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FT-IR, Raman, and SERS Spectra of Arcaine Sulfate

Antony Eapen and I. Hubert Joe

Department of Physics, Mar Ivanios College, Trivandrum 695015, India

and

G. Aruldhas[1]

Regional Research Laboratory (CSIR), Pappanamcode, Trivandrum 695019, India

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Vibrational spectral analysis of arcaine sulfate has been carried out using FT-IR, Raman, and SERS spectra. Raman and FT-IR spectra suggest protonation of the imino groups of the arcaine molecule at the expense of the proton from H_2SO_4. Analysis of SERS spectra shows that the molecule is adsorbed to the silver surface through the uncharged amino group and oxygen sites of the sulfate groups. The large enhancement observed for the amino group bending vibrations suggests that the molecule is adsorbed perpendicular to the silver surface. © 1997 Academic Press

INTRODUCTION

Polyamines react with various acidic polysaccharides, such as heparin, chandroitin, and sulfate, compounds that may occasionally contaminate nucleic acid preparations (1). Arcaine is a diamidino putrescine found in several organisms (2). Arcaine is also reported to possess steriod like anti-inflammatory activity (3). In view of their importance in biological process, FT-IR, normal Raman, and SERS investigations of arcaine sulfate have been carried out to understand the vibrational characteristic features of different groups, their bondings, and conformations.

EXPERIMENTAL

The sample arcaine sulfate (ArS) was procured from Sigma chemicals with a purity of 99.99%. Silver sol was prepared by the method described by Creighton *et al.* (4).

Raman spectra of polycrystalline sample (Fig. 1) were recorded on a Dilor Z-24 spectrometer with 300 mW laser power of a Spectra Physics model 165 argon ion laser (514.5 nm). Nicolet-510P (4000–400 cm^{-1}) and Bruker IFS-66 V (500–50 cm^{-1}) FT-IR spectrometers were used to obtain the FT-IR spectra (Figs. 2 and 3).

SERS spectra (Figs. 4 and 5) were recorded for concentrations 10^{-4} and 10^{-3} M in the stable greenish yellow colloid. To record the SERS spectra equal volumes of colloid and $10^{-3}\,M/10^{-4}\,M$ ArS were added and shaken well. The resulting solutions were taken in a rectangular quartz cell.

CRYSTAL STRUCTURE

ArS is monoclinic and crystallizes in the space group $P2_1/n$ with 12 formula units in the unit cell (5). Of these, three amine sulfate molecules per asymmetric unit lead to interesting amine sulfate interactions through an extensive N–H ⋯ O type hydrogen bond network. The molecule exhibits a layered packing with the zigzag amine chains arranged in planes parallel to **bc**. The three butyl amine segments in *all-trans* configurations are approximately in parallel planes. The sulfate ions interleave these planes.

In all of the polyamine derivatives reported, the amino molecule is protonated and presents as a positive ion whereas the sulfate, phosphate, or chloride, as the case may be, is negatively charged. In this case there are eight protons from the amine and two from H_2SO_4 for hydrogen bonding per molecule, out of which eight of molecule I and nine of molecules II and III are involved N–H ⋯ O type of hydrogen bonding (6). The crystal structure of arcaine sulfate is given in Scheme 1.

FACTOR GROUP ANALYSIS

The factor group analysis (Table 1) using the correlation method (7) gives the distribution of normal modes (exclud-

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[1] To whom correspondence should be addressed.

