NIR–FT Raman, FT–IR and surface-enhanced Raman scattering and DFT based theoretical studies on the adsorption behaviour of (S)-Phenylsuccinic acid on silver nanoparticles

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Abstract.   Single crystals of (*S*)-phenylsuccinic acid (SPSA) were grown by the slow evaporation technique and vibrational spectral analysis was carried out using near-IR Fourier transform Raman and Fourier transform IR spectroscopy. The density functional theoretical (DFT) computations were also performed at the B3LYP/6–311G(d, p) level to derive the equilibrium geometry, vibrational wavenumbers and intensities. Vibrational spectral investigation confirmed the formation of cyclic dimers in the crystal, with the carboxyl groups of each acid molecule being hydrogen bonded to those of the adjacent molecules. The Raman vibrational wavenumbers of the adsorption geometry of (S)-phenylsuccinic acid (SPSA) on a silver surface have been simulated using DFT-B3PW91 with lanl2dz basis set and it compared with the experimental spectrum. The large enhancement of in-plane bending and ring breathing modes in the surface-enhanced Raman scattering spectrum indicates that the molecule is adsorbed on the silver surface in an 'at least vertical' or slightly tilted orientation, with the ring perpendicular to the silver surface. The calculated vibrational spectra are in agreement with experimental values confirming the validity of the proposed adsorption configurations.

Keywords.   NIR–FT Raman; FT–IR SERS spectra; adsorption behaviour; (S)-Phenylsuccinic acid; DFT calculations.

1.   Introduction

Surface-enhanced Raman scattering (SERS) has recently evolved as an important laser spectroscopic characterization technique applied to biomedically significant molecules to study structural functional properties. SERS is widely used to elucidate information about the behaviour of biomolecules adsorbed at the metal surfaces, orientation of adsorbed species and the changes in the orientation induced by external factors.[1–3] However, with the change in the characteristics of the surface of the substrates, the SERS spectrum of adsorbates will also be different, which makes the analyses difficult.[4–6] The common analytical method is based on the shift of Raman frequencies, enhancing or weakening of intensity to hypothesize the adsorption ori-

entation, geometry configuration, and adsorption essence of adsorbates on the surfaces of substrates.[7–10] Surface-enhanced Raman scattering spectroscopy is now a well-established technique whereby unusually intense Raman signals are obtained from molecules adsorbed on or placed near rough metal surfaces, periodic metal structures produced lithographically or by coating gratings, metal island films, and colloidal metal particles.[11–14] The SERS spectra of many carboxylic acids have shown that the acid is adsorbed on the surface as the carboxylate ion. Carboxylic acid can bind to metal via either the oxygen lone pair electrons or the carboxylate systems.[15–17] Depending on the binding mechanism, the adsorbed carboxylic acid will assume different orientations on the surface. In order to deepen our understanding of the interaction of carboxylic acid with the metal surface, a more thorough investigation than that hitherto performed seems necessary. Owing to its rather

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rigid structure, benzoic acid can be regarded as a good model compound in the investigation of interaction of carboxylic acids with metal surfaces.[8] Vibrational and SERS spectral investigations of (RS)-phenylsuccinic acid[19,20] supported by *ab initio* density functional theory studies have been reported. Though the crystal structure of the title compound, (S)-phenylsuccinic acid (SPSA) has been reported,[21] the vibrational spectral features of SPSA crystal have not been subject of detailed analysis so far. SPSA is an aromatic dicarboxylic acid used as a classical resolving agent for pharmaceuticals. The present contribution reports the IR, Raman and SERS spectral studies of SPSA (figure 1) which can provide information on the adsorption geometry along with the geometry optimization and vibrational calculation using DFT to investigate other molecular bonding features.

2. Experimental

2.1 *Preparation of silver colloid*

Silver colloid was prepared by reduction of silver nitrate by sodium citrate, using the Lee and Meisel's method.[2,23] In 500 ml of deionized water, 90 mg of silver nitrate was dissolved and the solution was heated to boiling. Then 10 ml of a 1% trisodium citrate aqueous solution was added into the boiling silver nitrate solution drop-wise, accompanied by vigorous stirring. The mixed solution was kept boiling for a further 10 min. Finally, a green–gray silver colloid was obtained, which was stable for several days or weeks. The stability of the colloid was ascertained using an Ocean Optics model S2000 fibre optic UV-Visible-NIR spectrometer.
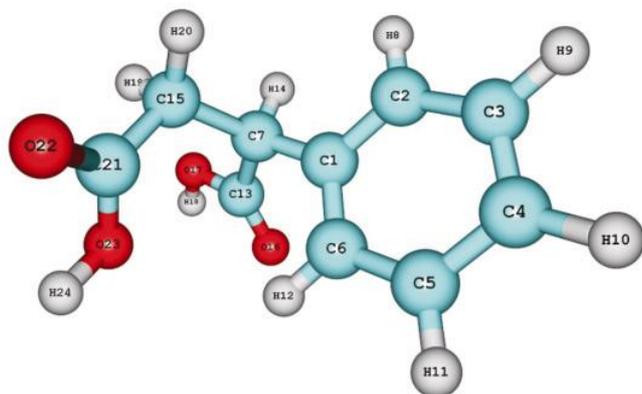

Figure 1. The structures of (S)-phenylsuccinic acid molecule.

