JOURNAL OF SOLID STATE CHEMISTRY **116**, 217–223 (1995)

Vibrational and Surface Enhanced Raman Scattering Spectra of Sulfamic Acid

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Received March 9, 1994, in revised form August 2, 1994; accepted August 3, 1994

The analysis of the Raman and FTIR spectra of sulfamic acid suggest a structure between that of zwitterion and molecular form. SERS spectra have been analyzed in two types of silver colloids. As S $\cdots$ O ····· Ag linkages are formed in one colloid, $S = 0$ fundamentals are enhanced in intensity and shifted in frequency. Appearance of a δ SOH band indicates the retention of SOH bonds in the metal–molecule adsorbed system. Further, splitting of the fundamentals, which arises from the lowering of the symmetry of the molecule on adsorption, is noticed. In the second colloid, the ν S–O band is shifted in frequency and enhanced in intensity. No band corresponding to δ SOH is noticed, indicating the removal of protons and formation of S–O ····· Ag linkages. © 1995 Academic Press, Inc.

INTRODUCTION

The study of the structure of sulfamic acid, NH_2HSO_3, has been of interest (1–6) as its physical properties are considerably different from those of other substituted sulfuric acids. It has been suggested (2, 4) that it exists as a zwitterion, $NH_3^+ SO_3^-$, in the solid state and as NH_2–SO_2–OH in aqueous solution (5). In the Raman spectrum (6) of sulfamic acid, the bands in the 2800–3200 cm^{-1} region are assigned to hydrogen bonded NH stretching vibrations of NH_3^+. However, Vuagnant and Wagner (4) assigned some of the IR bands in this region to overtones of δNH_3^+. In the present investigation, a number of additional bands and shifts of some of the IR and Raman frequencies have been observed and hence a complete vibrational spectral analysis is taken up.

The surface enhanced Raman scattering (SERS) spectrum of sulfamic acid has not yet been studied, though detailed reports (7–11) of other oxyacid derivatives are available. A study of its SERS spectrum in silver colloid is expected to give informations regarding the coordination, geometry, and orientation of the adsorbed molecule (10, 11).

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EXPERIMENTAL

Silver colloid was prepared by two different methods. A stable greenish-yellow colloid (colloid 1) having a sharp absorption maximum at 400 nm was prepared from sodium borohydride and silver nitrate by the method described by Creighton *et al.* (12). A greenish-grey colloid (colloid 2) with a broad absorption band around 430 nm was prepared from silver nitrate and sodium citrate (13).

Absorption spectra of the silver colloids, sulfamic acid, and adsorbed sulfamic acid (Fig. 1) were recorded on a UV-240 Shimadzu UV–visible recording spectrophotometer. To get samples for SERS spectral measurements equal volumes of colloid 1/colloid 2 and 10^{-4} *M* sulfamic acid were added and shaken well. The resulting solutions were placed in rectangular quartz cells and the Raman spectra (Fig. 2) recorded on a Dilor GMBH Z24 spectrometer with 200 mW laser power (514.5 nm). Raman spectra of sulfamic acid in polycrystalline and aqueous forms (Fig. 2) were also recorded. PE 7600 FTIR (4000–400 cm^{-1}) and PE 983 (4000–200 cm^{-1}) spectrometers were used to record the IR spectrum (Fig. 3) with the sample in KBr pellets. The Raman spectrum in the high wavenumber region is given in Fig. 4. Fig. 5 shows the IR spectrum in the 400–200 cm^{-1} region.

RESULTS AND DISCUSSION

UV–Visible Spectra

Sulfamic acid has a characteristic absorption band at 398 nm. In colloid 1, it gives a light pink color and absorbs at 400 and 540 nm (Fig. 1). In colloid 2 it has absorption bands at 350, 440, and 630 nm (Fig. 1). The additional broad absorption band on the long wavelength side around 540 nm (colloid 1) and around 630 nm (colloid 2) are in agreement with the reported results for aggregated colloids (10).

Crystal Structure and Factor Group Analysis

Sulfamic acid crystallizes in the orthorhombic system *Pbca* (D_{2h}^{15}) with eight formula units in the unit cell (1, 2).