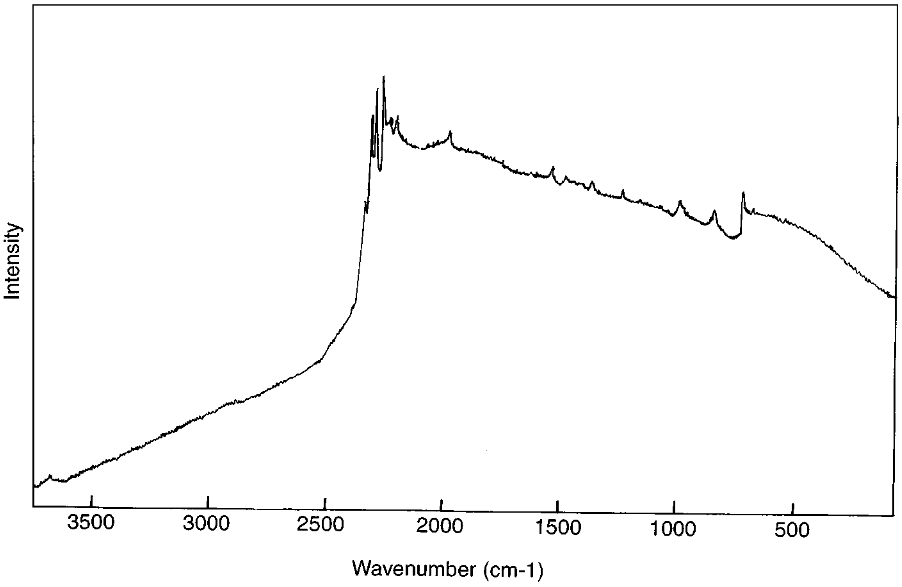


FIG. 1. Raman spectrum of arcaine sulfate (polycrystalline form).

ing acoustic modes) as

$$\Gamma_{\mathrm{ArS}} = 315A_g + 315B_g + 314A_u + 318B_u$$

where the "*g*" modes are Raman active and "*u*" modes are IR active. Detailed splittings of the vibrational modes are given in Tables 2–4.

SPECTRA OF ARCAINE MOLECULE

The crystal structure investigations (5) reveal that the amine molecule presents as positive ion after protonation. In such a case one can expect the characteristic vibrations of the NH_2^+ group in the spectrum. The other groups that are vibrationally significant in the organic complex are the CH_2

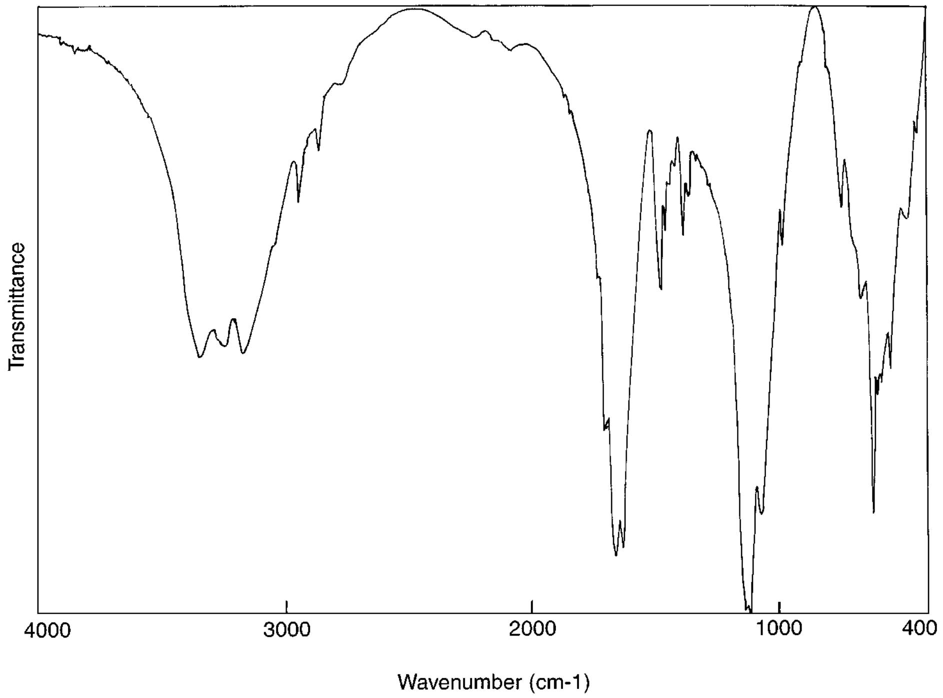


FIG. 2. FT-IR spectrum of arcaine sulfate in the region of 400–4000 cm^{-1}.

