Surface Enhanced Raman Spectroscopic Study of 2- and 3-Bromothiophenes in Silver Hydrosol

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Surface enhanced Raman spectra (SERS) of 2- and 3-bromothiophene molecules in silver sol are compared with those of molecules in acetonitrile solution. The experimental results suggest that the 2-isomer is adsorbed on the metal surface through both the sulfur and the bromine atoms, with the thiophene molecular plane almost normal to the surface, whereas the 3-isomer is adsorbed principally through the sulfur atom. The Raman excitation profile of the molecules in the surface adsorbed state follows surface plasmon resonance frequency, reflecting the contribution of classical electromagnetic effect to SERS in silver sol. The observed "first layer effect", i.e. maximum enhancement on a monomolecular layer formation on the metal surface, suggests charge transfer contribution to SERS of these molecules. Further, appearance of Ag–Br and Ag–S stretching modes in the SER spectra of 2-isomer indicates chemisorption of the adsorbate molecules on the metal surface.

Surface enhanced Raman spectroscopy is an useful technique for studying physical and chemical adsorption of molecules on metals. Several factors[1] are reported to influence the enhancement of Raman signals of molecules adsorbed on the metal surface. The enhancement factor depends on the excitation wavelength. If the exciting radiation frequency coincides with the surface plasmon resonance frequency of the metal, maximum enhancement is observed. This is termed the electromagnetic effect.[2] The other effect that contributes to the enhancement is charge transfer between adsorbate and the metal which modulates Raman scattering polarizability through molecular vibration. The charge transfer effect often leads to the formation of a monolayer of the absorbates on the metal surface and chemisorption.[3—5]

In this paper we report the SERS study of 2- and 3-bromothiophenes (BrT) possessing several sites of adsorption (sulfur and bromine atoms and the π-donor thiophene ring). In these systems both the electromagnetic effect and the first layer effect have been observed. Moreover, selective enhancement of different modes of bromothiophenes give insight into the geometry and orientation of the molecules on the silver surface.

Experimental

Instruments: The excitation source used is an argon-ion laser (Spectra Physics Model 2020-05) at a power of 0.25 W. The sample was placed in a standard 1-cm cubette. Raman scattering was collected at a right angles to the excitation and detected with a Spex double monochromator (model 1403) fitted with a holographic grating of 1800 groves/mm and a thermoelectriacally cooled photomultiplier tube of Hamamatsu Photonics, Japan. The operation of the photon counter, data acquisition and analysis were controlled by Spex datamate 1B. The acquisition time for each spectral element was 0.5 s. The absorption spectra were recorded by a Shimadzu UV-vis spectrophotometer (model UV-vis 210A).

Chemicals and Procedure: Bromothiophenes (Aldrich Chemical Co.) were purified by vacuum distillation. Silver hydrosols were prepared following the method of Creighton et al.[6] The yellowish sol with a single extinction maximum at 395 nm was aged for several hours before using it in the SERS experiments. Distilled and deionized water from Milli-Q-plus system of M/S Millipore Corporation, USA was used for sol-preparation.

The desired concentration of the subject bromothiophenes in silver hydrosol was attained by mixing a specific volume of a stock solution (2 M, 1 M, 10^{-1}—10^{-6} M) (1 M = 1 mol dm^{-3}) in acetonitrile (ACN) with an appropriate volume of silver hydrosol. Fractional concentrations were attained by mixing stock solutions with hydrosol in different ratios. For example, for making a concentration of 1×10^{-3} M of bromothiophenes in hydrosol, 1 ml of 10^{-2} M stock solution was added to 9 ml of hydrosol. Mixing of these in 1 : 4 ratio is considered to result in a concentration of 2×10^{-3} M.

Results and Discussion

Bromothiophenes are practically insoluble in water but are highly soluble in acetonitrile (ACN). Raman spectra of 2- and 3- bromothiophenes in acetonitrile (with concentration 2 M and 1 M respectively) are shown in Figs. 1(a) and 2(a) respectively. Surface enhanced Raman spectra of the two molecules in the adsorbed state on Ag sol with concentration 8×10^{-3} M (2-BrT) and 1×10^{-3} M (3-BrT) are shown in Figs. 1(b) and 2(b), respectively. In all these cases, the amount of acetonitrile in Ag sol has been kept constant so that the intensities of the ACN bands (921 and 1377 cm^{-1}) remain equal, facilitating normalization of the bromothiophene bands with reference to the ACN bands. A separate experiment showed that ACN bands do not show any surface enhancement under adsorption on silver particles.

The apparent enhancement factor of the various vibrational modes of the molecules have been calculated using the relation[7] A.E.F. = $\frac{\alpha_2 C_1}{\alpha_1 C_2}$, where α_2 and α_1 are the normal-

ized intensity value of the Raman modes in arbitrary units in silver sol and in ACN solution with molecular concentration of C_2 and C_1, respectively. Real enhancement will be a few orders of magnitude higher than the calculated value, because not all the molecules that are present in the sol are adsorbed and the intensity of the laser radiation is significantly reduced due to absorption and scattering by silver particles.[8] Assignments made on the basis of earlier reports[9—11] of different Raman bands along with their A.E.F. values are shown in Tables 1 and 2.

