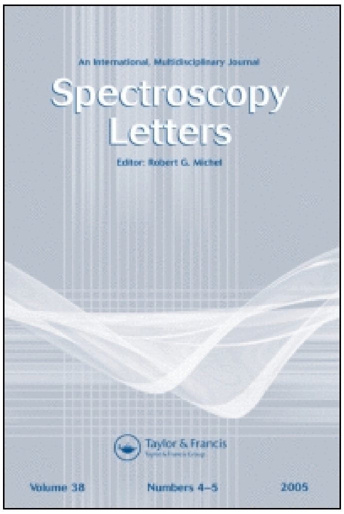

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Infrared, Raman, and SERS Spectra of Betaine Arsenate

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To cite this Article Haresh, R. , Philip, Daizy and Aruldhas, G.(1995) 'Infrared, Raman, and SERS Spectra of Betaine Arsenate', Spectroscopy Letters, 28: 1, 11 — 28

To link to this Article: DOI: 10.1080/00387019508011651

URL: http://dx.doi.org/10.1080/00387019508011651

SPECTROSCOPY LETTERS, 28(1), 11-28 (1995)

INFRARED, RAMAN, AND SERS SPECTRA OF BETAINE ARSENATE

Key words: Betaine arsenate, Infrared spectrum, Raman spectrum, SERS spectrum, Silver colloid, Adsorption.

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ABSTRACT

Infrared and Raman spectra of betaine arsenate are recorded and analyzed. It is found that protonation of betaine occurs at the expense of proton from H_3AsO_4. Further, H_2AsO_4 and H_3AsO_4 groups coexist in the crystal. SERS spectrum is recorded in silver colloid. Chemisorbed arsenate species is found to have a C_{3v} symmetry. Betaine arsenate molecule has two adsorption sites.

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INTRODUCTION

Betaine arsenate, $(CH_3)_3NCH_2COO.H_3AsO_4$, belongs to a group of compounds consisting of an amino acid and an inorganic compound. It shows interesting physical properties with temperature and several studies have been made in this respect[1-5]. Structural investigations indicate that the arsenate tetrahedra are chained by disordered hydrogen bonds and the molecular motions are hindered by hydrogen bond coupling between the inorganic and organic components. Therefore, one may expect significant changes in the vibrational frequency regions of orthoarsenate and betaine groups. However, very limited vibrational data are available for both betaine and arsenate compounds. Hence, an analysis of the infrared and Raman spectra of the compound has been carried out to characterise the vibrational bands due to betaine and arsenate groups and to understand the nature of their co-ordination in the crystal. Its SERS spectrum has also been investigated since it is expected to give informations regarding the nature of adsorption and orientation of the adsorbed species on the metal surface.

EXPERIMENTAL

Betaine arsenate is grown from aqueous solution containing betaine and arsenic acid in the molar ratio 1:1 at room temperature[6,7]. Raman spectrum of the powder sample (Figs. I and II) in the region 50-4000 cm^{-1} is recorded using a Dilor GMBH Z24 Raman spectrometer equipped with a Spectra Physics model 165 Ar^+ laser. 488.0 nm radiation of 40 mW power is used for excitation. IR spectrum (4000-200 cm^{-1}) is

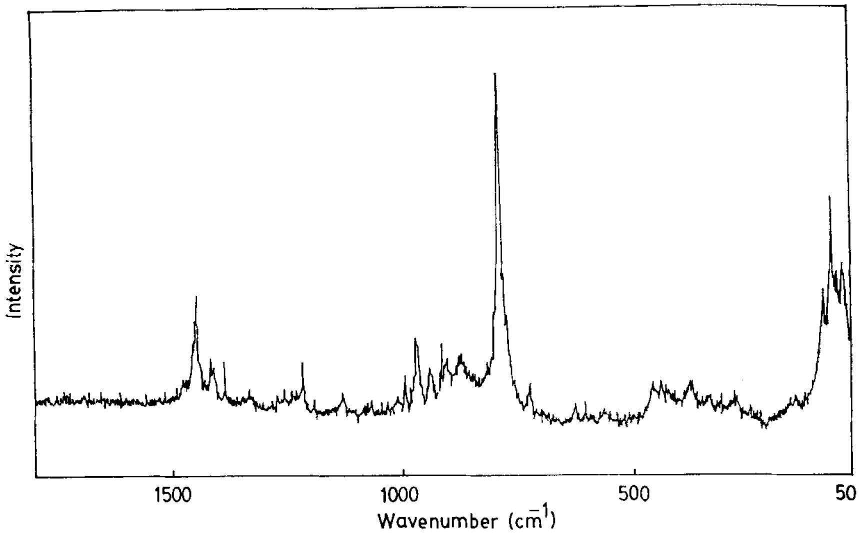

FIG. I - Raman spectrum of betaine arsenate in the 50-1750 cm^{-1} region.