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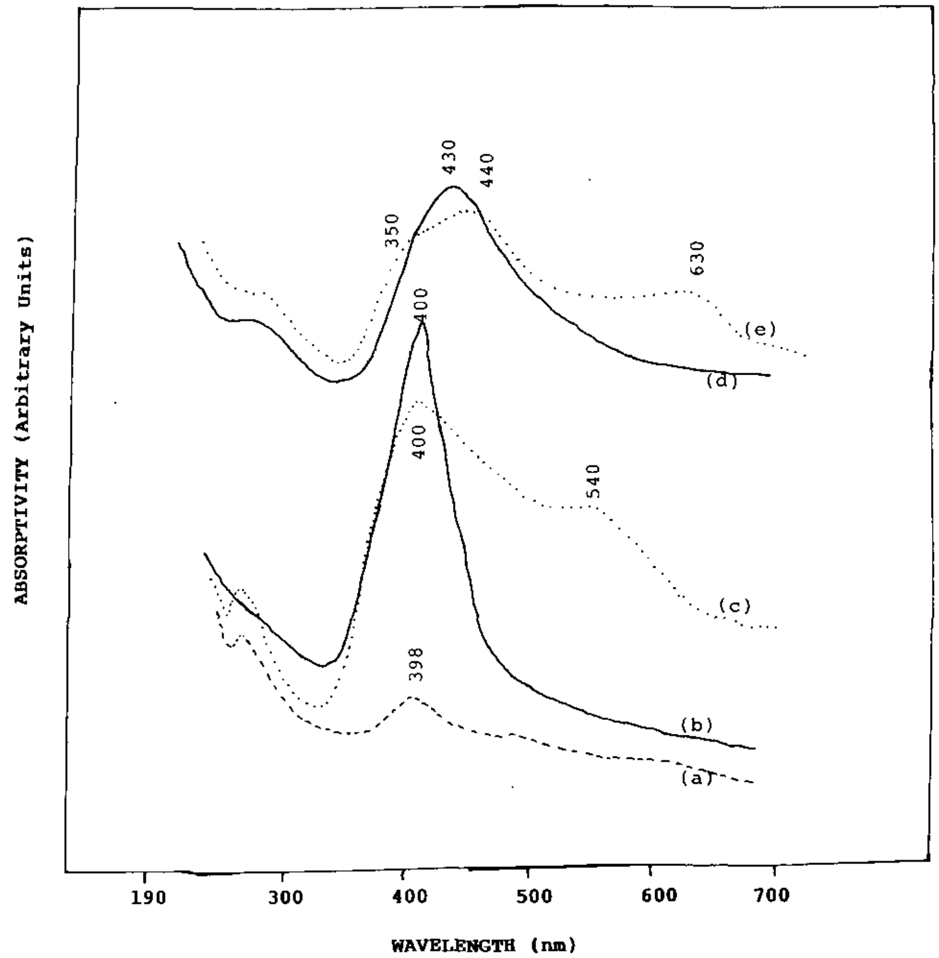

FIG. 1. UV-Visible spectrum of (a) sulfamic acid, (b) colloid 1, (c) sulfamic acid in colloid 1, (d) colloid 2, (e) sulfamic acid in colloid 2.

All the atoms are in general positions. Sulphur atom is approximately tetrahedrally coordinated to three oxygen atoms and a nitrogen atom. The average S–N distance is 1.76 Å, the S–O bond length varies from 1.42 to 1.45 Å, and the N–H bond lengths are 1.013, 1.028, and 1.032 Å. Consequently the formula is written as NH_3SO_3. Each nitrogen atom has six oxygen neighbors at distances ranging between 2.824 and 2.984 Å. The hydrogen atoms lying between them form hydrogen bonds N–H ····· O. The distribution of irreducible representations (14) at $k = 0$ is

$$\Gamma = 24A_g + 24B_{1g} + 24B_{2g} + 24B_{3g} + 24A_u + 23B_{1u} + 23B_{2u} + 23B_{3u}.$$

