

FT-IR, FT-Raman and SERS spectra of anilinium sulfate

P. L. Anto,^a R. J. Anto,^b H. T. Varghese,^c C. Y. Panicker,^{d*} D. Philip^e and A. G. Brolo^f



The FT-IR and FT-Raman spectra of anilinium sulfate were recorded and analyzed. The surface-enhanced Raman scattering (SERS) was recorded from a silver electrode. The vibrational wavenumbers of the compound have been computed using the Hartree-Fock/6-31G* basis and compared with the experimental values. The molecule is adsorbed on the silver surface with the benzene ring in a tilted orientation. The presence of amino and sulfate group vibrations in the SERS spectrum reveal the interaction between amino and sulfate groups with the silver surface. The direction of the charge transfer contribution to SERS has been discussed from the frontier orbital theory. Copyright © 2009 John Wiley & Sons, Ltd.

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Keywords: anilinium sulfate; FT-IR spectra; FT-Raman spectra; SERS; Hartree-Fock *ab initio* calculations

Introduction

Surface-enhanced Raman scattering (SERS) is a useful technique in surface chemistry and physics because of its high sensitivity and the potential in providing some useful information about the nature and orientation of adsorbed molecular species and the adsorbate-metal interaction mechanism.^[1] Several pharmaceutical and industrial processes use aniline and its derivatives as starting materials because they can serve as precursors in the synthesis of dyes and sensitizer molecules, pesticides and antioxidants.^[2,3] They are also used in electro-optical industry, for the synthesis of technological materials with non-linear optical responses.^[4] The structures and the vibrational spectra of aniline and substituted aniline complexes are being studied extensively, since elucidation of their molecular properties as well as nature of reaction mechanism is of utmost importance. The structural, electronic and vibrational parameters of the aniline molecule change with inclusion of substituent groups because it leads to the variation of charge distribution in the molecule. Tzeng *et al.*^[5,6] reported extensive experimental and theoretical investigations focused on elucidating the structure and normal vibrations of aniline and its derivatives. The NH₂ vibrational modes of aromatic amines, such as benzidine, aniline and paraphenylenediamine, are found to have much effect on complex formation through amino nitrogen lone pairs. For instance, whilst the frequencies of the NH₂ stretching and NH₂ bending modes were found to decrease upon complexation, the NH₂ twisting and NH₂ wagging vibrational frequencies increased in all aniline, benzidine or paraphenylenediamine complexes.^[7-12] Sulfuric acid is an important industrial chemical, widely used in the production of fertilizers and in the synthesis of a variety of common products. The renewed interest in its properties originates from environmental concerns, such as acid rain and stratospheric ozone depletion. The infrared spectra of sulfuric acid complexes are reported by Givan *et al.*^[13-16] Hintze *et al.*^[17] reported the vibrational and electronic spectroscopy of sulfuric acid vapor, Tomykawa and Kanno^[18] reported the Raman study

of sulfuric acid at low temperatures, the *ab initio* vibrational calculations of sulfuric acid are reported by Miller *et al.*^[19] and the equilibrium structure of sulfuric acid is reported by Demaison *et al.*^[20] So far there is no report on the vibrational spectral analysis of the title compound. In the present study, the IR, Raman and SERS spectra of anilinium sulfate were investigated. The objectives were to produce a reliable vibrational assignment for that compound and determine its orientation, when adsorbed on a silver surface. The vibrational assignment was supported by theoretical study carried out using the Gaussian'03 software package.^[21]

Experimental

Anilinium sulfate was procured from Sigma-Aldrich, USA. The FT-IR and FT-Raman spectra were recorded using a Bruker IFS 66v FT-IR/FT-Raman spectrometer. The FRA 106 module attached to the IFS66v FT-IR spectrometer extended the capabilities of that system to FT-Raman. A Nd:YAG laser operating at 1064 nm was used as the excitation source. SERS spectra were obtained for anilinium sulfate adsorbed on an electrochemically roughened silver surface. The activation (roughening) procedure for the silver

