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Potential-dependent SERS profile of orthanilic acid on silver electrode

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FT-IR and FT-Raman spectra of orthanilic acid were recorded and analyzed. Surface-enhanced Raman scattering (SERS) spectrum was recorded on a silver electrode surface. The vibrational wavenumbers were computed by the *ab initio* method using HF/6−31G* basis and they were found to be in good agreement with the experimental values. Potential dependence of the SERS profile was studied. The profile was prominent at electrode potentials of −0.3 and −0.8 V. The selective enhancement of different bands showed a change in orientation of the molecule on the silver surface. Copyright © 2006 John Wiley & Sons, Ltd.

INTRODUCTION

The use of aniline derivatives has been pursued to obtain conducting polymers with a variety of physical and chemical characteristics: increased solubility in a range of solvents, increased stability, wider color changes, etc.[1] Orthanilic acid has a number of applications in the synthesis of organic dyes.[2] IR spectral analysis of dipolar isomeric aminobenzene sulfonic acids was reported by Ganguly *et al.*[3] X-ray diffraction studies on *meta*,[4] *para*[5] and *ortho*[2] anilic acids have confirmed their dipolar structures in the solid state. In the present study, the IR, Raman and potential-dependent surface-enhanced Raman scattering (SERS) profile of orthanilic acid were investigated to get an idea regarding the orientation of the molecule on the silver surface and the optimum electrode potential for SERS activity. Theoretical calculations of the IR and Raman vibrational wavenumbers were made using Gaussian'03 software package.[6]

EXPERIMENTAL

Orthanilic acid was procured from Sigma-Aldrich, USA. The FT-IR and FT-Raman spectra (Figs 1 and 2) were recorded using a Bruker IFS 66v FT-IR/FT-Raman spectrometer. The FRA 106 module attached to the IFS 66v FT-IR spectrometer provided the FT-Raman spectral measurements. An Nd:YAG laser operating at 1064 nm was used as the excitation source. The detector was a Ge diode cooled to liquid-nitrogen temperature. SERS spectra (Fig. 3) were recorded using a confocal microprobe Raman system (LabRam I, Dilor, France).[7] The excitation wavelength in this case was 632.8 nm from an air-cooled He–Ne laser. The potentials applied to cells during Raman measurements were controlled by a PAR 173 Potentiostat (EG & G). Square waves were generated by a GFB-8016G function generator (Good Will Instrument, Co. Ltd). The reference electrode was the saturated calomel electrode (SCE); thus all the potentials are quoted *vs* SCE. The details of the Raman system and pretreatment of the silver electrode can be found elsewhere.[7,8]