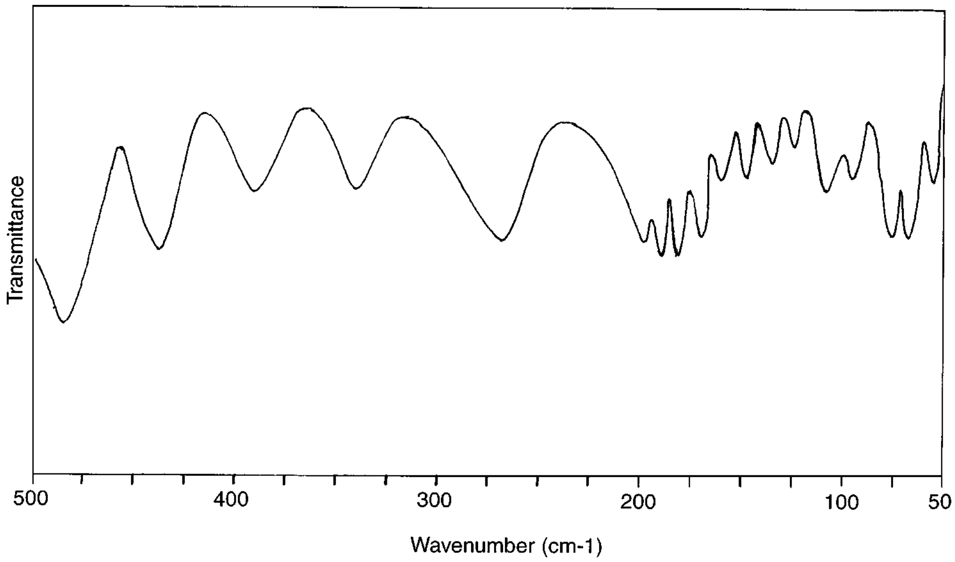


FIG. 3. FT-IR spectrum of arcaine sulfate in the region of 50–500 cm^{-1}.

and NH_2 groups. Identification and interpretation of the vibrational frequencies can reveal information regarding the presence of NH_2 (charged and uncharged) and CH_2 groups.

It is well established that the uncharged NH_2 group has stretching frequencies in the region 3400–3200 cm^{-1} while the charged group has frequencies in the range 3000–2800 cm^{-1} (8, 9). Observation of IR bands in the region 2750–3350 cm^{-1} shows the presence of both charged and uncharged NH_2 groups in the compound. The wagging, twisting, scissoring, and rocking modes of NH_2 are identified and assigned (Table 5). In the IR spectrum of ArS (Fig. 2), the stretching vibrations of NH_2 and CH_2 groups together give rise to a strong broad band extending from 2700 to 3500 cm^{-1} (FWHM ~ 430 cm^{-1}) with five peaks at 2882, 2946, 3177, 3245, and 3348 cm^{-1}. The normal Raman spectrum (Fig. 1) shows a very intense background due to strong fluorescence.

The CH stretching mode of the CH_2 group is normally found in the region 3100–2800 (8). Since this broad frequency range contains NH_2^+ and CH_2 group vibrations,