* Correspondence to: C. Y. Panicker, Department of Physics, TKM College of Arts and Science, Kollam, Kerala, India. E-mail: cyphyp@rediffmail.com

a Department of Physics, St. Thomas College, Thrissur, Kerala, India

b Molecular Carcinogenesis and Chemoprevention Laboratory, Division of Cancer Research, Rajiv Gandhi Centre for Biotechnology, Thiruvananthapuram, Kerala, India

c Department of Physics, Fatima Mata National College, Kollam, Kerala, India

d Department of Physics, TKM College of Arts and Science, Kollam, Kerala, India

e Department of Physics, Mar Ivanios College, Trivandrum, Kerala, India

f Department of Chemistry, University of Victoria, Victoria, BC, Canada

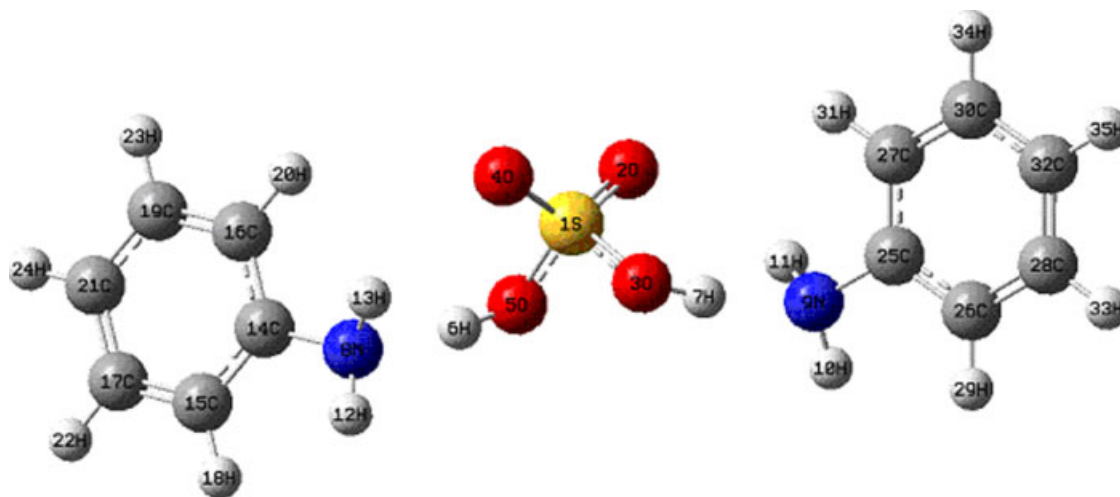


Figure 1. Optimized geometry of anilinium sulfate. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

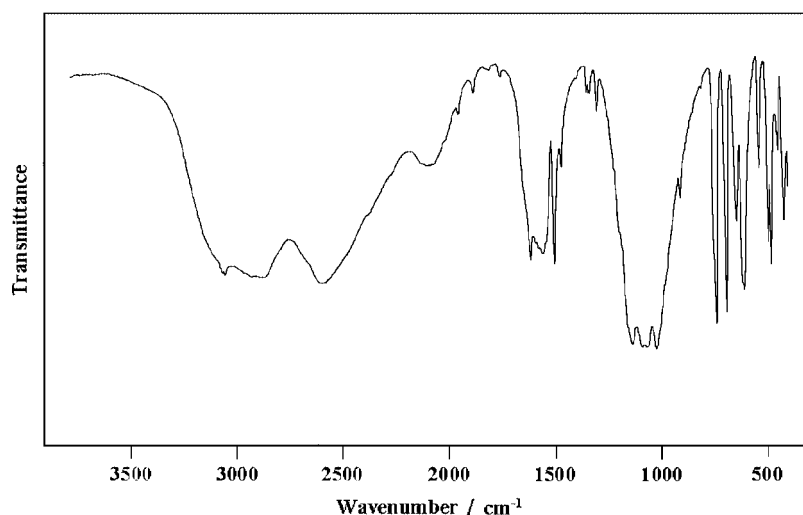


Figure 2. FT-IR spectrum of anilinium sulfate.

surface was described elsewhere.^[22] The roughened silver surface was immersed in a 1 mM solution of anilinium sulfate in 0.1 M KCl and the SERS was recorded *in situ*. The excitation source was a 17 mW He-Ne laser from Melles Griot. The excitation wavelength was 632.8 nm and the experiments were realized in backscattering geometry. The residual laser excitation and the Rayleigh scattering were removed using a super notch filter from Kaiser. The Raman radiation was then directed into a Kaiser Holospec f/1.4 spectrograph coupled with an Andor CCD detector (model DV-401-BV).