COMPUTATIONAL DETAILS

The vibrational wavenumbers were calculated using Gaussian'03 software package on a personal computer. The wavenumbers computed at the Hartree−Fock level contain known systematic errors owing to neglecting the electron correlation.[9] We, therefore, have used the scaling factor value of 0.8929 for HF/6−31G* basis. Parameters corresponding to optimized geometry of orthanilic acid (Fig. 4) are given in Table 1. The calculated vibrational spectrum had no imaginary wavenumbers, which helped us to confirm that the structure of the title compound deduced following optimization corresponded to energy minimum. In total there are 48 vibrations from 3542 to 70 cm^{-1}.
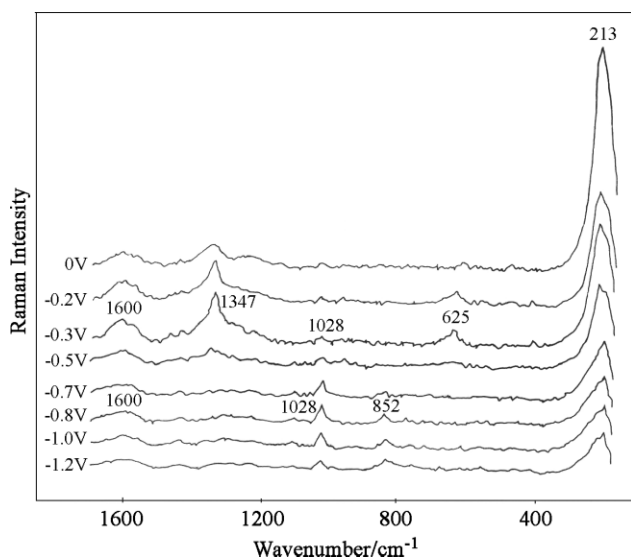
*Correspondence to: C. Yohannan Panicker, Department of Physics, TKM College of Arts and Science, Kollam, Kerala, 691 005, India. E-mail: cyphyp@rediffmail.com
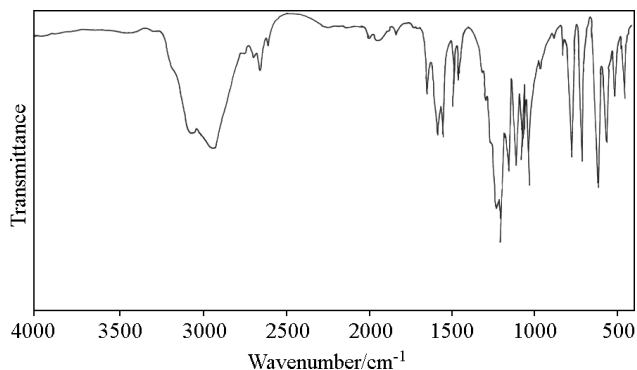
Figure 1. FT-IR spectrum of orthanilic acid 400–4000 cm^{-1}.
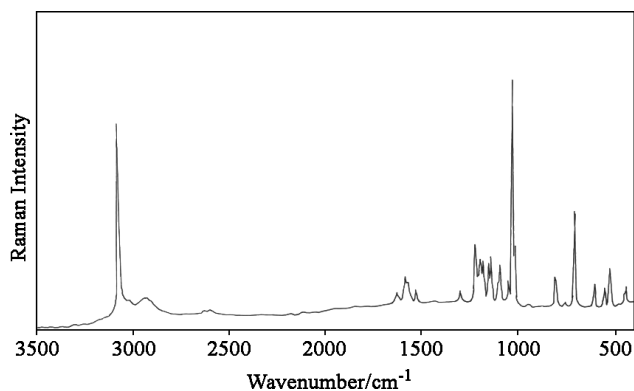
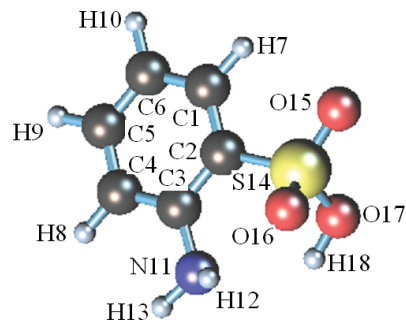**Figure 2.** FT-Raman spectrum of orthanilic acid 400–3500 cm^{-1}.

Figure 3. SERS spectrum of orthanilic acid 200–1800 cm^{-1}.

RESULTS AND DISCUSSION

IR and Raman spectra

Band assignments have been made on the basis of the published work on selected organic structures,[10] selected

Figure 4. Optimized geometry of orthanilic acid.

benzene derivatives,[11] Colthup *et al*.[12] and Silverstein and Webster.[13] The observed Raman and IR bands with their relative intensities, calculated values and assignments are given in Table 2. The modes are numbered as suggested by Miller.[14]

In sulfanilamide,[15] υ_{as} NH$_2$ is observed at 3478 cm^{-1} in the IR spectrum and δNH$_2$ at 1629 cm^{-1} in both the IR and Raman spectra. As suggested by Roeges,[10] the bands seen at 3400 and 3233 cm^{-1} in the IR spectrum are assigned to the asymmetric and symmetric NH$_2$ stretching modes. The calculated values for these modes are 3443 and 3350 cm^{-1}, respectively. The NH$_2$ scissoring vibration of the aniline ring, expected[10] around 1650 cm^{-1}, appears at 1637 cm^{-1} in the IR spectrum and at 1642 cm^{-1} from calculations.

The CH stretching vibrations in the IR spectrum are observed at 3150 and 3069 cm^{-1}, while in the Raman spectrum a very strong band is observed at 3080 cm^{-1} with weak bands at 3156 and 3040 cm^{-1}. According to Roeges[10] υCH is expected in the region 3000–3110 cm^{-1}. The calculated values for these modes are 3052, 3032, 3017 and 3001 cm^{-1}. The strong, broad band at 2936 cm^{-1} in the IR spectrum and the weak band 2948 cm^{-1} in the Raman spectrum can be typically observed[12] in the spectra of sulfonic acid and are due to OH stretching. The bands in the range 2713–1700 cm^{-1} in the IR spectrum are assigned to overtones/combinations of the hydrogen-bonded OH bending modes that arise from proton tunneling and Fermi resonance interaction.[16–20] The υPh[10] vibrations are observed in the range 1343–1608 cm^{-1}. The values are in agreement with the results given by Varghese *et al*.[15] and Topacli and Kesimli[21] for sulfanilamide, and Panicker *et al*.[22] for sulfanilic acid.