IR and Raman Spectra

For an NH_2 group one expects both the stretching bands to be above 3200 cm^{-1}, and for an NH_3^+ group they should appear below 3200 cm^{-1} (4, 6, 15, 16). In the present case, the asymmetric stretching mode appears around 3361 cm^{-1} and the symmetric one around 3163 cm^{-1} (IR). In Raman, spectroscopy, a very weak broad band is observed around 3380 cm^{-1} which corresponds to the asymmetric NH stretching mode. The symmetric mode appears at 3115 and 3042 cm^{-1}. Further, in both Raman and IR spectra there is a medium intensity band around 2870 cm^{-1} which is due to a strongly hydrogen bonded NH stretching mode. It may be noted here that Katiyar and Krishnan (6) have made a similar assignment for the band at (2876 cm^{-1}). The wide range of frequencies observed for the NH stretching modes is due to the presence in the compound of hydrogen bonds of different strengths.

In strongly hydrogen bonded systems with X(:O)–OH grouping (X = P, As, S, Se and C) a trio of well defined IR bands (A, B, C bands) are expected in the regions 2800–2400, 2350–1900, and 1720–1600 cm^{-1} (15, 17–20) which arise from proton tunnelling and Fermi resonance interactions with the overtones/combinations of hydro-

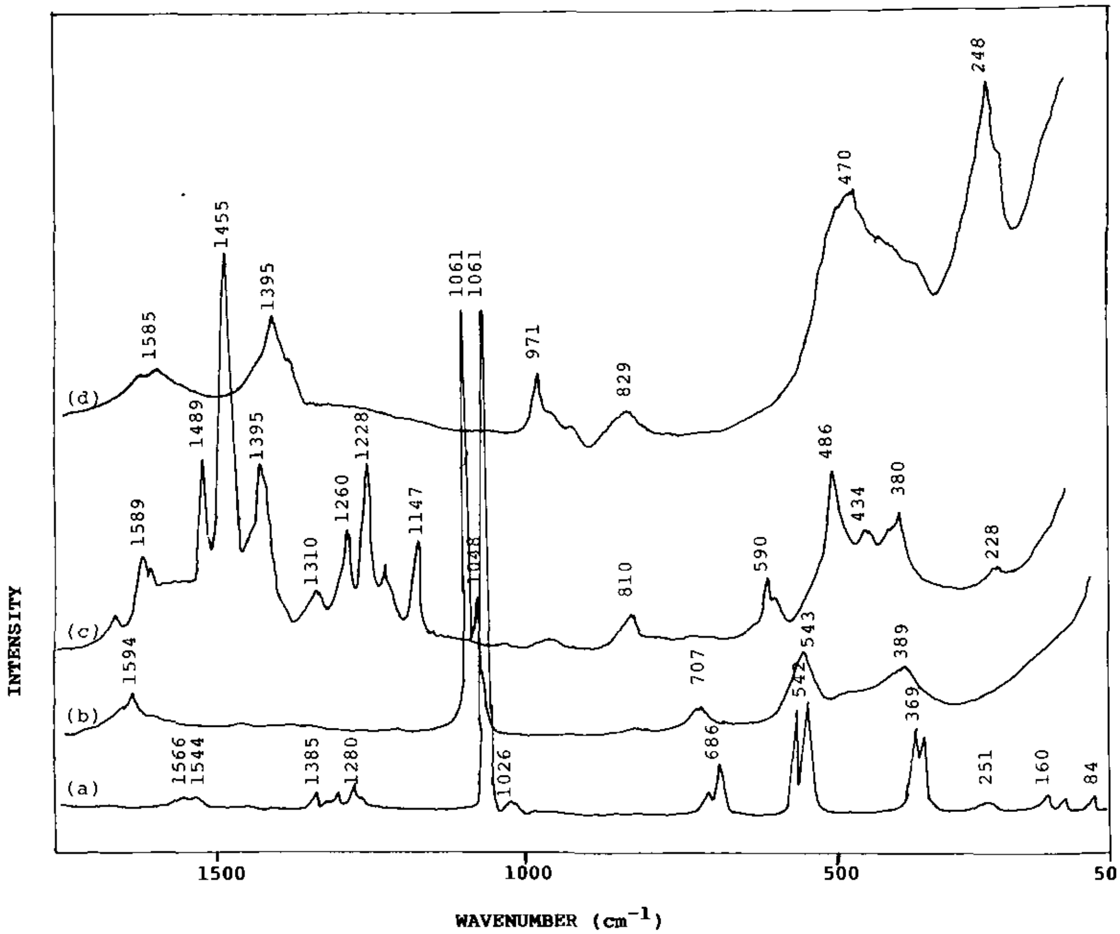

FIG. 2. (a) Raman spectrum of sulfamic acid (powder); (b) Raman spectrum of sulfamic acid (aqueous solution); (c) SERS spectrum of sulfamic acid in colloid 1; (d) SERS spectrum of sulfamic acid in colloid 2.

gen bonded OH bending modes. Therefore, the assignment of all the bands in the 1700–3100 cm^{-1} to overtones and combinations as given by Vuagnant and Wagner (4) is probably not correct. Some of them can be due to the triobands.