Computational Details

The vibrational wavenumbers were calculated using the Gaussian'03 software package on a personal computer. The geometry of anilinium sulfate was fully optimized without imposing external symmetry constraints using the 6-31G* basis set at the Hartree-Fock level of theory (Fig. 1). Since errors within this type of calculation are systematic, it is common practice to use empirical correction factors.^[23] In this study a unique scale factor of 0.8929 was employed to generate the final wavenumbers. The parameters corresponding to the optimized geometry of

anilinium sulfate are given as supplementary material (Table S1, Supporting Information). The calculated vibrational spectrum had no imaginary wavenumbers, which confirms that the calculated structure following optimization corresponded to an energy minimum. The spectral assignment was aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes.^[24,25]

Results and Discussion

IR and Raman spectra

Figures 2 and 3 show the FT-IR and FT-Raman of anilinium sulfate powder. The wavenumbers of the observed IR and Raman bands, their relative intensities, calculated values and the assignments are given in Table 1. The NH₂ scissoring vibrations of aromatic amines, expected^[26] around 1650 cm⁻¹ appear at around 1608 cm⁻¹ in both spectra and at 1641 and 1615 cm⁻¹ from the calculation. The δ NH₂ scissoring vibrations are reported at 1629 cm⁻¹ for sulfanilamide^[27] and at 1637 cm⁻¹ in IR, 1634 cm⁻¹ in Raman and 1642 cm⁻¹ in HF for orthanilic acid.^[28] The δ NH₂ scissoring modes

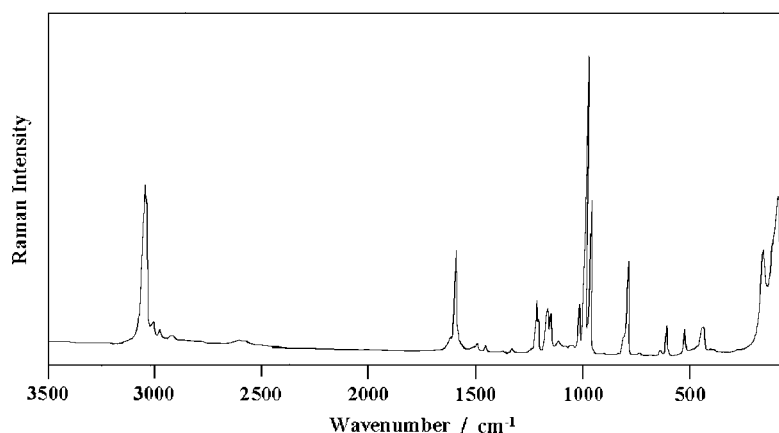


Figure 3. FT-Raman spectrum of anilinium sulfate.

are reported at 1621, 1597 cm^{-1} (IR), 1621, 1602 cm^{-1} (Raman) for para substituted halogeno anilines^[29] and at 1630 cm^{-1} for 2-aminobenzyl alcohol.^[30] According to Roeges,^[26] $\rho/\tau\text{NH}_2$ vibration is expected in the region $1070 \pm 50 \text{ cm}^{-1}$ and in the present case the bands observed at 1068, 1023 cm^{-1} (IR) and 1028 cm^{-1} (Raman) are assigned as $\rho/\tau\text{NH}_2$ modes. The HF calculations predict these modes at 1063 and 1044 cm^{-1} , respectively. For orthanilic acid^[28] these modes are reported at around 1101 cm^{-1} experimentally and at 1112 cm^{-1} theoretically. Krishnakumar and Balachandran^[31] and Altun *et al.*^[32] reported these modes at 1130, 1126, 1089, 1085 cm^{-1} for dibromo, nitro and methylthioaniline complexes, and at 1040, 1030, 1008 cm^{-1} for methyl aniline complexes, respectively. Kurt *et al.*^[33] observed the ωNH_2 vibration for chloromethylaniline at 667 cm^{-1} in IR spectrum and at 695 cm^{-1} in HF calculation. Tzeng *et al.*^[5] calculated the wavenumber of wagging vibration of amino group at 649 cm^{-1} and experimentally at 665 cm^{-1} and established the mixing between the out-of-plane amino group wagging and the δPh bending of aniline.^[5,33] For the title compound, the wagging vibrations of NH_2 are observed at 606 cm^{-1} in the IR spectrum, at 619 cm^{-1} in the Raman spectrum and at 608 cm^{-1} theoretically, which is consistent with its expected presence in the region^[26] of $620 \pm 100 \text{ cm}^{-1}$.