Bands at 1230, 1204, 1065 and 1043 cm^{-1} in the IR spectrum and 1225, 1208, 1062 and 1040 cm^{-1} in the Raman spectrum derive from the presence of the SO$_3$H group.[3,23] The in-plane CH deformation vibrations are assigned in the range 1027–1287 cm^{-1} in the IR and Raman spectra.[10] The out-of-plane CH deformations are observed at 954, 865 and 771 cm^{-1} in the IR spectrum.[10] The γCH band at 954 cm^{-1} is not pure but contains significant contribution of the mode γCN.[15,24]

Substituent-sensitive out-of-plane ring deformation is observed at 504 cm^{-1} in the IR spectrum and at 532 cm^{-1} in the Raman spectrum.[10] The band at 706 cm^{-1} in the IR

Table 1. Optimized geometrical parameters of orthanilic acid, atom labeling is according to Fig. 4

Bond lengths (Å)

C_1-C_2	1.3849	C_1-C_6	1.3833	C_1-H_7	1.0728
C_2-C_3	1.3987	C_2-S_{14}	1.7615	C_3-C_4	1.3881
C_3-N_{11}	1.4035	C_4-C_5	1.3848	C_4-H_8	1.0757
C_5-C_6	1.3848	C_5-H_9	1.0752	C_6-H_{10}	1.0737
$N_{11}-H_{12}$	1.0021	$N_{11}-H_{13}$	0.9988	$S_{14}-O_{15}$	1.4180
$S_{14}-O_{16}$	1.4303	$S_{14}-O_{17}$	1.5796	$O_{17}-H_{18}$	0.9582

Bond angles (°)

A(2,1,6)	119.8718	A(2,1,7)	119.0525	A(6,1,7)	121.0717
A(1,2,3)	121.4866	A(1,2,14)	119.1910	A(3,2,14)	119.3100
A(2,3,4)	117.9295	A(2,3,11)	120.0715	A(4,3,11)	121.8961
A(3,4,5)	120.5090	A(3,4,8)	119.4335	A(5,4,8)	120.0564
A(4,5,6)	121.0869	A(4,5,9)	119.0652	A(6,5,9)	119.8463
A(1,6,5)	119.1012	A(1,6,10)	120.2213	A(5,6,10)	120.6757
A(3,11,12)	113.0619	A(3,11,13)	112.7995	A(12,11,13)	110.2917
A(2,14,15)	109.6987	A(2,14,16)	108.4778	A(2,14,17)	102.3724
A(15,14,16)	120.6601	A(15,14,17)	106.3121	A(16,14,17)	107.7558
A(14,17,18)	109.7528	–	–	–	–

Dihedral angles (°)

D(6,1,2,3)	−0.716	D(6,1,2,14)	177.994	D(7,1,2,3)	−179.9911
D(7,1,2,14)	−1.2811	D(2,1,6,5)	−0.4043	D(2,1,6,10)	−179.9160
D(7,1,6,5)	178.8559	D(7,1,6,10)	−0.6558	D(1,2,3,4)	1.3368
D(1,2,3,11)	177.7196	D(14,2,3,4)	−177.3717	D(14,2,3,11)	−0.9889
D(1,2,14,15)	−3.1982	D(1,2,14,16)	130.4891	D(1,2,14,17)	−115.7773
D(3,2,14,15)	175.5403	D(3,2,14,16)	−50.7724	D(3,2,14,17)	62.9611
D(2,3,4,5)	−0.8543	D(2,3,4,8)	179.5224	D(11,3,4,5)	−177.1671
D(11,3,4,8)	3.2096	D(2,3,11,12)	54.8778	D(2,3,11,13)	−179.1188
D(4,3,11,12)	−128.8867	D(4,3,11,13)	−2.8832	D(3,4,5,6)	−0.2388
D(3,4,5,9)	−179.7831	D(8,4,5,6)	179.3822	D(8,4,5,9)	−0.1622
D(4,5,6,1)	0.8814	D(4,5,6,10)	−179.6092	D(9,5,6,1)	−179.5778
D(9,5,6,10)	−0.0684	D(2,14,17,18)	−65.9754	D(15,14,17,18)	178.9525
D(16,14,17,18)	48.2887	–	–	–	–