2.2 *Instrumentation*

The FT–IR spectrum of this sample was recorded using Perkin-Elmer Spectrum One FT–IR spectrometer in the region of 450–4000 cm^{-1} with the standard KBr pellet technique. The spectral resolution was 1 cm^{-1}. The NIR–FT Raman spectrum was obtained on a Bruker RFS 100/s spectrophotometer with the powder sample taken in a capillary tube and the Raman spectra were recorded with an Nd : YAG laser at 1064 nm with an output of 300 mW used as the excitation source and with a liquid nitrogen-cooled Ge-diode detector; 1000 scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 1 cm^{-1}. A correction according to the fourth-power scattering factor was performed, but no instrumental correction was made. The upper limit for the wavenumbers is 3500 cm^{-1} owing to the detector sensitivity and the lower limit is around 10 cm^{-1} owing to the Rayleigh line cut-off by the notch filter.

The SERS measurements were performed on a single stage imaging spectroscope (ISA Jobin-Yvon Spex HR-320,f/4.1) fitted with a liquid nitrogen cooled CCD detector (Spectrum one,2000x 800 pixels with an active area of 30x 12 mm).The spectra were recorded with a 600g/mm grating blazed at 1 μm (7 cm^{-1}). NIR laser excitation of 785 nm was provided by an SDL-8350 diode laser. To a 5 ml of silver colloid, an equal volume of 10^{-4} M aqueous solution of SPSA was added. The resultant solution having dark-green colour was transferred to quartz cuvettes and the SERS spectra is recorded.

2.3 *Computational details*

All *ab initio* molecular orbital calculations were carried out using the Gaussian'98 suite of programs.[24] At first, the structure of the SPSA molecule (figure 1) and the SPSA–Ag complex (figure 2) were optimized, and then the Raman wavenumbers were calculated with the B3LYP/6-311G (d,p) and B3PW91/ lanl2dz basis sets, respectively. B3PW91 functionals have proven to be superior to the traditional functionals defined so far.[25] All optimized structures were confirmed to be minimum energy conformations. Harmonic vibrational wave numbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies. At the optimized structure of the examined species

no imaginary frequency modes were obtained, proving that a true minimum on the potential energy surface was found. The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The theoretical spectrum of (S)-phenylsuccinic acid–Ag complex was scaled with a 0.9573 factor.[26] The assignment of vibrational modes was done on the basis of the GaussView 3.0 package.

2.4 *Vibrational analysis*

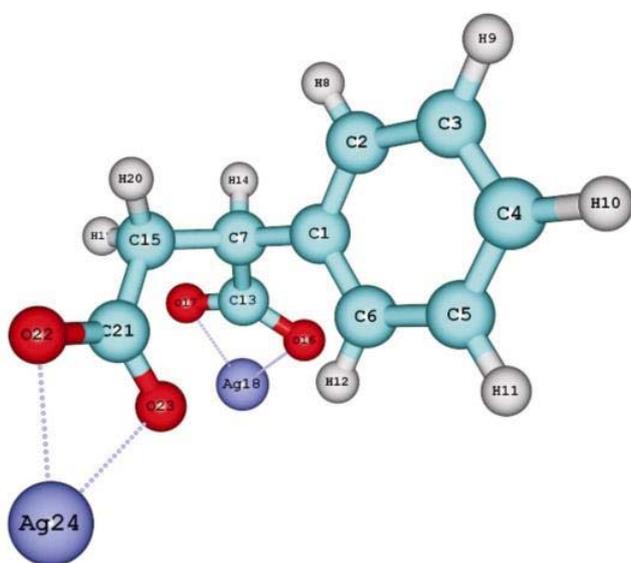The vibrational spectral analysis of SPSA is based on simulated and experimental FT–IR (figure 3) and