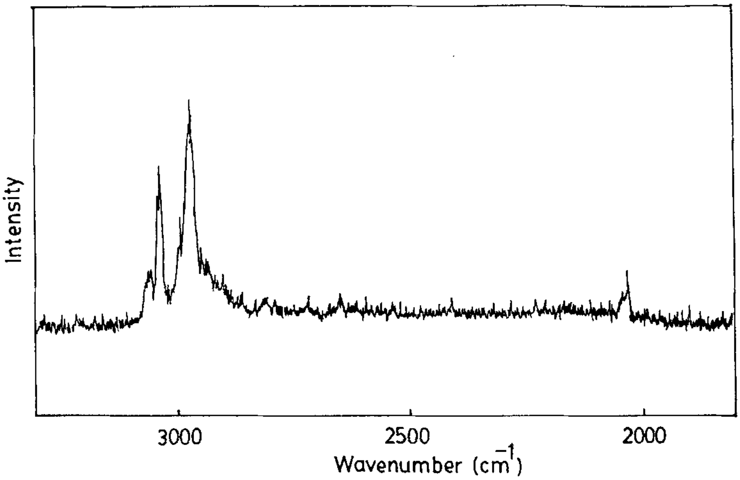

FIG. II - Raman spectrum of betaine arsenate in the 1750-3600 cm^{-1} region.

obtained on a Perkin Elmer 577 spectrometer with the sample in KBr (Fig.III).

The SERS spectrum (Fig,.IV) has been investigated in the stable greenish-yellow colloid having a sharp absorption maximum at 400 nm prepared by the method described by Creighton et al[8]. A 100 ml silver nitrate solution (6×10^{-4}M) is added dropwise to a 300 ml sodium borohydride solution (1.2×10^{-3}M) with slow stirring. Prior to mixing, both solutions have been chilled by ice-cold water. Chemicals are procured from Sigma, U.S.A. Deionised water has been used throughout.

The electronic absorption spectra (Fig.V) of the silver colloid, betaine arsenate and adsorbed betaine arsenate have been recorded on a UV-240 Shimadzu UV-Visible recording spectrometer. When betaine arsenate gets adsorbed onto the silver surface, the colour changes to light pink and the strong sharp band at 400 nm becomes broad and an additional broad band appears around 490 nm. These features are usually observed in aggregate colloids[9,10]. To record the SERS spectra, 1 ml of 10^{-4}M betaine arsenate solution has been added to 100 ml of the colloid. The resulting solution with a slight change in colour is taken in a rectangular quartz cell and the Raman spectrum is recorded on a Dilor GMBH Z24 spectrometer with 400 mW laser power.

RESULTS AND DISCUSSION

Factor group Analysis

Betaine arsenate crystallizes in the monoclinic system $P2_1/n$ with four formula units in the unit

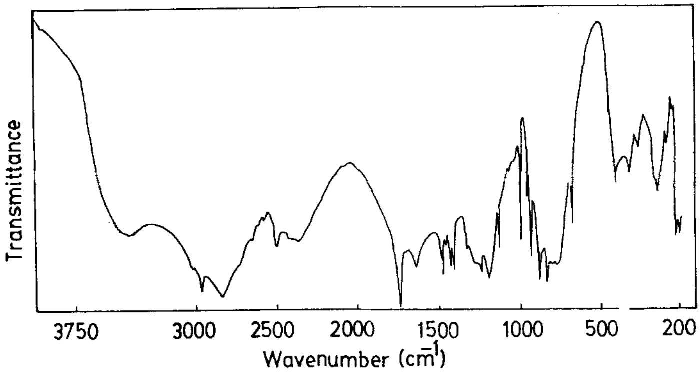

FIG. III - IR spectrum of betaine arsenate in the 4000-200 cm^{-1} region.