spectrum and 711 cm^{-1} in the Raman spectrum is assigned as the υC–S stretching mode.[3,13] Usually the SO_2 asymmetric stretching vibration[10,13] lies within the region 1415 ± 85 cm^{-1} and esters of organic sulfonic acids absorb at 1385 ± 35 cm^{-1}. We have observed υ_a SO_2 at 1313 cm^{-1} in IR and at 1315 cm^{-1} in Raman spectra of sulfanilamide.[15] Previous reports give the symmetric υ_s SO_2 at 1147 cm^{-1} in IR and at 1157 and 1136 cm^{-1} in Raman spectrum.[15] In the title compound the band seen at 1309 cm^{-1} in the Raman spectrum and at 1301 cm^{-1} by calculations is assigned to the asymmetric υ_a SO_2 mode.[10,13] The SO_2 symmetric vibration[10,13] is observed in the region 1195 ± 60 cm^{-1}. The band around 1208 cm^{-1} is assigned as υ_s SO_2 mode for the title compound.

Usually absorption bands of the SO_2 deformations appear with weak to moderate intensity. The SO_2 scissoring mode (565 ± 45 cm^{-1}) absorbs near 613 cm^{-1} in the IR spectrum and is observed at 619 cm^{-1} in the Raman spectrum.[10] A second SO_2 deformation, often assigned as a wagging vibration, is found in a neighboring region (535 ± 35 cm^{-1}) but clearly separated from the scissoring mode.[10] This wagging mode is observed at 561 cm^{-1} in the IR spectrum, 565 cm^{-1} in the Raman spectrum and 552 cm^{-1} by *ab initio* calculation. The phenyl ring deformation bands[10] are expected in the range 390–740 cm^{-1}.

SERS spectrum

SERS spectra of orthanilic acid (0.1 M) on silver electrode in 0.1 M KCl were recorded in the wavenumber range 200–1800 cm^{-1} at electrode potentials between 0 and −1.2 V. Prominent bands are observed at 1600, 1445, 1347, 1234, 1028, 625 and 213 cm^{-1} for −0.3 V and at 1600, 1234, 1028, 852, 771 and 213 cm^{-1} for −0.8 V.

The relative intensities of the bands from SERS spectra are expected to differ significantly from those of normal Raman spectra owing to the specific selection rules.[25] Moreover, the relative intensities are also potential dependent.[25,26] Surface selection rule suggests that for a molecule adsorbed flat on