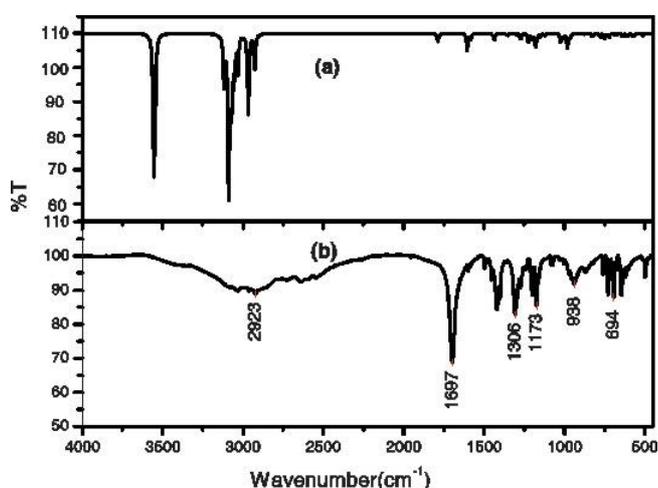**Figure 2.** The structures of (*S*)-phenylsuccinic acid – Ag complex.

simulated and experimental Raman spectra (figure 4) using density functional theory at B3LYP/6-311G(d, p) level. The vibrations of methylene, carboxylic acid, and phenyl ring modes have been separately analysed. The calculated vibrational wavenumbers, measured infrared and Raman band positions and their assignments are given in the table S1 (supplementary information).

2.4a *Phenyl ring vibrations:* The aromatic C–H stretching[27–29] vibrations in mono substituted benzene rings are generally observed in the region 3000–3100 cm^{-1}. For SPSA crystal, the weak bands at 3064, 3031 and 3012 cm^{-1} in IR correspond to ring modes **2**, **20b** and **20a** respectively, based on the eigen vector distribution of the computed vibrational modes while the weak bands in Raman at 3063 cm^{-1} and at 3026 cm^{-1} belong to the ring mode **2** and **20a** respectively.

The tangential C–C stretching mode **8** splits and **8a** vibration can be observed[27–29] as a very strong band in Raman at 1602 cm^{-1} and as a medium shoulder in IR at 1593 cm^{-1}. Its relatively weaker companion **8b** can be found as a medium band in the infrared spectrum at 1584 cm^{-1} and as a weak band in Raman spectrum at 1590 cm^{-1}. The ring modes **19a** and **19b**, found respectively in the frequency intervals (1470–1515 cm^{-1}) and (1440–1470 cm^{-1}) for mono substituted ring, have been reported to be insensitive to the substitution and the frequency can be altered only by the vibrational coupling with the substituents.[18] In the present compound **19a** can be

Figure 3. (**a**) Simulated IR spectrum of SPSA at B3LYP/6-311G(d, p) level and (**b**) experimental FT–IR spectrum of SPSA.
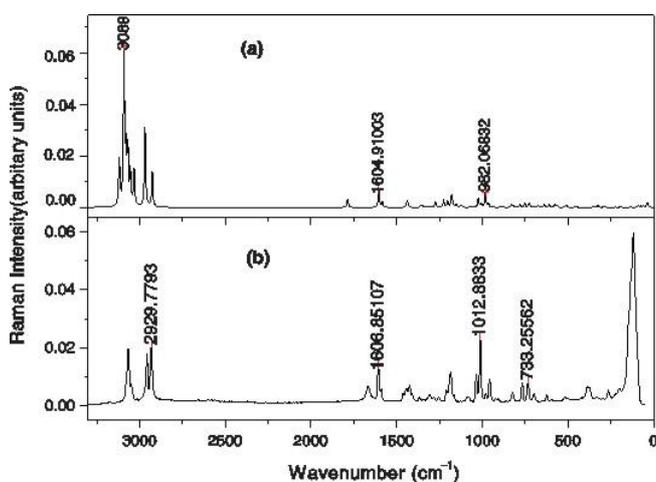

Figure 4. (**a**) Simulated Raman spectrum of SPSA at B3LYP/6-311G(d, p) level and (**b**) experimental NIR–FT Raman spectrum of SPSA.

observed as a weak band in Raman at 1503 cm^{-1} while **19b** appears as a strong band in Raman at 1450 cm^{-1} and in IR at 1455 cm^{-1} and the band positions are supported by computations.

The CH in plane bending modes **3**, **9a**, **15** and **18b** can be observed in Raman respectively as weak band at 1256 cm^{-1}, strong band at 1184 cm^{-1}, medium band at 1165 cm^{-1} and as weak band at 1078 cm^{-1}. The modes **15**, **18b** and **3** are active in IR, as a strong band at 1173 cm^{-1} as a medium band at 1071 cm^{-1} and as a strong band at 1263 cm^{-1} respectively. Normal vibration **1** of phenyl ring is usually referred to as a substitutent sensitive vibration. For a heavy substitution these modes found in the region of 1100–1000 cm^{-1} are strongly Raman active. This is confirmed by the strong intense Raman band at 1030 cm^{-1} and weak intense IR band 1029 cm^{-1}, which is supported by computed results. The inplane ring deformation or trigonal ring breathing vibration derived from the b_{1u} benzene vibration **12** (1010 cm^{-1}) gives rise to an intense Raman band in monosubstituted benzene[29–31] at 1010–990 cm^{-1}. In SPSA the radial skeletal mode **12** is identified as strong band in Raman at 1012 cm^{-1} and medium intense band in IR spectrum at 1008 cm^{-1}.

