

Potential dependent SERS profile of sulfanilamide on silver electrode

Hema Tresa Varghese,¹ C. Yohannan Panicker,^{2#} P. L. Anto³ and Daizy Philip^{2*}

¹ Department of Physics, Fatima Mata National College, Kollam, Kerala, 691 001, India

² Mar Ivanios College, Nalanchira, Thiruvananthapuram, Kerala, 695 015, India

³ Department of Physics, St Thomas College, Trichur, Kerala, 680 001, India

Received 12 March 2005; Accepted 27 July 2005

FT-IR and FT-Raman spectra of Sulfanilamide were recorded and analysed. Surface-Enhanced Raman Scattering (SERS) spectrum was recorded on a silver electrode surface. Potential dependence of SERS profile was studied. The profile is most prominent at an electrode potential of -1.0 V. The molecule is adsorbed on the silver surface with the benzene ring in a 'tilted orientation'. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: sulfanilamide; vibrational spectra; SERS; silver electrode

INTRODUCTION

Sulfanilamides were the first effective chemotherapeutic agents to be employed systematically for the prevention and cure of bacterial infections in humans.¹ Furthermore, sulfa drugs and their complexes have many applications, such as diuretic, antiglaucoma or antiepileptic drugs, among others.^{2–4} The sulfanilamides exert their antibacterial action by the competitive inhibition of the enzyme dihydropterase synthetase towards the substrate *p*-aminobenzoate.⁵ Some metal sulfanilamides get much attention owing to their antimicrobial activity. The crystal structure of three forms of sulfanilamide^{6–9} and the characterization of sulfanilamide and its derivative complexes had been extensively studied.^{10–13} However, the number of well-documented IR and Raman studies on the structures of free sulfanilamide and its derivative complexes are very limited. IR spectra of SO₂ group in sulfonamide derivatives and related compounds had been reported by Rastelli *et al.*¹⁴ Narang and Gupta¹⁵ and Blasco *et al.*² had described IR characterization of Cu(II) complexes of sulfanilamide. SO₂ vibrations and NH₂ modes of amino and sulfonamide group of sulfanilamide had been investigated by Narang and Gupta.¹⁵ In addition to these vibrations, in order to deduce structural differences upon coordination, ν (SN) vibrations of sulfanilamide had been reported by Blasco *et al.*² *Ab initio* quantum mechanical calculations for the assignment of IR spectrum of sulfanilamide had been reported by Topaclı and Topaclı.¹⁶

However, there is no report on the surface-enhanced Raman scattering (SERS) spectrum of the title compound. In the present study, the IR, Raman and potential dependent SERS profile of sulfanilamide are reported to get an idea regarding orientation of the molecule on the silver surface and optimum electrode potential for SERS activity.

EXPERIMENTAL

Sulfanilamide was procured from Sigma-Aldrich, USA. The FT-IR and FT-Raman spectra (Figs 1 and 2) were recorded using a Bruker IFS 66 v FT-IR/FT-Raman spectrometer having a resolution of 0.1 cm⁻¹. SERS spectra (Fig. 3) were recorded using a confocal microprobe Raman system (LabRam I). The details of the Raman system and pretreatment of the Ag electrode can be found elsewhere.¹⁷

RESULTS AND DISCUSSION

IR and Raman spectra

In making assignments, we have been helped by the studies published on selected organic structures,¹⁸ selected benzene derivatives¹⁹ and sulfanilamide.^{2,20} The observed Raman and IR bands together with their relative intensities and band assignments are given in Table 1. The numbering of modes is as suggested by Miller.²¹

The strong band detected in the IR spectrum at 3478 cm⁻¹ is assigned to the asymmetric stretching mode NH₂ of aniline ring.²⁰ The region of IR and Raman spectra of sulfanilamide exhibiting the NH₂ stretching modes is around 3375–3264 cm⁻¹.¹⁸ The assignments of NH₂ stretching modes are in agreement with Topaclı and Topaclı.¹⁶ The CH

[#]Permanent address: Department of Physics, TKM College of Arts and Science, Kollam-5, Kerala, 691 005, India.