Primary aromatic amines with nitrogen directly attached to the ring absorb in the region 1330–1260 cm^{-1} due to the stretching of the phenyl carbon–nitrogen bond.^[5,34] We have observed this νCN mode at 1226 cm^{-1} in the Raman spectrum and at 1225 cm^{-1} theoretically. Akalin and Akyuz^[35] assigned C–N stretching vibration at 1268 cm^{-1} in the Raman spectrum for paraphenylenediamine, at 1226, 1227, 1229 cm^{-1} for paraphenylenediamine complexes and at 1266, 1263 and 1216 cm^{-1} theoretically.

The asymmetric and the symmetric stretching vibrations of $\text{S}=\text{O}_2$ are reported in the range 1433–1446 cm^{-1} and 1172–1214 cm^{-1} respectively.^[13–16] For the title compound, the *ab initio* calculations give these modes at 1420 and 1156 cm^{-1} , respectively while no bands were observed experimentally. Givan *et al.*^[13,15] reported S-(OH)₂ deformation bands at 1178 cm^{-1} and 1148 cm^{-1} as weak bands. The weak bands observed at 1161 cm^{-1} in Raman spectrum and at 1162 cm^{-1} in HF calculation are assigned as the deformation bands S-(OH)₂ for the title compound. In the present case, the calculated band at 861 cm^{-1} is assigned as S-(OH)₂ stretching vibration, which is in agreement with the reported values.^[13–16] The bands at around 532 cm^{-1} and 444 cm^{-1} are assigned as the deformation bands of $\text{S}=\text{O}_2$ group.

For H_2SO_4 complexes these deformation bands are reported in the range^[13–16] 450–550 cm^{-1} .

The existence of one or more aromatic rings in a structure is normally readily determined from the C–H and C=C–C ring related vibrations. The C–H stretching occurs above 3000 cm^{-1} and is typically exhibited as a multiplicity of weak to moderate bands compared with the aliphatic C–H stretch.^[36] In the present case, the *ab initio* calculations predict the $\nu\text{C–H}$ modes at 3017, 3028 and 3092 cm^{-1} . The bands observed at 3051 cm^{-1} in the IR spectrum and at 3017 and 3070 cm^{-1} in the Raman spectrum are assigned as the $\nu\text{C–H}$ modes of the phenyl ring. The benzene ring possesses six ring-stretching vibrations, of which the four with the highest wavenumbers (occurring respectively near 1600, 1580, 1490 and 1440 cm^{-1}) are good group vibrations. In the absence of ring conjugation, the band near 1580 cm^{-1} is usually weaker than that at 1600 cm^{-1} . The fifth ring stretching vibration is active near $1355 \pm 35 \text{ cm}^{-1}$, a region which overlaps strongly with that of the C–H in-plane deformation and the intensity is in general, low or medium high.^[26,37] The sixth ring stretching vibration or ring breathing mode appears as a weak band near 1000 cm^{-1} in mono substituted benzenes.^[26] The very strong band observed at 1005 cm^{-1} in the Raman spectrum is assigned as ring breathing mode. The *ab initio* calculations give this mode at 1010 cm^{-1} . The bands observed at 1608, 1498 and 1462 cm^{-1} in the IR spectrum and at 1609 and 1458 cm^{-1} in the Raman spectrum are assigned as νPh ring-stretching modes. As seen from Table 1, the *ab initio* calculations give these modes^[26] in the range 1615–1345 cm^{-1} .