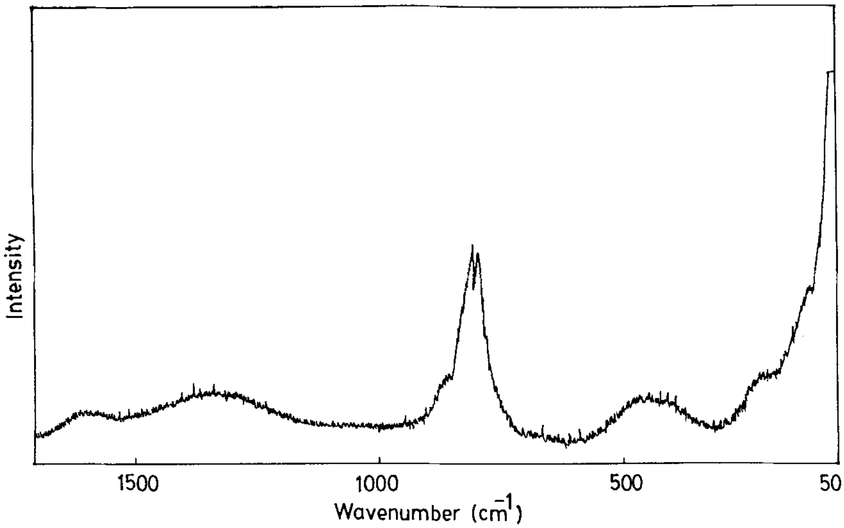

FIG. IV - SERS spectrum of betaine arsenate.

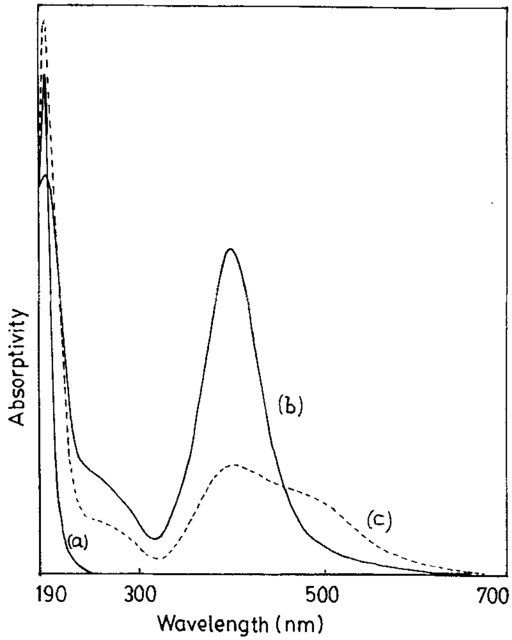

FIG. V - UV-Visible spectrum of
(a) betaine arsenate
(b) silver colloid and
(c) adsorbed betaine arsenate

cell[11]. All the atoms occupy the general site C_1 in the crystal. The factor group analysis by the correlation method gives the distribution of irreducible representation at k = 0 as

$$\Gamma = 81A_g + 81B_g + 80A_u + 79B_u$$

where A_g and B_g modes are Raman active while A_u and B_u are IR active.

The AsO_4 tetrahedron is asymmetrically surrounded by hydrogen atoms (Fig.VI) with two long As-O bonds ($As-O_3$ and $As-O_5$). The betaine molecule is coupled to the arsenate group by two hydrogen bonds $O_2 \cdots H_{12}$ and $O_1 \cdots H_{14}$ which are not so much different[11]. The symmetry of AsO_4 is lowered from T_d to C_1 in the crystal and the correlation diagrams for its internal modes through the site group to the factor group are shown in Tables I and II. The observed bands and their probable assignments are given in Table III.