In the NH deformation mode region, three bands are observed in IR (1570, 1540, 1451 cm^{-1}). If these are due to the symmetric and asymmetric bending modes of NH_3^+, one should observe a comparatively strong band around 1450 cm^{-1} in Raman for the symmetric NH_3^+ bending mode. However, this is not observed in the spectrum. As the observed stretching and bending modes of NH are not in the expected regions of NH_3^+ or NH_2 it may be inferred that sulfamic acid has a structure in between the two. It may be noted that in the Raman spectrum of aqueous solution, δNH appears at 1594 cm^{-1}, which is the expected region for δNH_2 (18, 21). The large splitting of about 120 cm^{-1} observed for the bending mode of NH can be attributed to hydrogen bonds of different strengths.

The medium intense IR band at 1257 cm^{-1} with the shoulder at 1230 cm^{-1} is assigned to δOH, the in-plane OH bending mode (15, 22, 23). The out-of-plane OH bending mode (γOH) appears at 798 and 890 cm^{-1} in IR (15, 22, 23). The spectral data and the complete band assignments are given in Table 1. The earlier authors (4, 6) did not observe the bands at 1257, 1230, 1191, 1130, 1055, 910, 890, 798, 607, 595 and 555 cm^{-1} in the FTIR spectrum (Fig. 3) and at 2126, 1280, 1075 and 706 cm^{-1} in the Raman spectrum.

If the structure is NH_2SO_2–OH the vibrational spectrum should show S–O(H) and S=O stretching bands. In the Raman spectra of both powder and aqueous solution samples two bands are observed between 1000 and 1100 cm^{-1}. Of these, the band at 1061 cm^{-1} does not show decrease in intensity or lowering of frequency on passing from solution to solid state (Fig. 2). Therefore, it can easily be assigned (18) to the symmetric stretching mode of S=O. However, the band at 1048 cm^{-1} shows a lowering of about 22 cm^{-1} and a decrease in intensity on pass-