The C–H out-of-plane deformations^[26] are observed between 1000 and 700 cm^{-1} . Generally, the C–H out-of-plane deformations with the highest wavenumbers have a weaker intensity than those at lower wavenumbers. The out-of-plane C–H deformation γCH at 736 cm^{-1} and the out-of-plane ring deformation δPh at 688 cm^{-1} in the IR spectrum form a pair of strong band characteristics of mono substituted benzene derivatives.^[26,38] From the study of phenyl ammonium hexafluorosilicate,^[39] there are several very weak, medium and strong bands relative to the in-plane bending of C–H vibration in the IR spectrum in a range 1320–1040 cm^{-1} and in the Raman spectrum in a range 1211–1030 cm^{-1} . For aniline complexes, Rai *et al.*^[40] reported the C–H in-plane bending between 1303 and 1048 cm^{-1} in the IR spectrum and in a range 1308–1048 cm^{-1} in the Raman spectrum. The multiplicity of the bands appearing in this region can be explained by such splitting of some IR degenerate modes corresponding to the free benzene ring as well as by the eventual activation of some Raman bands

Table 1. Calculated vibrational wavenumbers (in cm^{-1} , scaled), measured infrared and Raman band positions and assignments for anilinium sulfate

$\nu(\text{HF})$ (cm^{-1})	$\nu(\text{IR})$ (cm^{-1})	$\nu(\text{Raman})$ (cm^{-1})	$\nu(\text{SERS})$ (cm^{-1})	Assignments
3425	–	–	–	$\nu_a\text{NH}_2$
3343	–	–	–	$\nu_s\text{NH}_2$
3118	–	–	–	$\nu\text{OH}(\text{H-bond})$
3092	–	3070 s	–	νCH
3028	3051 mbr	–	–	νCH
3017	–	3017 w	–	νCH
–	2933 m	–	–	Overtone/combination
–	2875 mbr	–	–	Overtone/combination
–	2595 mbr	–	–	Overtone/combination
–	2097 w	–	–	Overtone/combination
–	1725 w	–	–	Overtone/combination
1641	–	–	1669 m	δNH_2
1615	1608 m	1609 m	1591 vs	$\delta\text{NH}_2, \nu\text{Ph}$
1494	1498 s	–	–	νPh
1466	1462 w	1458 vw	–	νPh
1420	–	–	1428 w	$\nu_a\text{S}=\text{O}_2$
1345	–	–	1372 m	$\delta\text{CH}, \nu\text{Ph}$
1335	1328 vw	–	1317 w	δCH
1277	1292 vw	–	1278 w	δCH
1225	–	1226 w	1223 vs	νCN
1162	–	1175 w	1184 m	$\delta\text{CH}, \delta\text{S}(\text{OH})_2$
1156	–	–	1145 w	$\delta\text{CH}, \nu_s\text{S}=\text{O}_2$
1134	1137 sbr	–	–	δCH
1063	1068 sbr	–	1036 m	$\delta\text{CH}, \gamma\text{NH}_2$
1044	1023 sbr	1028 w	1028 vs	$\delta\text{CH}, \gamma\text{NH}_2$
1010	–	1005 vs	981 s	$\delta\text{CH}, \text{ring breathing}$
978	–	978 m	–	γCH
927	–	–	919 m	γCH
900	905 m	–	–	γCH
861	–	–	864 w	$\nu_s\text{S}(\text{OH})_2$
841	–	–	825 m	γCH
808	–	801 w	778 m	γCH
740	736 s	–	740 m	γCH
690	688 vs	–	700 m	γPh
608	606 sbr	619 w	606 m	$\delta\text{Ph}, \omega\text{NH}_2$
608	–	–	583 w	$\delta\text{Ph}, \omega\text{NH}_2$
551	–	–	–	$\omega\text{S}=\text{O}_2$
545	532 w	534 w	–	$\delta\text{S}=\text{O}_2$
505	490 m	–	489 m	$\gamma\text{Ph}(\text{X})$
502	477 m	–	473 w	$\gamma\text{Ph}(\text{X})$
444	444 w	445 w	445 w	$\gamma\text{Ph}(\text{X}), \delta\text{O}=\text{S}=\text{O}$
416	418 w	–	–	γPh
155	–	173 m	–	$\tau\text{Ph}, \tau\text{H}_2\text{SO}_4$
94	–	108 s	–	$\tau\text{Ph}, \tau\text{H}_2\text{SO}_4$