Vibrations of Betaine Molecule

The internal modes of betaine molecule may be separated as CH_3, CH_2, COO^- and various chain vibrations. Independent assignments of bands due to CH_3 and CH_2 are difficult. However, the most intense bands observed in Raman centred around 2972 and 3032 cm^{-1} are given to symmetric stretching vibrations of CH_2 and CH_3 respectively. In the bending mode region[12,13] (1300-1460 cm^{-1}) of C-H four bands are observed in Raman. The weak band at 1336 cm^{-1} is assigned to the symmetric bending vibration. The bands appeared at 1387 and 1482 cm^{-1} with weak intensity and the band at 1416 cm^{-1} with medium intensity are given to their asymmetric bending. In IR, two strong bands are observed at 1403 and 1425 cm^{-1} corresponding to this vibration. Though the frequencies and number of splitting observed for CH_3 in betaine arsenate are similar to those in betaine phosphate[14], it is different from that observed in betaine phosphite.[14]

The observation of symmetric stretching mode of $C = 0$ at 1738 and C-O at 1235 cm^{-1} in IR, which are

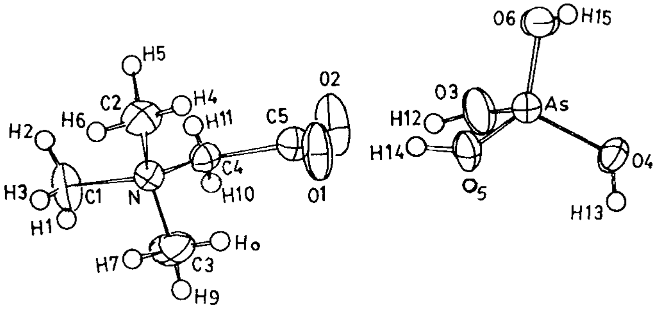

FIG . VI - Structure of betaine arsenate molecule.

characteristic bands[15] for the existence of COOH indicates the possibility of protonation of COO^- group in the crystal. In an ionized carboxyl group COO^-, the bands due to $\nu_{as}COO^-$ appears in the region 1550-1650 cm^{-1}. The strong band at 1637 cm^{-1} in IR is assigned to this mode. The strong band in the Raman spectrum at 1447 cm^{-1} and the medium intense band at 1457 cm^{-1} in IR can be readily assigned to the symmetric stretching of COO^-. The bands observed in the bending region (Table III) in the 450-700 cm^{-1} also supports the coexistence of both COO^- and COOH groups in the crystal. For this to happen, one hydrogen from the acid group has to be associated with the COO^- group giving rise to the existence of both $H_2AsO_4^-$ and H_3AsO_4 groups in the crystal.

Vibrations of Arsenate

Assuming the free rotation of the hydroxyl groups about their As-O bonds, the H_3AsO_4 molecule can be described as having C_{3v} symmetry[16,17]. Group theory

TABLE I

Correlation scheme for the internal vibrations of AsO_4^{3-} ion in Betaine arsenate

Free ion symmetry of AsO_4^{3-} T_d	H_3AsO_4 free ion symmetry C_{3v}	Site symmetry C_1	Factor group C_{2h}, $Z^B = 4$
ν_s As-O (ν_1)A_1(818)	νAs-O A_1(923)	A	$A_g+B_g+A_u+B_u$
δ_sOAsO (ν_2)E(341)	δ_{as}As(OH)$_3$ E(270)	A	$A_g+B_g+A_u+B_u$
		A	$A_g+B_g+A_u+B_u$
ν_{as}As-O (ν_3)F_2(786)	ν_sAs(OH)$_3$ A_1 (769)	A	$A_g+B_g+A_u+B_u$
	ν_{as}As(OH)$_3$ E (808)	A	$A_g+B_g+A_u+B_u$
		A	$A_g+B_g+A_u+B_u$
δ_{as}OAsO (ν_4)F_2(399)	δ_sAs(OH)$_3$ A_1 (350)	A	$A_g+B_g+A_u+B_u$
	r As(OH)$_3$ E (350)	A	$A_g+B_g+A_u+B_u$
		A	$A_g+B_g+A_u+B_u$

TABLE II

Correlation scheme for the internal vibrations of AsO_4^{3-} ion in Betaine arsenate