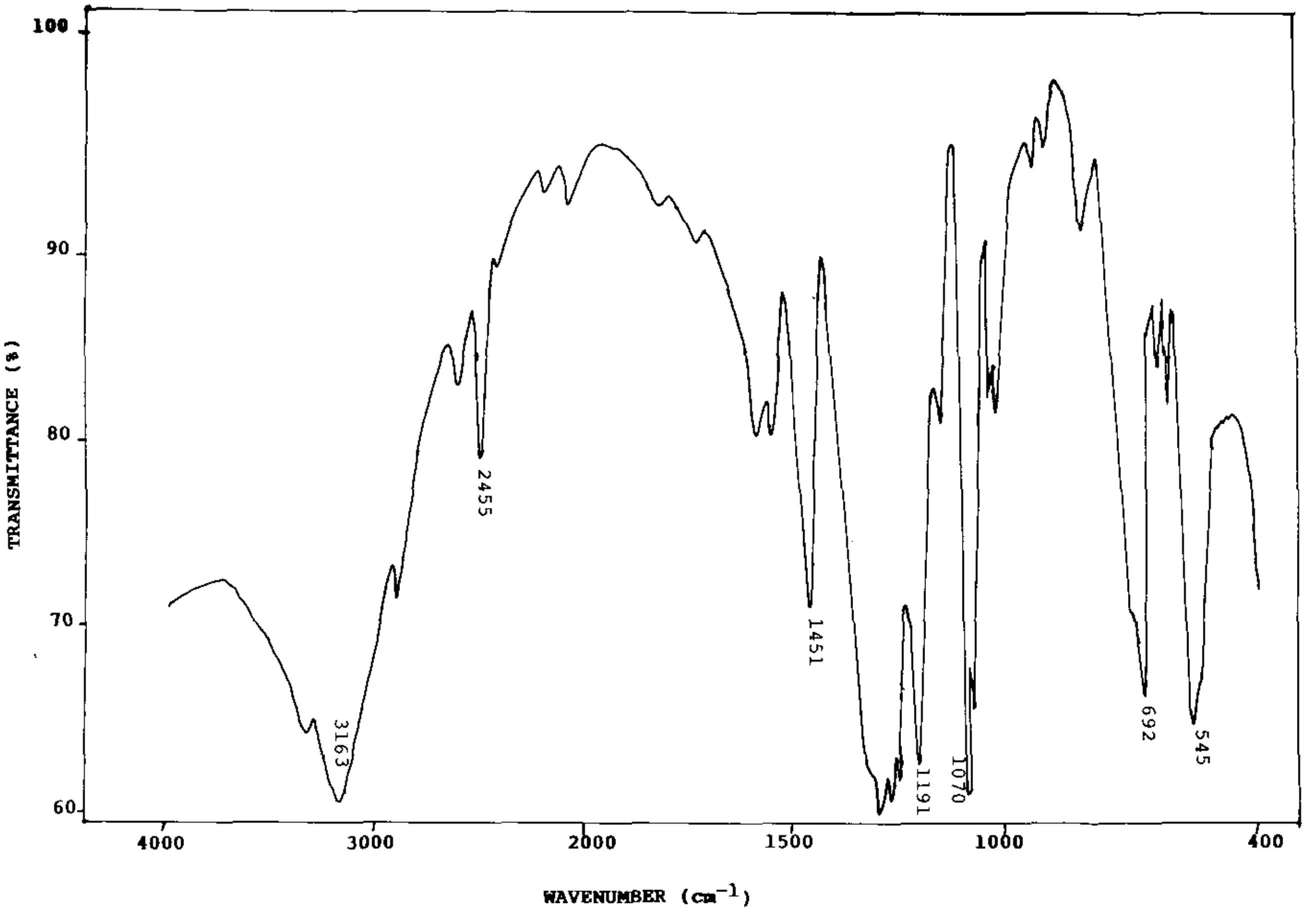

FIG. 3. FTIR spectrum of sulfamic acid.

ing from the solution to the solid state. Therefore, this band is assigned (18) to the S–O(H) stretching mode. The presence of νS–O(H) as a strong band and the appearance of the δNH_2 mode at 1594 cm^{-1} suggests the structure NH_2–SO_2–OH for sulfamic acid in solution. In the powder spectrum νS–O(H) appears as a weak band at 1026 cm^{-1}. The S–N stretching band could be identified easily as it appears at 707 cm^{-1} in the Raman spectrum of the solution. Its low frequency value compared with sulfamates (4, 6, 24) is because of the larger S–N bond length (1, 2) in sulfamic acid.

Summarizing, the observation of δOH, γOH, νS–O(H), the triobands and the wide range of frequencies for the NH fundamentals leads to the conclusion that in the solid state the sulphamic acid molecule is neither fully in the zwitterion form nor in the molecular form. It has an in between structure with N–H ····· O bonds of varying strengths giving rise to large splitting for the NH fundamentals. The splittings observed for the fundamentals is due to crystal field effects. However, in solution, the molecular form predominates as δNH appears at a higher frequency and νS–O appears as a strong band at a higher frequency (1048 cm^{-1}) than in the solid state (1026 cm^{-1}).