*Correspondence to: Daizy Philip, e-mail: daizyp@rediffmail.com

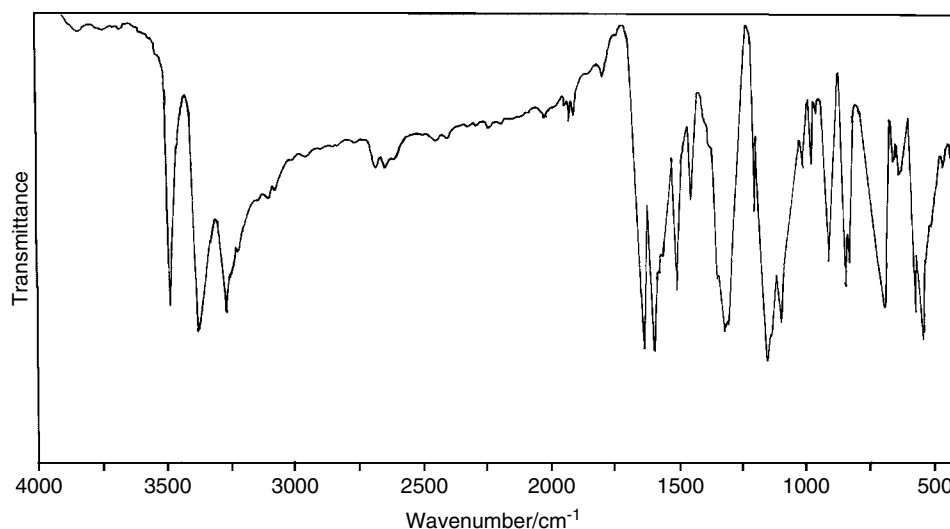


Figure 1. FT-IR spectrum of sulfanilamide in the spectral range 500–4000 cm^{-1} .

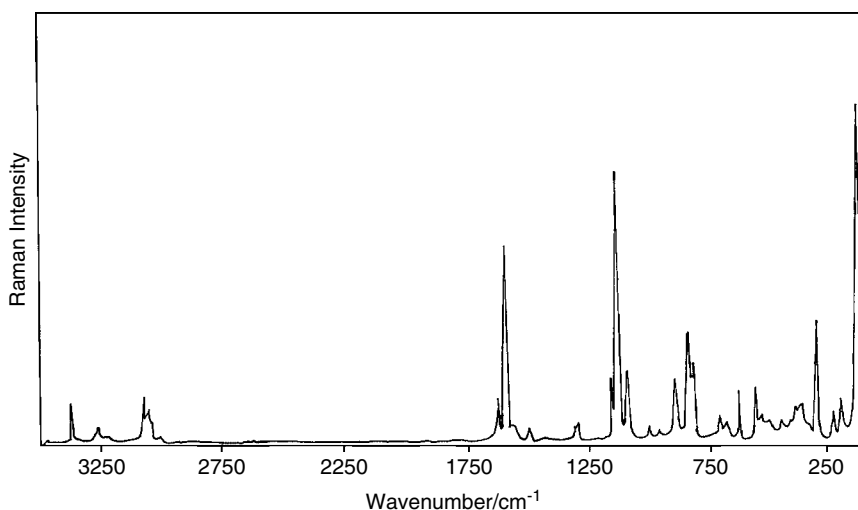


Figure 2. FT-Raman spectrum of sulfanilamide in the spectral range 100–3500 cm^{-1} .