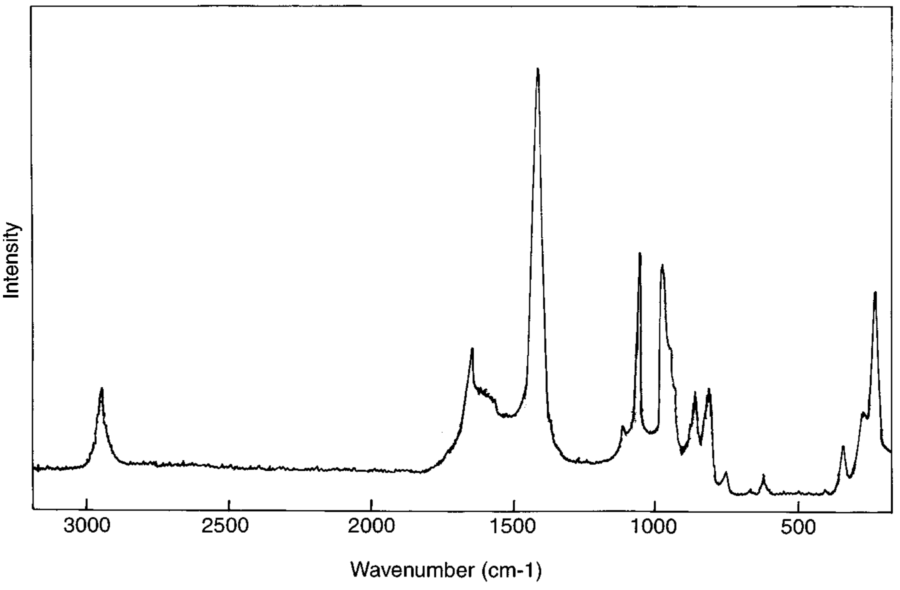


FIG. 4. SERS spectrum of 10^{-4} *M* arcaine sulfate in the silver sol.

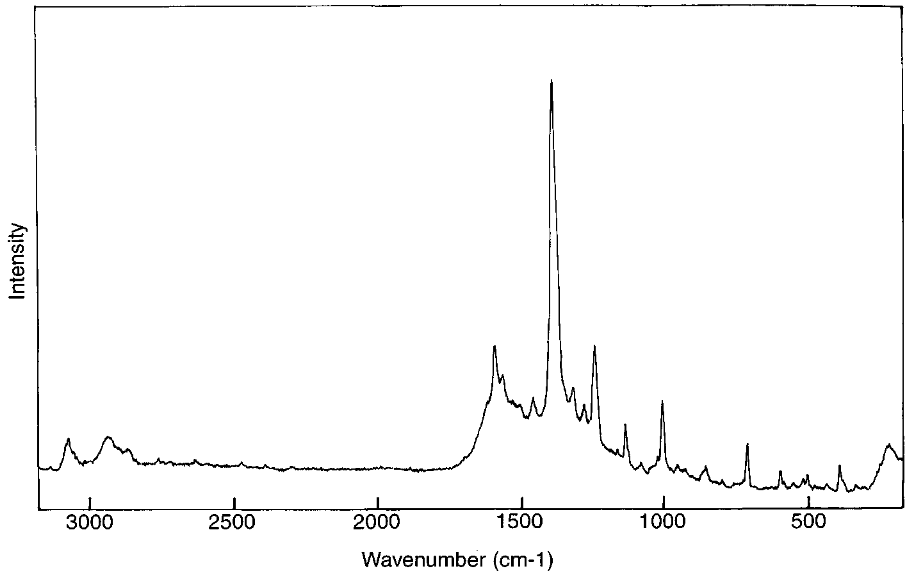


FIG. 5. SERS spectrum of 10^{-3} *M* arcaine sulfate in the silver sol.

unambiguous identification of their vibrational modes has not been possible. The deformation modes of the CH_2 group are observed at 1479 cm^{-1} in Raman and at 1444 and 1475 cm^{-1} in IR.