The absorption bands arising from C–H out-of-plane bending vibrations are usually observed in the region[29–33] at 1000–675 cm^{-1}. The weak band at 820 cm^{-1} in IR spectrum and medium band at 822 cm^{-1} in Raman belong to vibration **10b** while the medium nitense bands at 762 cm^{-1} and at 766 cm^{-1} in IR and Raman spectrum correspond to vibration **10a** where the assignments are in accordance with the computed vibrational modes. The strong band at 726 cm^{-1} and medium band at 732 cm^{-1} respectively for IR and Raman spectrum belong to mode **11**. The out-of-plane skeletal mode **4** can be observed as strong band in IR at 694 cm^{-1} and as weak band in Raman at 696 cm^{-1}, supported by computed result. The C–H out-of-plane bending vibrations **16a** and **16b** are observed as a weak band at 500 cm^{-1} and 387 cm^{-1} in Raman spectrum among which IR active mode **16b** is found at 496 cm^{-1}. The radial skeletal mode **6a** can be observed around 606 cm^{-1} for a phenyl ring carrying heavy substituents and here the weak band at 596 cm^{-1} belong to **6a** mode of C–C–C bending vibration. The phenyl ring modes **6b** can be observed in Raman spectrum at 626 cm^{1} and IR spectrum at 620 cm^{-1}.

2.4b Methylene group vibrations: The asymmetric C-H stretching mode of methylene group is expected in the region[27–31] around 2940 cm^{-1} and the symmetric around the region 2860 cm^{-1}. In SPSA the CH$_2$ asymmetric stretching mode is found to be medium intense bands in both Raman and infrared spectrum respectively at 2956 cm^{-1} and 2964 cm^{-1}. The symmetric stretching modes also observed as intense sharp band in Raman spectrum at 2929 cm^{-1} and medium intense band in IR spectrum at 2925 cm^{-1}. The calculated wavenumbers of the above modes are 2947 cm^{-1} and 2910 cm^{-1} respectively for methylene asymmetric and symmetric stretching modes.

The CH$_2$ scissoring vibrations are normally appears in the region of 1455–1435 cm^{-1} and consist of medium intense bands[30,31]. The weak bands at 1442 cm^{-1} are Raman spectrum and the medium intense band at 1456 cm^{-1} in IR spectrum corresponds to the CH$_2$ scissoring mode. The methylene wagging vibrations are generally found around 1321 cm^{-1}. In SPSA the wagging vibrations of CH$_2$ are found in both IR and Raman spectrum at 1274 cm^{-1} which is justified by our DFT calculation also. The bands corresponding to twisting and rocking vibrations of CH$_2$ appears at 1073 cm^{-1} and 727 cm^{-1} in Raman spectrum. The wavenumbers at 1078 cm^{-1} and 730 cm^{-1} in Raman spectrum are attributed to CH$_2$ twisting and rocking modes, respectively which is supported by the results reported in literature[27–28].

2.4c Carbonyl group vibrations: In a non-ionized carboxylic (COOH) group, the carbonyl [C=O] stretching vibration[34] usually appears in the wavenumber region of 1755–1700 cm^{-1}. When the dimer is considered as a whole, there will be two carbonyl stretching vibrations in the IR spectrum at 1720-1680 cm^{-1} for asymmetric stretch and at 1680–1640 cm^{-1} for symmetric stretch in the Raman spectrum.[27,28] The asymmetric and symmetric stretching vibrations of carbonyl modes in SPSA are found to be very strong at 1697 cm^{-1} and medium intense band at 1661 cm^{-1} respectively for infrared and Raman spectrum.

2.4d. Hydroxyl group vibrations: The hydroxyl stretching and bending bands can be identified by their broadness and strength of the band which is dependent on the extend of hydrogen bonding. In the hydrogen bonded dimer form, the O–H stretching band in the IR spectrum centers around 3000 cm^{-1} and is superimposed on the C–H stretching bands.[27,28] The SPSA in the condensed state is characterized by a strongly bonded (O–H...O = 2·65 Å),

broad O–H stretching band near 3000 cm^{-1}, which is superimposed on the C–H stretching bands. The broad wings of the O–H stretch can be seen on either side of the C–H bands. The broadening in the O–H stretching of SPSA is due to combination bands between the low wavenumber vibrations and ν_{O-H} and between the ring vibrations and excited binary combination of δ_{COH} and ν_{C-O}. The weak bands in infrared spectrum 2700–2500 cm^{-1} region, correspond to overtones and combinations of the 1322 and 1423 cm^{-1} bands due to interacting C–O stretch and O–H deformation vibrations.[19,27–36] The very strong Raman peak at 1292 cm^{-1} is due to the O–H in-plane deformation mode as expected. The out-of-plane deformation mode of O–H group is observed as a very strong peak at 986 cm^{-1} in Raman and as a weak peak at 978 cm^{-1} in IR spectrum. The C–O (H) stretching mode is observed as a strong band at 1176 cm^{-1} in IR and the corresponding Raman band is observed as a medium intense band at 1180 cm^{-1}.