stretching modes are observed at 3147, 3086 and 3062 cm^{-1} in the IR spectrum and at 3068 and 3050 cm^{-1} in the Raman spectrum of sulfanilamide¹⁶ with very weak intensities. The NH_2 scissoring vibrations belonging to the sulfonamide group and aniline ring are expected¹⁸ near 1650 cm^{-1} . The strong band observed at 1629 cm^{-1} is assigned to NH_2 scissoring mode of aniline ring. For sulfonamide group, this vibration occurs¹⁸ at 1573 cm^{-1} . The ring stretching modes of aniline ring are observed at 1595, 1503, 1440 and 1096 cm^{-1} in the IR spectrum and at 1594, 1502 and 1093 cm^{-1} in the Raman spectrum of sulfanilamide. This result is in agreement with Topaçli and Kesimli²² for the strong IR bands at 1595 and 1503 cm^{-1} .

The asymmetric and symmetric stretching modes of SO_2 group appear in the region 1360–1310 and 1165–1135 cm^{-1} , respectively.¹⁸ The observed bands 1313 cm^{-1} in IR and 1315 cm^{-1} in Raman spectra were assigned to the $\nu(\text{SO}_2)_{\text{asym}}$

modes and 1147 cm^{-1} in IR and 1157 and 1136 cm^{-1} in Raman spectra were assigned to the $\nu(\text{SO}_2)_{\text{sym}}$ modes. The weak band observed at 1003 cm^{-1} in IR spectrum and 1002 cm^{-1} in Raman spectrum is assigned to δCH vibration.

The C–H out-of-plane-bending vibrations are expected¹⁸ in the range 1000–900 cm^{-1} . The γCH bands 969 and 900 cm^{-1} are not pure but contain significant contributions of other modes ($\gamma(\text{CN})$ and $\nu(\text{SN})$).¹⁶ The ring planar deformation mode is observed at 824 cm^{-1} . The S–N stretching vibration¹⁸ is in the region $905 \pm 30 \text{ cm}^{-1}$. The band observed at 900 cm^{-1} in both spectra is not pure $\nu(\text{SN})$ vibration and contains a contribution of $\gamma(\text{CH})$ mode. Evans²³ reported a wavenumber of 670 cm^{-1} , which was assigned to the wagging mode of NH_2 group in aniline. But, this vibration appears in the region $690 \pm 40 \text{ cm}^{-1}$ for sulfonamide group.¹⁸ In the IR spectrum, it is observed at 683 cm^{-1} and, in the Raman spectrum, at 689 and 715 cm^{-1} . Although

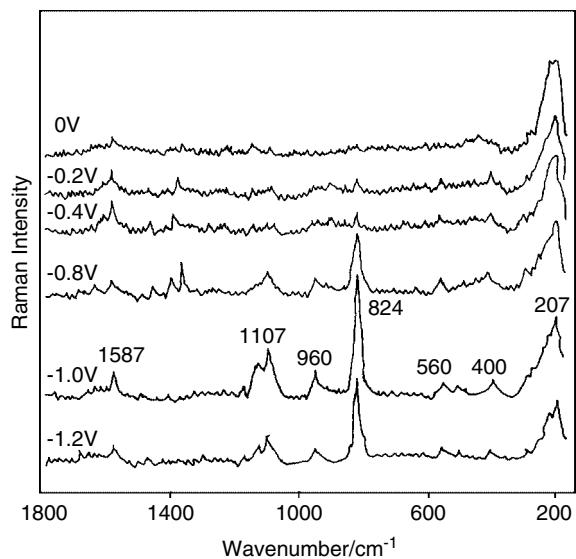


Figure 3. SERS spectrum of sulfanilamide in the spectral range 200–1800 cm^{-1} .

the region of the SO_2 scissors ($570 \pm 60 \text{ cm}^{-1}$) and that of SO_2 wagging vibration ($520 \pm 40 \text{ cm}^{-1}$) partly overlap, the two vibrations appear separately.¹⁸ The scissoring modes are observed at 626 and 563 cm^{-1} in IR spectrum and at 564 cm^{-1} in the Raman spectrum of sulfanilamide. The wagging mode is observed at 540 cm^{-1} in IR spectrum only. The torsional NH_2 modes of sulfonamide are observed at 371 and 298 cm^{-1} and torsional SO_2 modes are observed at 450 and 400 cm^{-1} in the Raman spectrum.¹⁸