ν , stretching; δ , in-plane bending; γ , out-of-plane bending; ω , wagging; τ , torsional; X, substituent sensitive; Ph, phenyl; s, strong; w, weak; br, broad; v, very; m, medium; sh, shoulder; s, symmetric a, asymmetric.

under the lowering of symmetry effect when benzene ring is mono substituted. We have observed the $\delta\text{C}-\text{H}$ vibrations between 1328 and 1023 cm^{-1} in the IR spectrum and between 1175 and 1005 cm^{-1} in the Raman spectrum. The theoretical calculations show excellent coincidence giving $\delta\text{C}-\text{H}$ vibrations in a range 1345–1010 cm^{-1} .

Geometrical parameters

The reported values of $\text{S}=\text{O}$ in SO_2 and SO_3 molecules are 1.4308, 1.4469 Å and 1.4173, 1.4261 Å, respectively.^[41,42] In the present case, the *ab initio* calculations give $\text{S}=\text{O}$ bond length as 1.4205 Å and $\text{S}-\text{O}$ as 1.5537 Å. Clerbaux and Colin^[43] reported the $\text{S}-\text{O}$ bond length as 1.4811 and 1.4931 Å, and Demaison *et al.*^[20] reported $\text{S}-\text{O}$ in the range 1.5750–1.6119 Å, $\text{S}=\text{O}$ in the range 1.4111–1.4301 Å and according to Miller *et al.*^[19] $\text{S}=\text{O}$ = 1.446 Å and $\text{S}-\text{O}$ = 1.627 Å. According to Natsheh *et al.*^[44] the bond length $\text{O}-\text{H}$ = 0.98, $\text{S}-\text{O}$ = 1.626, $\text{S}=\text{O}$ = 1.441 Å and Hintze *et al.*^[17] give the corresponding lengths as 0.968, 1.593 and 1.423 Å. According to Anderson *et al.*^[45] the SO bond lengths lie in the range 1.452–1.5666 Å and the CN bond lengths in the range 1.472–1.467 Å. The $\text{O}-\text{S}-\text{O}$ angles are reported in the range^[20,44] 101.4–102.3° whereas in the present case, the corresponding value is 103.0°. The bond angles for SO_4 moiety are reported^[45] in the 104.9–113.6° range. The CCN bond angles are reported^[45] as 118.6–119.5°. For the title compound, the *ab initio* calculations give an $\text{S}-\text{O}-\text{H}$ angle at around as 111.1° whereas the reported values are in the range^[20,41,44] 106.5–108.5°. The difference between the reported experimental values and calculated values is observed. This must be due to the fact that the experimental results belong to the solid phase and the theoretical calculations belong to the gaseous phase of a single molecule. For sulfuric acid^[19,20] the $\text{O}-\text{S}=\text{O}$ angle is reported in the range 105.2–108.5° whereas in the present case the corresponding range is 106–108.7°. For the title compound the *ab initio* calculation give $\text{O}=\text{S}=\text{O}$ as 121.1° whereas in sulfuric acid, the corresponding value^[20,44] is 125° and 124°. In the present case, the dihedral angles (Table S1, Supporting Information) of the H_2SO_4 moiety is in agreement with the reported values.^[20,44] The $\text{C}-\text{C}-\text{N}$ bond angle values (Table S1, Supporting Information) of anilinium sulfate are in agreement with the bond angle reported for aniline and transition metal aniline complexes.^[36,46] The bond angles $\text{C}-\text{C}-\text{N}$, $\text{H}-\text{N}-\text{H}$ and $\text{C}-\text{N}-\text{H}$ of anilinium sulfate are in agreement with the bond angles reported for aniline derivatives.^[5,46] In the amino group, the nitrogen atom is likely out-of-plane, with a torsional angle $\text{C}-\text{C}-\text{C}-\text{N}$ around 177° or (around 3°). Existence of this angle has been interpreted to be caused by the asymmetric interaction between the NH_2 group and the benzene ring plane. This interaction is common to all aniline derivatives.^[5,47] The $\text{C}-\text{N}$ distance in anilinium sulfate, 1.4196 Å, is similar to the measured value in aniline^[48] and (1.43 Å and calculated 1.414 Å) in *t*-methyl aniline.^[49,50] The $\text{C}_{14}-\text{C}_{16}$ ($\text{C}_{25}-\text{C}_{27}$) bond found to be slightly longer than $\text{C}_{14}-\text{C}_{15}$ ($\text{C}_{25}-\text{C}_{26}$) bond of the ring by 0.0025 Å.