2.4e *External modes:* The lattice vibrations usually appear in the region of 0–300 cm^{-1}. These modes are due to the rotational and translational vibrations of the molecules and vibrations involving hydrogen bonds. The low wavenumber bands of the hydrogen bond vibrations are generally found to be weak, broad and asymmetric in the Raman spectrum. The lattice vibrations of rotatory type are generally stronger in intensity than the translatory type.[36] The low wavenumber intermolecular vibrations involving two OH⋯O bonds of the dimer at 57, 120 and 171 cm^{-1} have been attributed to a twist motion of the two molecules involving in-plane rotation of the molecules against each other, an out-of-plane vibration of the two hydrogen bonds and an anti-symmetric dimer stretching mode involving stretching motion along the two hydrogen bonds of the cyclic dimer respectively.

3. SERS spectral analysis

The SERS spectrum of SPSA figure 5, has been recorded and the vibrational analysis is performed by comparing it with the normal Raman spectrum. The vibrational spectrum calculated at B3PW91/lanl2dz is used to determine the vibrational modes (figures 6 and 7) unambiguously. The calculated vibrational wavenumbers, measured SERS and Raman band positions and their tentative assignents are given in table 1.

The adsorption mechanism of an adsorbate can be deduced from its SERS spectrum. The possible potential sites available for the adsorption of SPSA on a silver surface are the ring π-system and the carboxylic acid group. The orientation of the molecule on the silver surface can be inferred from aromatic C–H stretching vibrations, ring stretching vibrations, the ring breathing mode, in-plane and out-of-plane vibrations and the SERS surface selection rule.[37,38] It has also been documented in the literature that when a ring moiety interacts directly with a metal surface, the ring breathing mode **1** and **12** has to be red shifted by about 10 cm^{-1} along with substantial band broadening in the SERS spectra. The modes correspond to **1** and 12 were observed as a strong bands at 1028 and 1000 cm^{-1} in SER spectrum respectively corresponding Raman band can be observed in the same region. Neither a substantial red shift, nor significant band broadening was identified in the SERS spectra of SPSA implying that the probability of a direct ring π-orbital to metal interaction should be low. In the SERS spectrum of SPSA in silver colloidal solution (figure 4), the 1596 band and the 1581 cm^{-1} band, assigned to the CC stretching of benzene, are both very strong, indicating that the interaction between benzene rings of SPSA molecules and the surfaces of silver nanoparticles is strong. But there are no shifts of these two bands compared with the corresponding bands in the Raman spectrum of solid SPSA, indicating that it is still a physical interaction. Moreover, the medium intense band at 1666 cm^{-1} in the NIR–FT Raman spectrum assigned to the carbonyl stretching vibration is not observed in the SERS spectrum and this also supports the above assumption. The carbonyl stretching appears only as a very weak band at 1668 cm^{-1} in the SERS spectrum. The is probably due to the formation of SPSA dimmers in the crystalline network, which is corroborated by the appearance of a broad band at about 2600 cm^{-1} due to ν(O–H) vibrations of carboxylic groups involved in hydrogen bonds. The weakening of this carbonyl stretching vibration indicates that the C=O is not in direct interaction with the silver surface.