SERS spectrum

The SERS spectra of sulfanilamide on silver electrode in 0.1 M KCl are recorded in the wavenumber range 200–1800 cm^{-1} at electrode potentials between –1.2 and 0 V. At –1.0 V, prominent bands are observed at 1587, 1107, 960, 824, 560, 400 and 207 cm^{-1} . The in-plane-bending vibrations of the benzene ring observed as strong bands at 824 cm^{-1} in IR spectrum and at 822 cm^{-1} in the Raman spectrum are seen at 824 cm^{-1} in the SERS spectrum. The enhancement of this vibration suggests that the benzene ring is oriented perpendicular to the silver surface.^{24,25} Further, the wavenumber difference of this SERS band compared to the Raman band is not more than 5 cm^{-1} , which supports the above fact.²⁶ Also, the benzene ring vibration observed at 1587 cm^{-1} supports this fact. The out-of-plane CH vibration observed at 960 cm^{-1} in the SERS spectrum is found to be medium broad, indicating a surface π -interaction in accordance with a somewhat flat orientation on the silver surface.^{27,28} From the intensities of the out-of-plane and in-plane-bending vibrations of the benzene ring, it can be inferred that, for sulfanilamide adsorbed on silver, the benzene ring has a ‘tilted orientation’. Further, a very strong symmetric $\text{Ag} \cdots \text{O}$ stretching vibration is observed^{27,29} at 207 cm^{-1} . According to surface selection rule, vibrations

involving atoms that are close to the silver surface will be enhanced.^{24,25} Here, the presence of the SERS bands at 1107, 560 and 400 cm^{-1} due to SO_2 vibrations and the absence of the vibrations involving NH_2 group in the SERS spectra suggest that the vibration at 207 cm^{-1} is due to $\nu \text{Ag} \cdots \text{O}$ rather than $\nu \text{Ag} \cdots \text{N}$. The very strong symmetric stretching SO_2 vibration observed at 1147 and 1136 cm^{-1} respectively in the IR and Raman spectra is shifted in wavenumber to 1107 cm^{-1} in the SERS spectrum. This indicates the nearness of the SO_2 group to the metal surface. The wavenumber shift from normal value is due to the change of symmetry on adsorption.³⁰

Potential dependence of SERS profile

The electrode potential was varied between –1.2 and 0 V in steps of 0.2 V. At different electrode potentials, the SERS spectrum for an adsorbed compound appears to change.³¹ The electrode potential dependence is induced by changes of the surface adsorbates at the electrode surface. Several studies on electrode potential dependence confirm the fact that a particular vibrational band of a molecule can be highlighted by a change in the electrode potential.^{31–35} The weak band observed for ν ring in the SERS spectrum at 1593 cm^{-1} at 0 V remains with almost same intensity when the potential becomes more negative while the wavenumber shows a red shift to 1587 cm^{-1} .

The in-plane-bending vibration observed at 824 cm^{-1} is found to increase in intensity when the potential becomes more negative and it has a maximum intensity at –1.0 V. The out-of-plane-bending vibrations are also observed in the potential profiles. In the whole potential region, the in-plane- and out-of-plane-bending vibrations are detected at the same time, suggesting tilted orientation.^{28,32} The symmetric stretching vibration of SO_2 appearing at 1107 cm^{-1} in the SERS spectra is also found to be potential dependent, with increase in intensity when the potential becomes more negative. The enhancement of this band can be due to the charge transfer mechanism explained by Franck-Condon, in which only totally symmetric modes are surface enhanced.³²

CONCLUSIONS

- (1) The potential dependent SERS profile has maximum intensity at an electrode potential of –1.0 V.
- (2) The appearance of $\text{Ag} \cdots \text{O}$ stretching mode is indicative of the nearness of these atoms to the silver surface.
- (3) The molecule is adsorbed with the benzene ring in a tilted orientation

Acknowledgements

C. Yohannan Panicker would like to thank the University Grants Commission, India, for awarding a Teacher Fellowship. We thank Prof. Z.Q. Tian, State Key Laboratory for Physical Chemistry of Solid Surfaces, Institute of Physical Chemistry and Department of Chemistry, Xiamen University, Xiamen, 361005, China, for the valuable suggestions.