Table 2. Wavenumbers (cm^{-1}) and band assignments

Calculated (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	SERS −0.3 V (cm^{-1})	at −0.8 V (cm^{-1})	Assignments
3542	–	–	–	–	υOH
3443	3400 vwbr	–	–	–	υ_aNH$_2$
3350	3233 vwbr	3203 w	–	–	υ_sNH$_2$
3052	3150 sh	3156 w	–	–	υCH 12a
3032	3069 sbr	3080 vs	–	–	υCH 1,12a
3017	–	3040 w	–	–	υCH 1,12b,15b
3001	–	–	–	–	υCH 12b
–	2936 sbr	2948 wbr	–	–	υOH
–	2713 w	–	–	–	Overtone/combination
–	2683 w	–	–	–	Overtone/combination
–	2642 m	–	–	–	Overtone/combination
–	2600 w	–	–	–	Overtone/combination
–	1985 w	–	–	–	Overtone/combination
–	1931 wbr	–	–	–	Overtone/combination
–	1800 w	–	–	–	Overtone/combination
–	1700 w	–	–	–	Overtone/combination
1642	1637 m	1634 w	–	–	δNH$_2$
1608	–	–	–	–	υPh 16a,16b
1590	1577 s	1595 m	1600 mbr	1600 mbr	υPh 16a,16b
–	1546 s	1539 w	–	–	υPh 16a,16b
1480	1481 m	1504 w	–	–	υPh 13b
1450	1452 m	–	1445 w	–	υPh 13a
1343	–	–	1347 s	–	υPh 9
1301	–	1309 w	–	–	υ_aSO$_2$
–	1287 w	–	–	–	δCH 3,9
1233	1230 s	1225 m	1234 w	1234 w	υSO$_3$H
1209	1204 vs	1208 w	–	–	υ SO$_3$H
1188	–	1190 w	–	–	δCH 5
1151	1151 s	1166 w	–	–	δCH 5,10
1141	–	1152 m	–	–	δCH 5,17b
1112	1101 s	1102 w	–	–	ρNH$_2$
1074	1065 m	1062 w	–	–	υSO$_3$H
1038	1043 m	1040 vvs	1028 s	1028 s	υS−O(H)
1014	1027 s	1027 m	–	–	δCH 2,14b
1006	–	–	–	–	δCH 7
980	954 w	–	–	–	γCH, γCN 7,19b
882	–	–	–	–	γCH 19a
852	865 w	–	–	852 m	γCH 19a
833	812 w	810 w	–	–	γSOH
791	–	–	–	–	γCH 4,6
756	771 s	760 vw	–	771 w	γCH 4,6
722	706 s	711 m	–	–	υC−S 8,18a
691	–	–	–	–	γPh 8,18a
592	613 vs	619 w	625 mbr	–	δ SO$_2$
552	561 m	565 w	–	–	ωSO$_2$
536	–	532 w	–	–	γPh(X) 18b
515	504 w	–	–	–	γPh(X) 18b,20a
490	–	–	–	–	γPh 15a,18b,20b
451	446 w	452 w	–	–	γPh, δPh(X) 5a,18b,20b

Table 2. (*Continued*)

Calculated (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	SERS −0.3 V (cm^{-1})	at −0.8 V (cm^{-1})	Assignments
428	–	–	421 w	–	τSO_2
397	–	–	–	–	$\rho SO_2 \ \tau \ NH_2$
381	–	–	–	–	$\rho SO_2 \ \tau \ NH_2$
326	–	–	–	–	ρSO_2, $\delta CX(X)$ 15a,18b
307	–	–	–	–	τNH_2
287	–	–	–	–	τNH_2
–	–	–	213 vs	213 vs	$\upsilon Ag\cdots O$
212	–	–	–	–	τPh, $\tau NH_2$11a,17a
176	–	–	–	–	τPh, τSO_3H 11a,17a
120	–	–	–	–	τPh 11b
70	–	–	–	–	τPh, τSO_3H

υ, stretching; δ, in-plane bending; γ, out-of-plane bending; ω, wagging; τ, torsional; ρ, rocking; X, substituent sensitive; Ph, Phenyl; s, strong; w, weak; br, broad; v, very; m, medium; sh, shoulder.

Subscript: a, asymmetric; s, symmetric.

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.[27,28] It is further seen that vibrations involving atoms that are close to the silver surface will be enhanced. When the wavenumber difference between the Raman bands in the normal and SERS spectrum is not more than 5 cm^{-1}, the molecular plane will be perpendicular to the silver surface.[29]

At different electrode potentials the SERS spectrum for an adsorbed compound appears to change.[30] The electrode potential dependence is induced by changes of the surface adsorbates at the electrode surface. Several studies on the electrode potential dependence confirm the fact that a particular vibrational band of a molecule can be highlighted by a change in the electrode potential.[15,30–34] The band observed for υ-ring in the SERS spectrum at 1600 cm^{-1} changes in intensity when potential increases from 0 to −0.3 V, and after that the intensity decreases. Also the intensity of the band at 1347 cm^{-1} (υ-ring) is found to increase in the potential range 0 to −0.3 V, and the band decreases in intensity and disappears for further negative electrode potentials. It is also interesting to observe a broad background around 1300–1600 cm^{-1} in the SERS spectrum. This band is supposed to arise from carbon overlayers on silver, formed through photodecomposition of orthanilic acid.[35,36] In SERS, a strong, broad feature is often observed in the 1300–1600 cm^{-1} region that is usually ascribed to graphite formed by the photodecomposition of organic materials near the surface.[37–39] According to the Auger electron spectroscopic study of Cooney and Mernagh,[40] carbon is the dominant species on Ag electrode surfaces illuminated by laser. Naked silver was barely present. From the fact that SERS became effective after laser illumination, it was proposed that the photographitization of organic compounds

on the metal surface, rather than the metal itself, was responsible for the SERS phenomenon.[40,41] Cao *et al.*[42] also reported broad background features between 1300 and 1600 cm^{-1} and have attributed them to the presence of surface carbon impurities.