Free ion symmetry of AsO_4^{3-} T_d	H_2AsO_4 free ion symmetry C_{2v}	Site symmetry C_1	Factor group C_{2h}, $Z^B = 4$
ν_sAs-O (ν_1)A_1(818)	$\nu_s AsO_2$ A_1(875)	A	$Ag_g+B_g+A_u+B_u$
δ_sOAsO (ν_2)E(341)	$\delta_s As(OH)_2$ A_1(285)	A	$A_g+B_g+A_u+B_u$
	τAsO_2 A_2(315)	A	$A_g+B_g+A_u+B_u$
ν_{as}As-O (ν_3)F_2(786)	$\nu_s As(OH)_2$ A_1(745)	A	$A_g+B_g+A_u+B_u$
	$\nu_{as} AsO_2$ B_1(915)	A	$A_g+B_g+A_u+B_u$
	$\nu_{as} As(OH)_2$ B_2(765)	A	$A_g+B_g+A_u+B_u$
δ_{as}OAsO (ν_4)F_2(399)	$\delta_s AsO_2$ A_1(365)	A	$A_g+B_g+A_u+B_u$
	r AsO_2 B_1(365)	A	$A_g+B_g+A_u+B_u$
	w AsO_2 B_2(365)	A	$A_g+B_g+A_u+B_u$

considerations show that the nine fundamental skeletal vibrations are partitioned over the symmetry species as $\Gamma = 3A_1 + 3E$ which can be described as four stretching and five bending modes. On lowering the symmetry of AsO_4^{3-} from T_d to C_{3v}, a vibration of the F_2 species gives rise to A_1 and E modes, while that of E species gives rise to an E mode in C_{3v} (Table I). For a free $H_2AsO_4^-$ under C_{2v} symmetry, group theory predicts nine fundamental skeletal vibrations partitioned over the symmetry species as $\Gamma = 4A_1 + A_2 + 2B_1 + 2B_2$. Correlation scheme showing the lowering of the symmetry from T_d to C_{2v} is given in Table II.

In the As-O stretching region (700-950 cm^{-1}) three bands are expected corresponding to H_3AsO_4. The strong band in Raman spectrum at 970 cm^{-1} can be assigned to the symmetric As = 0 stretching vibration. The very strong band observed at 791 cm^{-1} in the Raman spectrum may have contributions from $\nu_s As(OH)_3$, $\nu_s CN^+$ and $\nu_{s,as} As(OH)_2$ as they occur in this region. A very strong broad band is observed around 780 cm^{-1} in IR corresponding to these vibrations. The asymmetric stretching vibration of $As(OH)_3$ is also identified. Observation of other bands in the stretching mode region, which are in agreement with the vibrational frequencies[16,17] of $H_2AsO_4^-$ confirms the existence of $H_2AsO_4^-$ in the crystal. The medium intense broad band at 874 cm^{-1} in Raman is assigned to $\nu_s AsO_2$. The C-C stretching vibration is expected[18] around 880 cm^{-1}. The strong band at 881 cm^{-1} in IR can be due to this vibration. The medium intense Raman band at 913 cm^{-1} arises from the asymmetric stretching vibration of AsO_2. Its IR counterpart is observed at 928 cm^{-1} with

TABLE III

Spectral data (cm^{-1}) and band assignments of $(CH_3)_3NCH_2COO.H_3AsO_4$

Raman	IR	Assignment
52 s		
64 m		
112 s		External modes
160 m		
	210 s	
	215 s	
244 w	230 w	
	260 m	
	280 sbr	δ_{as} As(OH)$_3$
295 m		δ_s As(OH)$_2$
	310 msh	τAsO$_2$
338 m	340 wsh	δ_s As(OH)$_3$
378 m	376 w	δ_sAsO$_2$ & δ_{as} AsO$_2$
	399 m	
432 m	432 sh	δCN
457 m	460 m	
556 wbr	540 sh	
	560 vsbr	δCO$_2$,δAsOH out-of-plane and δCOOH
	595 ssh	
	585 ssh	
606 w	610 ssh	
627 w		
727 m	725 sh	ν_s As(OH)$_2$
791 vs	780 sbr	ν_{as} As(OH)$_3$, ν_{as}As(OH)$_2$ and νCN
808 sh	833 vs	ν_{as} As(OH)$_3$
874 mbr	881 s	ν_sAsO$_2$ and νC-C