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

IR	Raman	SERS at -1.0 V	Assignments
3478 s	–	–	$\nu_{\text{asy}}(\text{NH}_2)$ Aniline
3375 s	3371 w	–	$\nu_{\text{asy}}(\text{NH}_2)$ Sulfonamide
3266 s	3264 w	–	$\nu_{\text{sym}}(\text{NH}_2)$ Sulfonamide
3147 w	–	–	νCH
3086 w	–	–	νCH , 12a, 12b
3062 w	3068 w	–	νCH , 1, 12a, 12b
–	3050 w	–	νCH , 1, 12a, 12b
2683 wbr	–	–	Overtone and combinations
2633 wbr	–	–	Overtone and combinations
1916 w	–	–	Overtone and combinations
1629 s	1629 s	–	δNH_2 (Aniline)
1595 s	1594 s	1587 m	ν ring, 16a, 16b
1573 w	–	–	δNH_2 (Sulfonamide), 16a, 16b
1503 s	1502 w	–	ν ring, 13a
1440 s	–	–	ν ring, 13b
1313 vsbr	1315 w	–	$\nu_{\text{asy}}(\text{SO}_2)$, 3, 9
1300 m	1303 w	–	νCN , 3, 9
1188 m	–	–	δCH , 5, 17a
–	1157 w	–	$\nu_{\text{sym}}(\text{SO}_2)$, 5, 17a
1147 vs	1136 vvs	1107 sbr	$\nu_{\text{sym}}(\text{SO}_2)$, 5
1096 s	1093 w	–	ν ring, 2
1003 w	1002 w	–	δCH , 14a
969 w	967 vw	960 mbr	$\gamma(\text{CH})$, $\gamma(\text{CN})$, 7, 19a
900 s	900 w	–	$\nu(\text{SN})$, $\gamma(\text{CH})$
837 s	842 m	–	$\gamma(\text{CS})$, $\gamma(\text{CN})$, 11a, 18a, 19b
824 s	822 w	824 vvs	δ ring, 11a, 18a, 19b
–	715 w	–	ωNH_2 sulfonamide, 8
683 s	689 w	–	ωNH_2 sulfonamide, 8
626 m	–	–	δSO_2 , 6, 18b
563 s	564 w	560 w	δSO_2 , 6
540 s	–	–	ωSO_2 , 6, 20b
–	450 w	–	Torsion SO_2 , 17b, 20b
–	400 w	400 w	Torsion SO_2 , 15a, 17b
–	371 w	–	Torsion NH_2 sulfonamide, 15a, 17b
–	298 m	–	Torsion NH_2 sulfonamide, 11b, 15a, 17b
–	226 w	–	External mode
–	–	207 s	$\nu\text{Ag} \cdots \text{O}$
–	193 w	–	External mode
–	117 vvs	External mode	–

ν , stretching; δ , in-plane bending; γ , out-of-plane bending; ω , wagging; s, strong; w, weak; br, broad; v, very; m, medium; asy, asymmetric; sym, symmetric.

