **1974**, 13(1), 36.
- (16) Arya, V. P.; Shenoy, S. *J. Indian J. Chem.* **1976**, 14B(10), 780.
- (17) Doppler, T.; Schmid, H.; Hansen, H. *J. Helv. Chim. Acta* **1979**, 62, 271.
- (18) He, Y. Z.; Cui, J. P.; Mallard, W. G.; Tsang, W. J. *Am. Chem. Soc.* **1988**, 110, 3754.
- (19) Dryhurst, C. G. *Electrochemistry of Biological Molecules*; Academic Press: New York, 1977; p. 473.
- (20) Lee, P. C.; Meisel, D. *J. Phys. Chem.* **1982**, 86, 3391.
- (21) Brandt, S. E.; Cotton, T. M. *Physical Methods of Chem. Series*, 2nd ed.; Wiley: 1993; Vol. IX B, p. 670.
- (22) 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.; Ciolowski, 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.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Repogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A7; Gaussian Inc.: Pittsburgh, PA, 1998.
- (23) Becke, A. D. *Phys. Rev.* **1988**, A38, 3098.
- (24) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, B45, 13244.
- (25) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 1372.
- (26) Legge, F. S.; Nyberg, G. L.; Peel, J. B. *J. Phys. Chem.* **2001**, A105, 7905.
- (27) Barone, V. *J. Phys. Chem.* **1995**, 99, 11659.
- (28) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, 100, 16502.
- (29) Wong, M. W. *Chem. Phys. Lett.* **1996**, 256, 391.
- (30) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, 99, 3093.
- (31) Muniz-Miranda, M. *Vib. Spectrosc.* **1999**, 19, 227.
- (32) Kim, S. Y.; Joo, T. H.; Suh, S. W.; Kim, M. Y. *J. Raman Spectrosc.* **1986**, 17, 381.
- (33) Chowdhury, J.; Ghosh, M.; Misra, T. N. *Spectrochim. Acta* **2000**, A56, 2107.
- (34) Blatchford, C. G.; Campbell, J. R.; Creighton, J. A. *Surf. Sci.* **1982**, 120, 435.
- (35) Sanchez-Cortes, S.; Garcia-Ramos, J. V.; Morcillo, G.; Tinti, A. *J. Colloid Interface Sci.* **1995**, 175, 358.
- (36) Hallmark, V. M.; Campion, A. *J. Chem. Phys.* **1986**, 84, 2933.
- (37) Moskovits, M.; DiLella, D. P. *J. Chem. Phys.* **1980**, 73, 6068.
- (38) Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1984**, 88, 5526.