SERS spectrum

The SERS spectrum of anilinium sulfate (Fig. 4) was recorded in the wavenumber range between 1950 and 450 cm^{-1} . The relative intensities of the SERS bands are expected to differ significantly from those of the normal Raman spectrum owing to the specific selection rules.^[51] According to the surface selection rules when a molecule is adsorbed flat on the silver surface, its out-of-plane bending modes will be more enhanced when compared with its in-plane bending modes and vice versa when it is adsorbed perpendicular to the surface.^[52,53] It is further seen that vibrations involving groups that are close to the silver surface will be more enhanced. It has been suggested that when the wavenumber difference of the aromatic modes between a normal Raman band and SERS is less than 5 cm^{-1} , the molecular plane will be perpendicular to the silver surface.^[54]

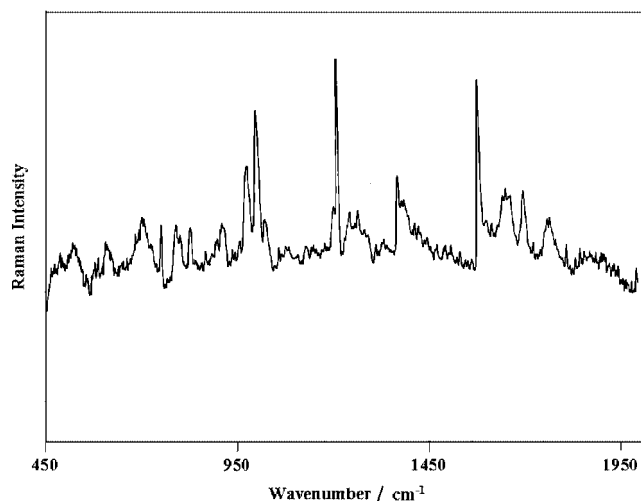


Figure 4. SERS spectrum of anilinium sulfate.

The $S=O_2$ stretching vibrations are observed in the SERS spectrum at 1428 and 1145 cm^{-1} but they are absent in the normal Raman spectrum. This indicates that the $S=O_2$ group is probably near to the metal surface. Also the presence of SERS bands at 864 and 445 cm^{-1} supports that assumption. Similarly, the enhanced medium intensity SERS band at 1184 cm^{-1} is assigned for $\delta S-(OH)_2$ the bending mode. This again supports the possibility of direct interaction between the sulfate group and the silver surface. This is justifiable because the modes of groups directly interacting with the metal surface will be prominent in SERS spectrum and undergo a wavenumber shift.^[55,56]

In the SERS spectrum of *p*-nitroaniline, the $\nu C-N$ is strongly enhanced, which indicates that the NH_2 group interacts more with metal surface.^[57] This interaction causes weakening of the $C-N$ bond. Hence more molecules are subjected to absorption and are responsible for strong enhancement of $\nu C-N$ in the SERS spectrum. Also, for *p*-nitroaniline, the enhanced band at 1630 cm^{-1} , corresponding to δNH_2 , suggests that the interaction between the amino group and the metal surface is strong.^[57] In the case of *p*-aminobenzoic acid, the $\nu C-N$ band is present in the SERS spectrum at 1253 cm^{-1} , and at 1279 cm^{-1} in the normal Raman spectrum.^[58] This means that this band shifted by ~ 26 cm^{-1} upon the surface adsorption of *p*-aminobenzoic acid onto silver. Such a shift was invoked by Holze^[59] to conclude that aniline interacts with the silver surface via its NH_2 group. In the present case, we observed δNH_2 in the SERS spectrum at 1669 and 1591 cm^{-1} . Also the $\nu C-N$ band is present at 1223 cm^{-1} as a very strong band in the SERS spectrum. The presence of these NH_2 modes indicates the interaction between the anilinium and the metal surface through the amino group. The presence of the deformation modes of the NH_2 group at 1036 and 583 cm^{-1} supports the argument. Also the substituent sensitive vibrations at 489, 473 and 445 cm^{-1} in the SERS spectrum support the interaction of amino group with the metal surface. The NH_2 group is almost pyramidal about the nitrogen atom in aromatic amine, and the N atom is sp^3 -hybridized, and the lone pair occupying p orbital is almost perpendicular to the plane of the molecule. The phenyl ring moiety of the aniline sulfuric acid is planar and is very well suited to π -bonding in a flat orientation. Since the NH_2 moiety is not planar, the phenyl ring moiety is not in a favored position to make π -bonding in a flat orientation. Therefore the phenyl ring makes π -bonding with silver surface in a slightly upward inclined