REFERENCES

- Munoz C. In *Farmacologia*, vol. 60, Mardones J (ed). Intermedica: Buenos Aires, 1979.
- Blasco F, Perello L, Latorre J, Borrás J, Garcia-Granda S. *J. Inorg. Biochem.* 1996; **61**: 143.
- Ferrer S, Borrás J, Garcia-España E. *J. Inorg. Biochem.* 1990; **39**: 297.
- Supuran CT, Mincoine F, Scozzafava A, Brigenti F, Mincione G, Ilies MA. *Eur. J. Med. Chem.* 1998; **33**: 247.
- Garcia-Raso A, Fiol JJ, Rigo S, Lopez-Lopez A, Molins E, Espinosa E, Borrás E, Alzuet G, Borrás J, Castineiras A. *Polyhedron* 2000; **19**: 991.
- O'Connor BH, Maslen EN. *Acta Crystallogr.* 1965; **18**(3): 363.
- O'Connell AM, Maslen EN. *Acta Crystallogr.* 1967; **22**(1): 134.
- Alleaume M, Decap J. *Acta Crystallogr.* 1965; **19**(6): 934.
- Alleaume M, Decap J. *Acta Crystallogr.* 1965; **18**(4): 731.
- Butt A. *Pharm. Weekbl. Sci.* (Ed. 3). 1981; **3**: 1.
- Butt A. In *Metal Ions in Biological systems*, vol. 16, Sigel H (ed). Marcel Dekker: New York, 1983.

12. Butt A, Uitterdijk JD, Klasen HB. *Transition Met. Chem.* 1979; **4**: 285.
13. Narang KK, Gupta JK. *Transition Met. Chem.* 1977; **2**: 83.
14. Rastelli A, Debenede PG, Albasins A, Vampa G, Melegari M. *Farm. Ed. Sci.* 1974; **29**(9): 654.
15. Narang KK, Gupta JK. *Indian J. Chem.* 1975; **13**: 705.
16. Topaclı C, Topaclı A. *J. Mol. Struct.* 2003; **644**: 145.
17. Chen YK, Zon SZ, Huang KQ, Tian ZQ. *J. Raman Spectrosc.* 1998; **249**: 749.
18. Roeges NPG. *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*. Wiley: New York, 1994.
19. Varsanyi G. *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*. Wiley: New York, 1974.
20. Topaclı C, Topaclı A. *Spectrosc. Lett.* 2002; **35**(2): 207.
21. Miller FA. *J. Raman Spectrosc.* 1988; **19**: 219.
22. Topaclı A, Kesimli B. *Spectrosc. Lett.* 2001; **34**(4): 513.
23. Evans JC. *Spectrochim. Acta* 1960; **16**: 428.
24. Gao X, Davies JP, Weaver MJ. *J. Phys. Chem.* 1990; **94**: 6858.
25. Creighton JA. *Adv. Spectrosc.* 1988; **19**: 37.
26. Levi G, Patigny P, Massault JP, Aubard J. *Proceedings of the 13th International Conference on Raman Spectroscopy*, 1992; Wurzburg, 652.
27. Yohannan PC, Hema TV, Annamma J, Daizy P, Kritina I, Gabor K. *Spectrochim. Acta* 2002; **A58**: 281.
28. Daizy P, Annamma J, Yohannan PC, Hema TV. *Spectrochim. Acta* 2001; **A57**: 1561.
29. Frederico C, Raul GJ, Francisco CN, Paola C, Marcia T. *J. Solid State Electrochem.* 2003; **7**: 576.
30. Daizy P, Antony E, Aruldas G. *J. Solid State Chem.* 1995; **116**: 217.
31. Michael MC, Robert BE, David Rauth R. *Anal. Chem.* 1987; **59**: 2559.
32. Eckhard K, Bert JK, Robert JM. *J. Phys. Chem.* 1996; **100**: 5078.
33. Arenas JF, Otero JC, Centeno SP, Lopez Tocon I, Sosto J. *Surf. Sci.* 2002; **511**: 163.
34. Peigen C, Renao G, Bin R, Zhongqun T. *Chem. Phys. Lett.* 2002; **366**: 440.
35. Cao PG, Yao JL, Zheng JW, Gu RA, Tian ZQ. *Langmuir* 2002; **18**: 100.