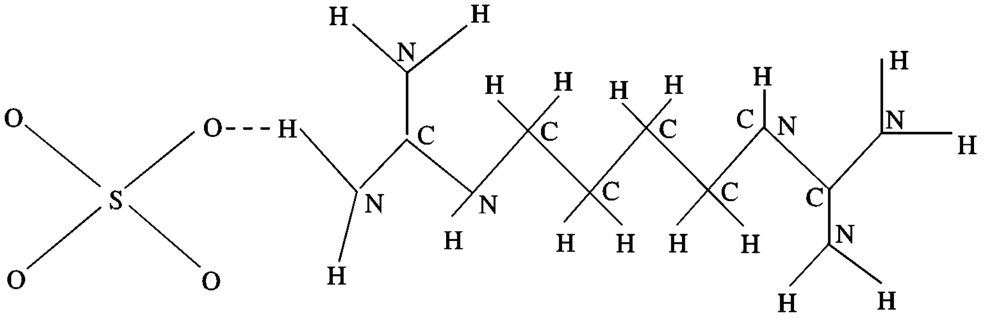
VIBRATIONS OF SO_4^{2-} ION

For an SO_4 tetrahedron having T_d symmetry, the normal modes of vibrations $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ usually appear around 981, 451, 1104, and 613 cm^{-1}, respectively (10). Of these ν_1 and ν_2 are active only in Raman while ν_3 and ν_4 are active in both Raman and IR. In the crystal, since the SO_4^{2-} ions occupy sites of lower symmetry than the free ion, anisotropic crystal fields may remove degeneracies of normal modes and allow inactive modes to become active.

In the IR spectrum, the band due to $\nu_3(F_2)$ modes is expected to be the most intense. The most intense band observed as a doublet (1111 and 1128 cm^{-1}) is assigned to this mode. For the nondegenerate ν_1 mode, a band at 994 cm^{-1} is observed in the Raman spectrum. A shoulder observed at 983 cm^{-1} in the IR spectrum corresponds to this mode. The activations of the inactive $\nu_1(A_1)$ mode in IR are due to the site symmetry effect. Three bands at 393, 440, and 486 cm^{-1} (IR) have been assigned to the doubly degenerate $\nu_2(E)$ mode. The splitting of this doubly degenerate mode is due to correlation field effect. In the $\nu_4(F_2)$ mode region, three intense bands at 597, 619, and 664 cm^{-1} (IR) have been observed.

SERS SPECTRA

Comparison of the SERS spectra for the two concentrations shows that the one corresponding to 10^{-4} *M* concentration is better than that of the other. Though the SERS spectrum for 10^{-4} *M* concentration (Fig. 4) is better than the 10^{-3} *M* concentration (Fig. 5) in general, in certain



SCHEME 1

TABLE 1
Factor Group Analysis of Arcaine Sulfate (Space Group $P2_1/n \equiv C_{2h}^5$; $Z = 12$)

Factor group species C_{2h}	NH_2		CH_2		SO_4		24 C	24 N	24 H	Optical modes	Acoustic modes	Activity	
	Internal modes	External modes	Internal modes	External modes	Internal modes	External modes						Raman	IR
A_g	36	36T, 36R	36	36T, 36R	27	9T, 9R	18	18	18	315		a	f
B_g	36	36T, 36R	36	36T, 36R	27	9T, 9R	18	18	18	315		a	f
A_u	36	36T, 36R	36	36T, 36R	27	9T, 9R	18	18	18	315	− 1	f	a
B_u	36	36T, 36R	36	36T, 36R	27	9T, 9R	18	18	18	315	− 2	f	a
	144	144T, 144R	144	144T, 144R	108	36T, 36R	72	72	72	1260	− 3		

Note. T, translations, R, librations; a, active; f, forbidden.

regions the 10^{-3} *M* concentration gives better details. For example, in the 10^{-3} *M* spectrum three bands have been observed at 1592, 1565, and 1506 cm^{-1} for the NH_2 scissoring whereas only two are observed in the 10^{-3} *M* spectrum. In the 10^{-4} *M* spectrum, two intense bands are observed in the region 950–1050 cm^{-1} which are weak in the 10^{-3} *M* spectrum. Spectral data and assignments are shown in Table 6. Observation of an intense band at 226 cm^{-1} and a shoulder at 281 cm^{-1} in the metal adsorbate stretching frequency region clearly shows the presence of metal adsorbate interaction. It is also evident that the molecule is adsorbed to the metal surface through two different sites.