Table III - contd

Raman	IR	Assignment	
913 m	928 m	ν_{as} AsO_2	
942 m	949 m	r CH_2 and rCH_3	
970 s 997 m	991 m	νAs=0	
	1015 wbr 1030 m	combination	
1134 w	1130 m 1190 mbr	δCOH in plane	
1222 w	1235 s	νCO	
1272 w	1275 br	δAsOH in-plane	
1336wbr	1325 msh	δ_s CH_3 & δ_s CH_2	
1387 w 1416 m	1403 s 1425 s	$\delta_{as}CH_3$	
1447 s	1457 m	ν_s COO^-	
1482 sh	1475 s	δ_{as} CH_2	
1535 vw	1637 sbr	ν_{as} COO^-	
	1738 sbr	ν_s C=O	
	1750 sh		
2044 vw	2180 sh 2360 mbr		Triobands
	2837 vsbr		
2900 w 2914 wsh 2972 s 2997 m	2983 vs	ν_s CH_2	CH stretching modes
2997 m 3032 s 3042 sh 3068 mbr	3000 sbr 3080 m	ν_s CH_3	

medium intensity. $\nu_s As(OH)_2$ is expected[16] at 745 cm^{-1}. The band at 727 cm^{-1} is assigned to this vibration.

In the bending region of the arsenate group, the low frequency band at 280 cm^{-1} in IR is assigned to the $\delta_{as} As(OH)_3$ which is expected to be very strong in IR. The medium intense band at 295 cm^{-1} in Raman corresponds to the symmetric $As(OH)_2$ vibration of $H_2AsO_4^-$. The other vibrations are also identified (Table III).

Although it is concluded in the structural study[11] that the two hydrogen bonds connecting the acid group and betaine molecule are of the same strength, the vibrational spectra indicate that, one hydrogen is strongly bonded to the betaine molecule. That is, protonation of COO^- may be at the expense of H_3AsO_4 giving rise to COOH and $H_2AsO_4^-$. Strong hydrogen bonding in the crystal is also supported by the observation of ABC bands in the expected region[13,15,19].

SERS SPECTRUM

In metal-oxygen chemisorbed systems, usually a low frequency band is observed for its stretching mode[20-22]. In the present case, the band observed at 214 cm^{-1} is assigned to νAg-O. Observation of three SERS bands (Fig.IV) for the stretching mode of the arsenate ions indicates a C_{3v} symmetry for the metal-arsenate adsorbed system. If an As-O(H) bond exists in the adsorbed system, its in-plane or out-of-plane bending modes or both would have been enhanced. The absence of these bands shows that the protons are displaced from the orthoarsenate ion in

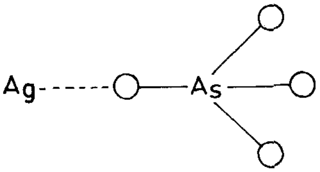

FIG. VII - Geometry of adsorption of betaine arsenate molecule on the silver surface.

TABLE IV

Spectral data (cm^{-1}) and band assignments of Betaine arsenate

SERS	ASSIGNMENTS	
122 sh	$\nu Ag-O_B$	
214 sh	$\nu Ag-O_A$	
468 mbr	δAsO_4^{3-}	
792 s	$\nu_s As-O \dots Ag(A_1)$	AsO_4^{3-}
802 s	$\nu_s AsO_3(A_1)$	
865 sh	$\nu_{as} AsO_3(E)$	
1368 wbr	$\nu_s COO^-$	
1609 wbr	$\nu_{as} COO^-$	

A - Arsenate; B - Betaine

solution and that the adsorbed species interacts with silver through the other oxygen forming a weak Ag.....O.....As linkage[9]. Therefore, the possible symmetry of adsorption is the one given in Fig.VII (C_{3v}) giving rise to three ($2A_1$+E) stretching bands (Table IV). Greaves and Griffith[9] have reported a similar SERS spectrum for Na_2HAsO_4.

The band observed at 122 cm^{-1} may be due to the ν Ag.....O of betaine molecule adsorbed on the silver surface. The observation of the weak bands at 1368 and 1609 cm^{-1} which are assigned to ν_s COO^- and ν_{as} COO^- respectively supports this argument. In conclusion, there are two adsorption sites for betaine arsenate on the silver surface namely the carboxylic oxygen and the free oxygen atom of H_3AsO_4.

CONCLUSION

Protonation of betaine occurs at the expense of proton of H_3AsO_4. $H_2AsO_4^-$ and H_3AsO_4 groups coexist in the crystal. The chemisorbed species has a C_{3v} symmetry. There are two adsorption sites for betaine arsenate molecule on the silver surface.

ACKNOWLEDGMENT

Daizy Philip thanks the CSIR, New Delhi for a Research Associateship.

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Date Received: July 18, 1994
Date Accepted: August 24, 1994