The relatively weak enhancement of the 1248 cm^{-1} band, assigned to the C–O stretching motions, indicate that the adsorption of SPSA takes place through carboxyl. In the SER spectrum a weak bands at 653 cm^{-1} that contain contributions of the in-plane COO$^-$ deformation vibrations. It is also informative to observe that the ν_s (COO$^-$) band at 1392 cm^{-1} with respect to the δ (COO$^-$) band at 857 cm^{-1} is
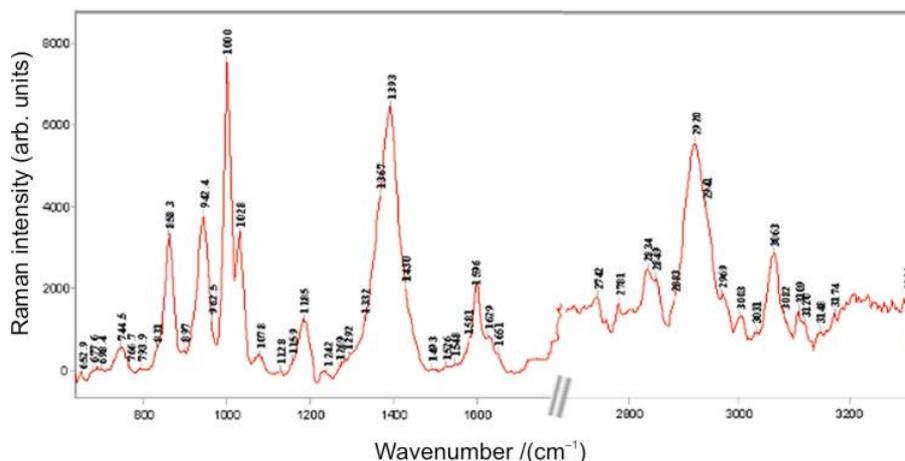
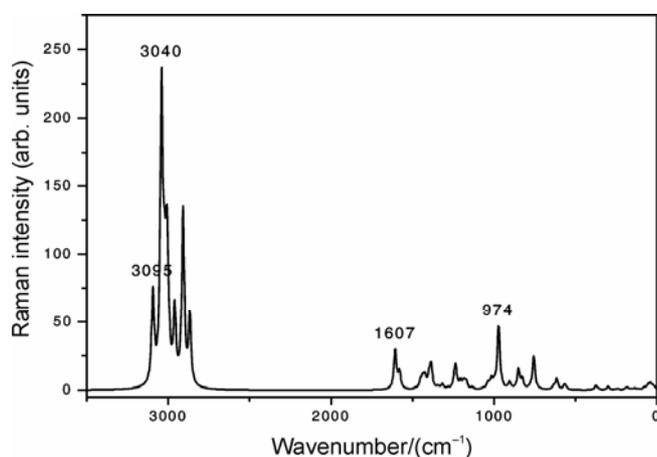**Figure 5.**   NIR–FT SERS Raman spectrum of SPSA (3400–600 cm⁻¹).

Figure 6.   Calculated SERS Spectrum of SPSA–Ag system at B3PW91/lanl2dz level.

much more intense.[37,38] In a tilted geometry, the relative intensity of the δ (COO⁻) band is stronger. From these results, it may be inferred that the relative intensity of the δ (COO⁻) band with respect to the ν_s (COO⁻) band increases as the tilt of the carboxylate to the silver surface, which indicates that the O–H bonds of carboxyl has broken down upon adsorption.[37,38] This indicates that the $A_g^+\ldots COO^-$ bonds formed by the adsorption of SPSA on silver are not ionic. The bonds should then posses a covalent character. There are two bonding schemes that may be considered, one being a σ-coordination via the donation of oxygen lone pair eletrons to silver and the other a π-coordination via the donation of π-electrons of carboxylate groups to silver accompanied by a metal-to-adsorbate π^* backdonation. In the present case, the simultaneous involvement of σ and π-type coordination may indicate that the SPSA

species has to assume a tilted orientation on the silver surface[37,38]. Such a tilted orientation was presumed to occur by the simultaneous σ and π-type coordination of carboxylate groups to silver surface caused by the steric hindrance and electrostatic repulsion between the two carboxylate groups, and thereby SPSA on silver was easily displaced with aromatic carboxylic acids.