The band observed around 1400 cm^{-1} corresponding to the NH_2 rocking mode is the most intense in the two concentrations. In the 10^{-3} *M* concentration, an additional weak line also appears at 1318 cm^{-1} for this mode. This is understandable since the C–N distance of the arcaine molecule has different values ranging from 1.33 to 1.50 Å. For the wagging mode of NH_2, three bands (673, 758, and 816 cm^{-1}) are observed in the 10^{-4} *M* and only one band at 717 cm^{-1} is observed in the 10^{-3} *M*) spectrum. Intensity enhancement is observed for the stretching and scissoring modes of NH_2. Further, the C–N stretching vibration which could not be observed in the normal Raman spectrum appears at 1041 cm^{-1} with intensity enhancement. The observation of intensity enhancement in all the amine group vibrations indicate strong interaction of the molecule to the silver surface through nitrogen. The splitting of the NH_2 wagging and rocking modes can be attributed to the change of symmetry of the molecule on chemisorption and the consequent breakdown of selection rules.

The stretching and deformation mode of CH_2 close to the amine group have also shown marked intensity enhancement in both the spectra. Hence it is reasonable to infer that the mechanism behind the interaction between the amine group (1244 and 2950 cm^{-1}) and the metal surface is the coordination through nitrogen lone pair electrons. From results reported (11–13) earlier on SERS spectra of compounds involving amine groups, it is clear that the band at 281 cm^{-1} is an Ag–N stretching vibration.

According to the surface selection rule (14, 15), when a molecule is adsorbed perpendicular to the metal surface, its in-plane bending modes will be more enhanced when compared with its out-of-plane bending modes while reverse is the case when it is adsorbed flat on the metal surface. In the present case, the in-plane bending modes of the NH_2 group (rocking and scissoring) adsorbed on the silver surface are more enhanced than its out-of-plane bending

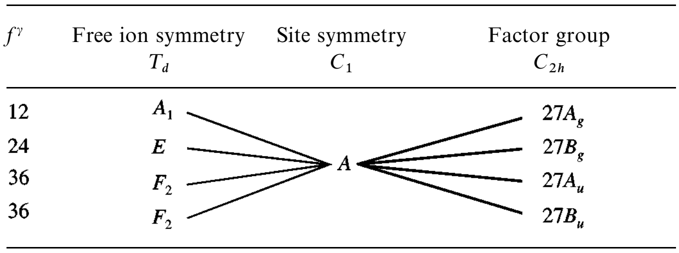
TABLE 2
Correlation Scheme for the Internal Vibrations of the NH_2 Group in the ArS Crystal

f^{γ}	Free ion symmetry C_{2v}	Site symmetry C_1	Factor group symmetry C_{2h}
48	A_1		$36A_g$
48	A_1	A	$36B_g$ $36A_u$
48	B_1		$36B_u$

TABLE 3
Correlation Scheme for the Internal Vibrations of the CH_2 Group in the ArS Crystal

f^{γ}	Free ion symmetry C_{2v}	Site symmetry C_1	Factor group symmetry C_{2h}
48	A_1		$36A_g$
48	A_1	A	$36B_g$ $36A_u$
48	B_1		$36B_u$

TABLE 4
Correlation Scheme for the Internal Vibrations of the SO_4 Group



modes. Therefore it is reasonable to assume that adsorption of the molecule is such that the bond is perpendicular to the silver surface.

TABLE 5
Vibrational Spectral Data (in cm^{-1}) and Band Assignments of Arcaine Sulfate