SERS Spectra

In the SERS spectrum recorded in colloid 1 (Fig. 2) there are a strong band at 1228 cm^{-1} and a medium intense band at 1260 cm^{-1} which do not appear in the normal Raman spectrum. In IR there are two corresponding bands at 1230 and 1257 cm^{-1} arising from δSOH. Appearance of these bands in the SERS spectrum without appreciable shift in frequency indicates that in colloid 1 the adsorbed molecule retains the SOH bond and the selection rules for SERS are different from that of normal Raman (25). Further, the δNH mode (1589 cm^{-1}) is not shifted in frequency when compared with that of the normal Raman spectrum of the solution (1594 cm^{-1}). Therefore, the NH and SOH parts are away from the silver surface since the vibrational modes involving atoms close to the silver surface will be shifted in frequency (11).

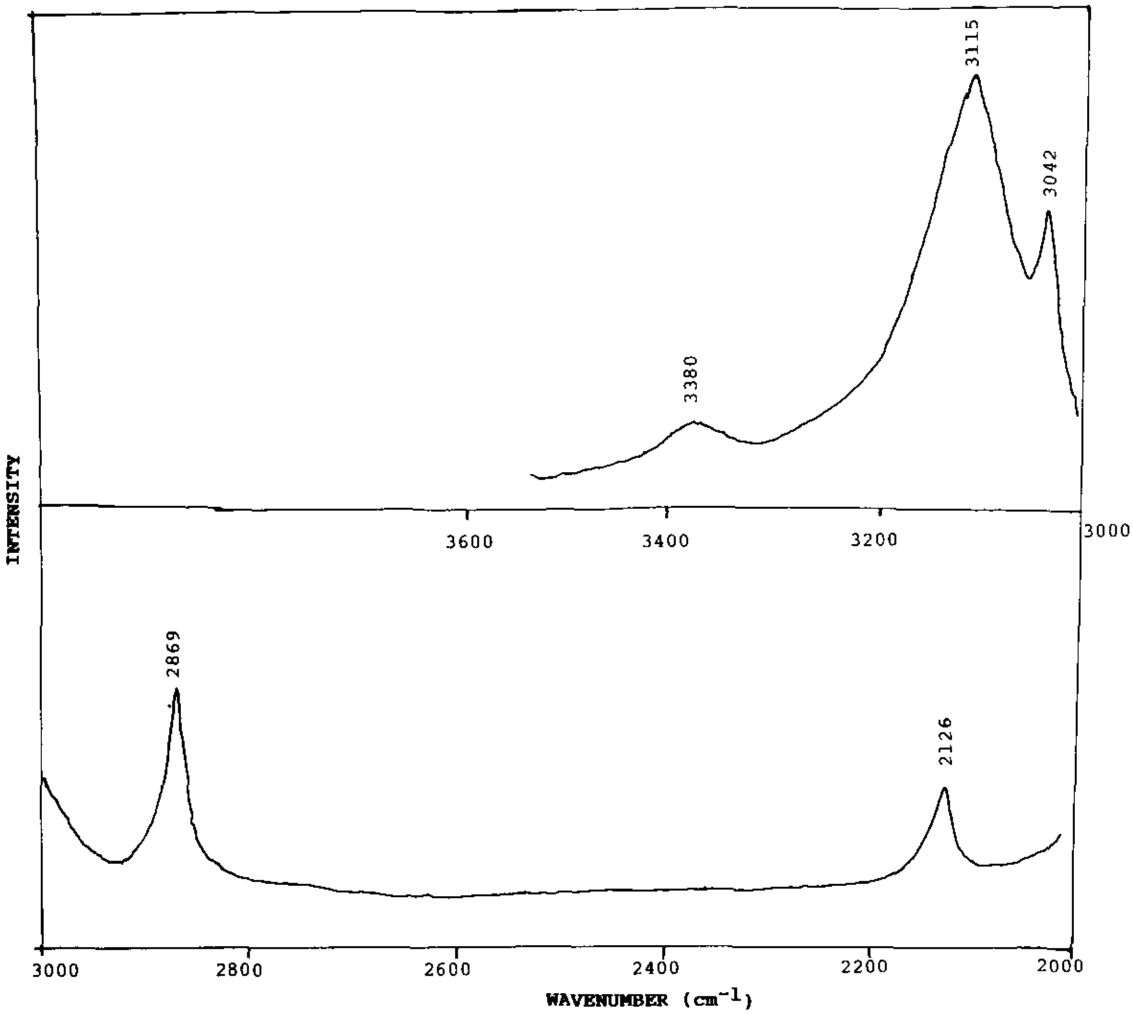

FIG. 4. Raman spectrum of sulfamic acid in the high wavenumber region.

The ν_{as} S=O is not observed in the Raman spectrum of the solution. In the powder spectrum four weak bands at 1280, 1306, 1341, and 1385 cm^{-1} are observed for this mode. The SERS spectrum in colloid 1 shows four bands at 1310, 1395, 1455 and 1489 cm^{-1} corresponding to this mode with considerable shift in frequency and enhancement in intensity. The high frequency shift from the normal values is due to the change of symmetry on adsorption. This indicates the possibility of S ⩦ O ····· Ag linkage since it is expected that the modes involving motions in groups directly interacting with the metal surface are rather prominent in the SERS spectrum and shifted in frequency (11). The appearance of the weak Raman band at 228 cm^{-1} which corresponds to Ag ····· O stretching mode (10, 11) supports this argument. The scissoring and wagging modes of SO_2 (δSO_2 and ωSO_2) are also enhanced, with appreciable shifts from the normal value (Table 1). This also supports the presence of the coordination S ⩦ O ····· Ag. It is reported (10, 11) that the symmetric stretching bands