The substituent-sensitive υCX vibration, which is a strong band in IR spectrum at 1230 cm^{-1} and a medium band in the Raman spectrum at 1225 cm^{-1}, is seen and shifted in wavenumber to 1234 cm^{-1} in the SERS spectrum. This indicates the possibility of SO_3H group involved in chemisorption and a change of symmetry on adsorption.[43,44] The υSO, observed as a medium band at 1043 cm^{-1} in the IR spectrum and as a very strong band at 1040 cm^{-1} in the Raman spectrum, appears at 1028 cm^{-1} in the SERS spectra. This indicates the nearness of the SO bond to the silver surface. This is justifiable because the modes of groups directly interacting with the metal surface will be prominent in the SERS spectrum and undergo a wavenumber shift.[45] Further, the SO band at 625 cm^{-1} observed in the SERS spectrum at −0.3 V supports this argument. In the whole potential range, a strong peak was observed at 213 cm^{-1}, which may be the Ag–O/Ag–Cl/Ag–N mode. In the present case the absence of vibrations involving NH_2 group in the SERS spectra suggests that this mode is not due to $\upsilon Ag–N$. Several authors[35,46–49] have reported the Ag–Cl stretching vibration above 230 cm^{-1}. We have observed the $\upsilon Ag–O$ band at 207 and 218 cm^{-1} for sulfanilamide[15] and sulfanilic acid,[22] respectively. Because of these reasons, for the title compound, the band at 213 cm^{-1} is assigned as $\upsilon Ag–O$ vibration. Further, the presence of the bands at 1234, 1028, 625, 421 cm^{-1} in the SERS spectrum of the title compound indicates the involvement of SO_3H group in the chemisorption process and the formation of metal–molecule adsorbate justifying the above argument.

According to the surface selection rule[27,28,50] 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. The out-of-plane vibrations observed at 852 and 771 cm^{-1} in the SERS spectrum at -0.8 V indicate a surface π-interaction in accordance with somewhat flat orientation on the silver surface.[51,52]

There is an increase in intensity of the SERS band at 1347 cm^{-1} (υCC mode) as the electrode potential changes from 0 to -0.5 V. This band is completely absent at about -0.8 V. However, the intensity of the band around 1028 cm^{-1} is maximum at -0.8 V. It is possible that at -0.3 V the molecule has a perpendicular orientation at the silver surface and at -0.8 V it assumes a somewhat flat orientation.[53,54] This is supported by the appearance of a medium SERS band at 852 cm^{-1} (-0.8 V), which is absent in the normal Raman spectrum. That is, there is a selective enhancement of different bands at -0.3 and -0.8 V, indicative of a change in orientation of the molecule on the silver surface.

Allen and Van Duyne[55] gave evidence for an orientation transition of cyanopyridine on a silver electrode. They explained this to be due to a change in the orientation of the molecule relative to the electrode from parallel to perpendicular upon potential increase. Olivier *et al.*[56] reported that the adsorption configuration of 4-cyanopyridine is potential dependent and presented two transitions in its orientation relative to the gold electrode. Panicker *et al.*[22] also observed a change of orientation for sulfanilic acid on a silver electrode with potential variation.

CONCLUSIONS

The FT-IR, FT-Raman and potential-dependent SERS spectra of orthanilic acid were studied. The molecular geometry and wavenumbers were calculated using the Hartree–Fock method with the 6–31G* basis set. The observed wavenumbers were found to be in agreement with the calculated values. The appearance of the υSO$_3$H, υS–O(H), δSO$_2$ and τSO$_2$ vibrations in the SERS spectra showed the nearness of SO$_3$H group to the silver surface. Further, the intense υAg–O vibration seen in all the SERS spectra substantiated metal–molecule interaction. The potential-dependent SERS profile gave maximum intensity at electrode potentials of -0.3 and -0.8 V. The change in intensities of the υPh and γCH vibrations with electrode potentials suggest a change in the orientation of the molecule on the silver surface.

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