According to the surface selection rules for Raman scattering,[12–18] the vibration of the adsorbed molecules, which has a polarizability tensor component normal to the surface, will be preferentially enhanced. Stretching vibrations are assumed to have large component of the polarizability along the bond axis. It has been well-established that presence and absence of the phenyl ring C–H stretching vibration is a reliable probe for the perpendicular or parallel orientation, respectively, of the benzene ring with respect to the surface[37,38]. The aromatic ring C–H stretching bands **2**, **20b** and **7a** are observed 3063, 3031 and 3003 cm⁻¹ in the SERS spectrum which is also observed in the same region in normal Raman. The computed wavenumbers of modes corresponds to the **2**, **20b** and **7a** to be 3063, 3031 and 3013 cm⁻¹ respectively. Hence the presence of the phenyl ring C–H stretching vibration in an SERS spectrum is indicative of a vertical or at least a tilted orientation of the benzene ring moiety on a silver substrate. The SERS spectrum of the molecule, which are adsorbed flat on the silver surface and its out-of-plane bending mode will be more enhanced when compared with its in-plane bending mode and vice versa when it is adsorbed perpendicular to the surface. Further, vibrations involving atoms that are close to the silver surface will be enhanced. The C–H in-plane
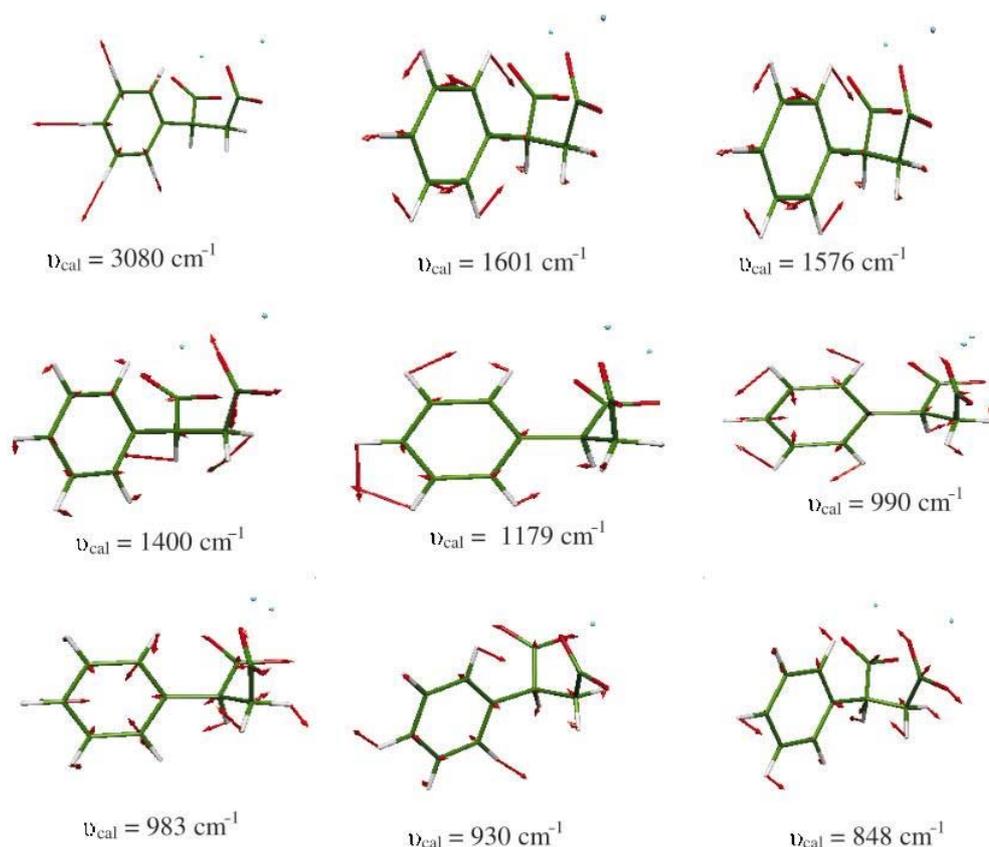
$\upsilon_{cal} = 3080$ cm^{-1} $\upsilon_{cal} = 1601$ cm^{-1} $\upsilon_{cal} = 1576$ cm^{-1}

$\upsilon_{cal} = 1400$ cm^{-1} $\upsilon_{cal} = 1179$ cm^{-1} $\upsilon_{cal} = 990$ cm^{-1}

$\upsilon_{cal} = 983$ cm^{-1} $\upsilon_{cal} = 930$ cm^{-1} $\upsilon_{cal} = 848$ cm^{-1}

Figure 7.   Selected normal modes of SPSA–Ag system computed at B3PW91/lanl2dz.

Table 1.   Calculated vibrational wavenumbers, measured SERS and Raman band positions (cm^{-1}) and assignments for SPSA.

B3PW91/lanl2dz	ν_{SERS} SPSA	ν_{Raman} SPSA	Assignments
3080	3056 *m*	3063 *vw*	2 arom. C–H stretch
3066	3031 *w*	3030 *vw*	20b arom. C–H stretch
3023	3003 *w*		7b arom C–H stretch
2996	2969 *s*	2969 *w*	CH$_2$ sym. stretch
2961	2941 *sh*	2950 *s*	C$_{12}$–H$_2$ stretch
2927	2920 *s*	2907 *vs*	CH$_2$ asym. stretch
	1629 *w*		COO$^-$ asym. stretch
1601	1596 *m*	1596 *s*	8a ring stretch
1576	1581 *vw*	1581 *s*	8b ring stretch
1400	1393 *vvs*		COO$^-$ sym. stretch
1298	1292 *w*	1292 *vvw*	CH$_2$ wagging
1261	1242 *w*	1242 *vvw*	C–O stretch
1179	1185 *m*	1179 *s*	C–H i.p bend + CH$_2$ twisting
990	1028 *s*	1028 *s*	1 ring breath
983	1000 *vvs*	1000 *vs*	12 ring i.p bend
930	942 *s*	922 *s*	10a C–H o.p bend
848	858 *vs*	867 *m*	COO$^-$ bend
810	794 *vw*	784 *w*	C–H o.p bend
764	746 *w*	732 *m*	11 C–H o.p bend
658	653 *w*	663 *w*	COO$^-$ in plane deformation