usually do not show appreciable shifts of frequency on chemisorption. Therefore, the enhanced band at 1147 cm^{-1} can be safely assigned to the wagging mode of NH_2. The enhancement in intensity of the twisting, wagging and scissoring modes of NH_2 (tNH_2, ωNH_2 and δNH_2) and the splitting of some of the modes are due to the change of symmetry of the molecule on chemisorption and the consequent breakdown of selection rules (10, 11, 25).

The SERS spectrum in colloid 2 (Fig. 2) shows a medium intensity band at 971 cm^{-1} which is not observed in colloid 1. Further, the δSOH band has not appeared. These facts indicate that the adsorbed molecule does not retain the SOH bond and that silver coordinates with the molecule by forming S–O ····· Ag linkage (10). This is the reason for the enhancement in intensity of the band at 971 cm^{-1} which corresponds to νS–O. Formation of S–O ·····

TABLE 1.
Spectral Data (cm^{-1}) and Band Assignments

IR	Raman (powder)	Raman (aqueous solution)	SERS in colloid 1	SERS in colloid 1	Assignments
3361 mbr	3380 vwbr				νNH
3163 sbr	3115 sbr				
2872 m	3042 m				
	2869 m				
2569 w					
2455 m					
2355 vw					triobands overtones and combinations
2135 vw	2126 w				
2030 w					
1820 wbr					
1570 m	1566 wbr	1594 w	1589 m	1585 wbr	δNH
1540 m	1544 wbr				
1451 s					
	1385 w		1489 s		
1320 sh	1341 w		1455 vs	1395 mbr	ν_{as} S = 0
1294 vs	1306 w		1395 s		
	1280 w		1310 wbr		
1257 m			1260 m		δOH
1230 sh			1228 s		
1191 vs			1147 m		ωNH_2 and ν_s S = 0
	1075 vw				
1130 m					
1070 vs	1061 vs	1061 vs			
1055 sh					
1020 sh	1026 w	1048 s		971 m	νS–O and rNH_2
1003 m					
910 vw					
890 w					γOH
798 m					
702 sh	706 w	707 w	810 w	829 wbr	νS–N
692 vs	686 m				
607 vw					
595 w					
555 sh	560 s	543 mbr	590 m		δSO_2 (scissoring)
545 s	542 s				
535 s			486 s		ωSO_2 (wagging)
435 sh			434 w		
				470 sbr	δSO_3
375 s	369 s				
365 sh	356 s	389 vwbr	380 m		tNH_2
355 sh					
335 w					
			228 w	248 s	νAg ····· O
245 m	251 vw				External modes
	160 w				
225 m	129 w				
	84 w				