position (tilted orientation). Also the sulfate moiety with negative charge can make interactions with the silver surface. This might explain the dominance of the benzene ring vibrations at 1591 and 1372 cm^{-1} in the SERS spectrum. We have argued that those vibrations, which result in the most charge transfer in and out of the metal in synchronism with the nuclear motion accompanying them, will be most enhanced.^[60] When π -bonded through the benzene ring, the ring vibrations become good candidates for such charge transfer, and should therefore be strongly present in the SERS spectrum.

The in-plane bending vibrations of the phenyl ring are present at 1372, 1317, 1278, 1184, 1145, 1036, 1028, 606, and 583 cm^{-1} and the out-of-plane bending modes are present at 919, 825, 778, 740, and 700 cm^{-1} in the SERS spectrum. From the intensities of the out-of-plane and in-plane bending of vibrations of the benzene ring, it can be inferred that, for anilinium sulfate adsorbed on silver, the benzene ring has a 'tilted orientation'.

Apart from the interaction of the amino group in the adsorption process, the SO_4^{2-} group can also bind to the silver surface through the oxygen atom or OH moiety or through both of them. A more favored adsorption site can be enumerated theoretically by estimating the partial atomic charges on each of these probable active sites.^[61,62] Since the silver surface is positively charged, it is possible that the sulfate site with more negative charge density on the atom will have higher probability of adsorption. Theoretical results estimated from the atom will have higher probability of adsorption. Theoretical results estimated from HF *ab initio* calculations show that the partial atomic charges on the nitrogen, oxygen atoms and OH moiety determined by natural population analysis are -0.979 , -0.662 and -0.797 respectively. The negative charge density is thus observed to be more appreciable on the nitrogen atom than others, thereby indicating the active involvement of the nitrogen atom on the adsorption process. The appearance of a strong band at 1223 cm^{-1} in the SERS spectrum ascribed to the $\nu C-N$ stretching indicates that the amino group of the title compound is indeed adsorbed through the nitrogen atom.

The charge transfer mechanism of SERS can be explained by the resonant Raman mechanism in which charge transfer excitations from the metal to the adsorbed molecule or vice versa occur at the energy of the incident laser wavenumber.^[63,64] The frontier orbital theory plays a significant role in the understanding of the charge transfer mechanisms of SERS.^[65,66] Two types of charge transfer mechanisms are predicted. One is molecule to metal and the other is metal to molecule. Molecule to metal charge transfer excitations occur when an electron is transferred from the highest occupied molecular orbital (HOMO) of the adsorbate to the Fermi level of the metal. Conversely transfer of an electron from the Fermi level of the metal to the lowest unoccupied molecular orbit (LUMO) results in metal to molecule charge transfer.^[65,67-69] The theoretical results shows that HOMO, LUMO and LUMO+1 energies of the molecule are -0.312 , 0.139 and 0.140 eV, respectively, which are energetically much lower than the Fermi level of the silver ($+5.48$ eV).^[70] Here we conclude that the metal to molecule charge transfer interactions is more preferred in our case. The electron is probably transferred from the metal to the LUMO of the molecule.

Conclusion

The FT-IR, FT-Raman and SERS spectra of anilinium sulfate were studied. The molecular geometry and wavenumbers have been

calculated theoretically. The presence of in-plane and out-of-plane modes of phenyl ring in the SERS spectrum suggest a tilted orientation of the molecule with respect to the silver surface. The presence of amino and sulfate group vibrations in the SERS spectrum show the interaction between these groups and the silver surface.

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Supporting information

Supporting information may be found in the online version of this article.

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