bending vibrations appear in the region of 1260–1050 cm^{-1}. The intense bands at 1185 and 942 cm^{-1} corresponds to in-plane bending mode and out of plane bending mode respectively. These modes have contribution of the polarizbility components α_{zz}, α_{xz} and α_{yz}. The SERS bands around 858, 794, 745 cm^{-1}

are correspond to out-of-plane C–H bending modes. The observed C–H in-plane bending and out-of-plane bending modes obtain their SERS intensity from these Raman polarizability components.[17,18] This leads to evidence for a tilted orientation of SPSA on the silver surface. The appearances of both in-plane modes and out-of-plane modes suggest that there is a certain angle between the ring plane and the surface of the silver nanoparticle. So the SPSA molecules are probably tilted on the silver nanoparticles through ionized carboxyl, and there is a certain angle between the benzene rings and the surfaces of silver nanoparticles. The observed SERS bands at 2969, 2920 cm^{-1} corresponds to CH_2 asymmetric and symmetric stretching modes respecively which is also observed in the same region in normal Raman and these modes shows that methyllene groups are close to the metal surface.

Analysing table 1 we can see that the calculated vibrational wavenumbers are very similar, only few vibrational wavenumbers have tiny differences, these tiny shifts are not regarded as discrimination in theoretical calculation. However, other theoretical values also are in good agreement with experimental values. We can see that a mean relative deviation (MRD) of 0·9% exists with experiment, which proves that our model is also probably reasonable. Other vibrational wavenumbers are all in good agreement with the experimental values; the good agreement shows us that the Ag atoms do interact with O atoms on carboxyl group of SPSA ion. However, their most vibrational wavenumbers are all the same, so, we speculate that all the stable experimental configurations exist actually. Although we used only two Ag atom as the substrate of the adsorbed molecules, the calculated vibrational spectra using
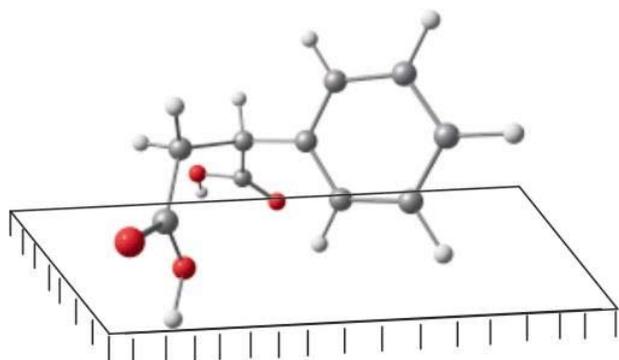
DFT-B3PW91 with lanl2dz are in good agreement with the experimental values and proved the proposed adsorption configurations (figure 8). So one can conclude that the model is reasonably good in describing the adsorption configurations.

4. Conclusions

Single crystals of (*S*)-phenylsuccinic acid (SPSA) were grown by the slow evaporation technique and vibrational spectral analysis was carried out using near-IR Fourier transform Raman and Fourier transform IR spectroscopy. The density functional theoretical (DFT) computations were also performed at the B3LYP/6–311G (d, p) level to derive the equilibrium geometry, vibrational wavenumbers, and intensities. Vibrational spectral investigation confirms formation of cyclic dimers, in the crystal, with the carboxyl groups of each acid molecule hydrogen bonded to those of adjacent molecules. The SER spectra of the SPSA sample in activated silver colloids and the corresponding Raman spectrum are compared. The SPSA molecules are bonded to the silver surface through lone pair of oxygen electrons of the carboxylate group, which has a perpendicular or slightly tilted orientation with respect to the silver surface. By analysing SER spectra, the SPSA molecules should be bound to silver surface as dicarboxylate with a strongly tilted orientation with respect to the normal surface. Such a tilted orientation was presumed to occur by the simultaneous σ- and π-type coordination of carboxylate groups to silver caused by the steric hindrance and electrostatic repulsion between the two carboxylate groups, and thereby SPSA on silver was easily displaced with aromatic carboxylic acids. In this sense, σ-type coordination seemed to be more important than a π-type coordination for aromatic carboxylic acid derivatives to assemble on a silver surface. The Raman vibrational wavenumbers of the adsorption geometry of (*S*)-phenylsuccinic acid (SPSA) on a silver surface have been simulated using DFT-B3PW91 with lanl2dz basis set and it compared with the experimental spectrum. The calculated vibrational spectra are in good agreement with experimental values and proved the proposed adsorption configurations.

Figure 8. Schematic model for the adsorption geometry of SPSA on the colloidal silver surface.

Manipal, India for their support in recording the SERS spectra.

Supplementary information

For supplementary information tables S1 and S2 see www.ias.ac.in/chemsci website.

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