Note. v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

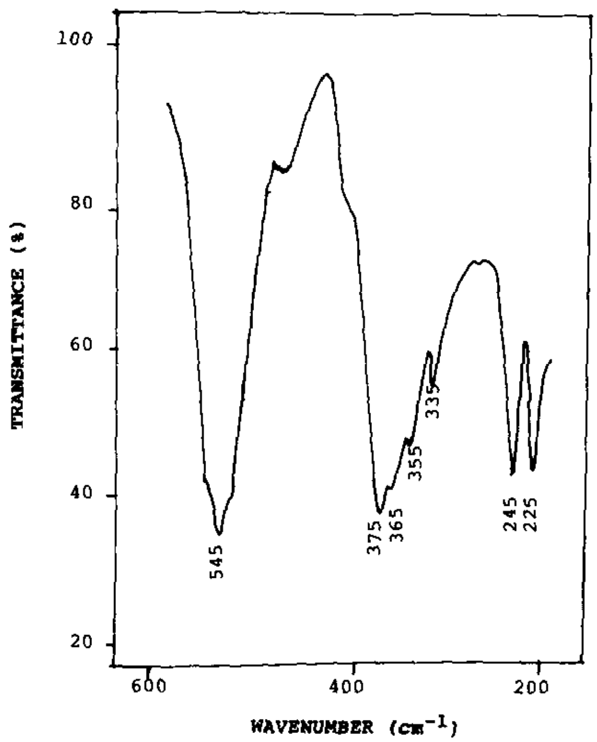

FIG. 5. IR spectrum of sulfamic acid in the 400–200 cm^{-1} region.

Ag linkages is further supported by the observation of the strong band at 248 cm^{-1} due to νAg ····· O (10, 11). The medium broad band around 1395 cm^{-1} and the strong broad band around 470 cm^{-1} are assigned to ν_{as} S=O and δSO_3. Splitting is not observed for most of the internal modes on chemisorption in colloid 2 (Table 1), which indicates that the symmetry of the molecule is not much changed on adsorption. The bands appearing at 810 cm^{-1} in colloid 1 and at 829 cm^{-1} in colloid 2 are due to S–N stretching mode. The possible orientations of the molecule at the silver surface are shown in Fig. 6.

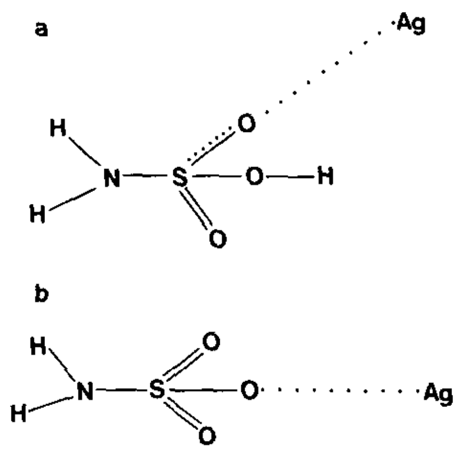

FIG. 6. Orientation of sulfamic acid molecule on the silver surface: (*a*) in collod 1, (*b*) in colloid 2.

CONCLUSION

The sulfamic acid molecule has a structure in between $NH_3^+SO_3^-$ and NH_2–SO_2–OH. On adsorption, in colloid 1 the molecules form S ⋯ O ····· Ag linkages, enhancing the S=O fundamentals in the intensity with shift in frequency. Further, the appearance of δSOH band indicates the retention of the SOH bond. Splitting and shifting of fundamentals observed are due to change of symmetry of the molecule on adsorption. In colloid 2, the νS–O band is shifted in frequency and enhanced in intensity, indicating the removal of a proton and the formation of S ⋯ O ····· Ag linkage.

ACKNOWLEDGMENT

Daizy Philip thanks the CSIR, New Delhi, for a research associateship.

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