Raman	IR	Assignments
	57 vw 69 w 75 w	Lattice modes
	96 vw 108 vw 117 vw 127 vw 134 vw 148 vw 159 vw	Translations and librations of SO_4^{2-}
	169 w 179 w 189 w 198 w 269 w	Translations and librations of cations
	339 vw	δ(CCN)
	393 vw 440 w 486 m	$\nu_2(SO_4)$
	548 s 582 s	$t(NH_2)$
	597 s 619 vs 664 s	$\nu_4(SO_4)$
722	742 m	$\omega(NH_2)$
844		ν(C–C)
994	983 sh	$\nu_1(SO_4)$
	1074 s	ν(C–N)
	1111 vvs 1128 vvs	$\nu_3(SO_4)$
1231	1230 sh	$\rho(CH_2)$
1361	1364 w 1388 m	$\omega(CH_2)$ $\rho(NH_2)$
1479	1458 m 1475 s 1506 w 1522 w	$\delta(CH_2)$
1527	1541 w 1557 sh 1633 vvs 1659 vs 1689 sh	NH_2^+ scissoring NH_2 scissoring
2199 2230 2241 2272 2300 2335	2231 vvw	Overtones and combinations of $\delta, \rho, \omega(CH_2)$ and $\delta, \rho, t(NH_2)$
	2752 vvw 2866 w 2882 w	$\nu_s(CH_2)$ $\nu_s(NH_2^+)$
	2946 m	$\nu_{as}(CH_2)$, $\nu_{as}(NH_2^+)$
	3177 vs, br 3245 vs, br	$\nu_s(NH_2)$
	3348 vs, br	$\nu_{as}(NH_2)$

Note. Relative intensities: v, very; s, strong; w, weak; m, medium; sh, shoulder, br, broad. ν, stretching; δ, bending; ω, wagging; ρ, rocking; t, twisting. Subscripts as and s refer to asymmetric and symmetric, respectively.

Intensity enhancement is also noticed in the symmetric stretching mode (970 cm^{-1}) of the SO_4^{2-} ion. This suggests adsorption of the molecule to the metal surface via oxygen atom of sulfate ion. The intense band at 226 cm^{-1} is assigned to Ag ··· O stretching vibrations.

TABLE 6
SERS Spectra Data and Vibrational Assignments for Arcaine Sulfate

10^{-3} *M*	10^{-4} *M*	Assignment
219 w	226 s	ν(Ag ··· O)
	281 sh	ν(Ag ··· N)
394 w	343 w 407 vvw	$\nu_2(SO_4)$
508 vvw 525 vvw		$t(NH_2)$
592 vvw 603 vw	613 vw	$\nu_4(SO_4)$

TABLE 6—*Continued*

10^{-3} *M*	10^{-4} *M*	Assignment
717 m	673 vvw 758 vw 816 m	$\omega(NH_2)$
856 vw 928 vvw 951 vvw	850 m 915 sh 943 sh	ν(C–C)
	970 s	$\nu_1(SO_4)$
1008 m 1025 vvw	1041 s	ν(C–N)
1082 vvw 1136 w 1166 vvw	1103 w	$\nu_3(SO_4)$
1244 m 1280 w		$\rho(CH_2)$
1318 w 1392 vvs	1422 vvs	$\rho(NH_2)$
1459 w		CH_2 scissoring
1506 vvw 1565 w 1592 m	1570 w 1651 w	NH_2 scissoring
2759 w 2867 vw		$\nu_s(CH_2)$
2936 w 3069 w	2950 m	$\nu_{as}(CH_2)$
3132		$\nu_s(NH_2)$
	3350 m, br	$\nu_{as}(NH_2)$

Note. Relative intensities: v, very; s, strong; w, weak; m, medium; sh, shoulder, br, broad. ν, stretching; δ, bending; ω, wagging; ρ, rocking; t, twisting. Subscripts as and s refer to asymmetric and symmetric, respectively.

RESULTS

1. The observation of vibrational frequencies of charged and uncharged NH_2 groups reveal that imino groups of arcaine molecule are protonated at the expense of proton from H_2SO_4.

2. Observed vibrational frequencies of the SO_4^{2-} group suggest the presence of both site symmetry and correlation field effects.

3. SERS spectra shows that the molecule is adsorbed to the silver surface through the uncharged amino groups and oxygen sites of sulfate groups.

4. Larger enhancement observed for amino group bending vibrations suggests that the molecule is adsorbed perpendicular to the metal surface.

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