Table 1. Observed Raman Shift and Intensities (Values in Parentheses) of 2-Bromothiophene in Normal and Surface Enhanced Raman Spectra

Liquid phase	Solution with adsorbate concn 2 M	Silver sol with adsorbate concn 8×10^{-3} M	Apparent enhancement factor ($\times10^3$)	Assignment of vibrational modes Ref. 9—12.
		161 (13)		ν (Ag–Br)
		174 (7)		ν (Ag–S)
197	199 (2)	191 (4)	0.50	π (C–Br)
210	213 (3)	205 (9)	0.75	β (C–Br)
329	330 (4)	324 (28)	1.75	ν (C–Br)
630	631 (6)	628 (48)	2.0	β (C–H)
678	667 (5)	—		π (C–H)
737	738 (11)	776 (30)	0.68	β (C–H)
840	843 (8)	846 (13)	0.41	Ring breathing
1080	1087 (6)	1092 (14)	0.58	β (C–H)
—	—	1128		Ag–BrT complex ?
1219	1184 (9)	1181 (46)	1.28	β (C–H)
—	—	1317		Ag–BrT complex ?
1341	1342 (6)	1368 (53)	2.21	ν (C_3–C_4)
1404	1406 (14)	1421 (14)	0.25	ν_{sym} (C=C)
1511	1521 (7)	1508 (70)	2.5	ν_{asym} (C=C)
3090		3083 (27)		ν_{sym} (C–H)
3110	3120 (3)	3111 (13)	1.08	ν_{asym} (C–H)

ν: Stretching; β: In-plane-bending; π: Out-of-plane bending.

Table 2. Observed Raman Shift and Intensities (Values in Parentheses) of 3-Bromothiophene in Normal and Surface Enhanced Raman Spectra

Liquid phase	Solution with adsorbate concn 1 M	Silver sol with adsorbate concn 1×10^{-3} M	Apparent enhancement factor ($\times10^3$)	Assignment of vibrational modes Ref. 9—12.
		179 (29)		ν (Ag–S)
198	200 (5)	—		π (C–Br)
243	242 (6)	226 (11)	1.83	β (C–Br)
322	321 (38)	—		ν (C–Br)
454	457 (4)	435 (6)	1.5	π (C–C)
624	624 (8)	634 (3)	0.38	β (C–H)
763	753 (4)	755 (8)	2.0	β (C–H)
800	799 (32)	—		β (C–H)
849	850 (20)	846 (28)	1.4	Ring breathing
884	886 (10)	874 (9)	0.9	Ring stretching
1076	1078 (sh)	1056 (15)		β (C–H)
1090	1093 (20)	1090 (6)	0.3	β (C–H)
1196	1202 (4)	1183 (9)	2.25	β (C–H)
1362	—	1365 (23)	Large	ν (C_3–C_4)
1403	1403 (23)	1399 (16)	0.7	ν_{sym} (C=C)
1499	—	1498 (22)	Large	ν_{asym} (C=C)
3095	3098 (3)	3085 (38)	12.7	ν_{sym} (C–H)
3115	3120 (13)	3109 (8)	0.61	ν_{asym} (C–H)

ν: Stretching; β: In-plane-bending; π: Out-of-plane bending.

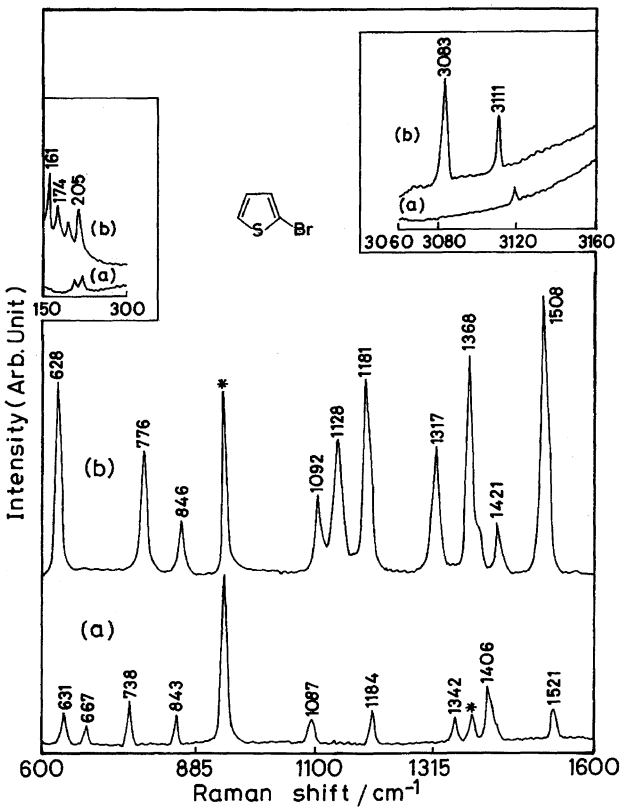

Fig. 1. (a) Raman spectrum of 2-bromothiophene in acetonitrile solvent (2 M); (b) SER spectrum of 2-bromothiophene adsorbed on silver sol (8×10^{-3} M). Left inset indicates the lower spectral range and the right inset is for higher spectral range. * denotes acetonitrile bands.

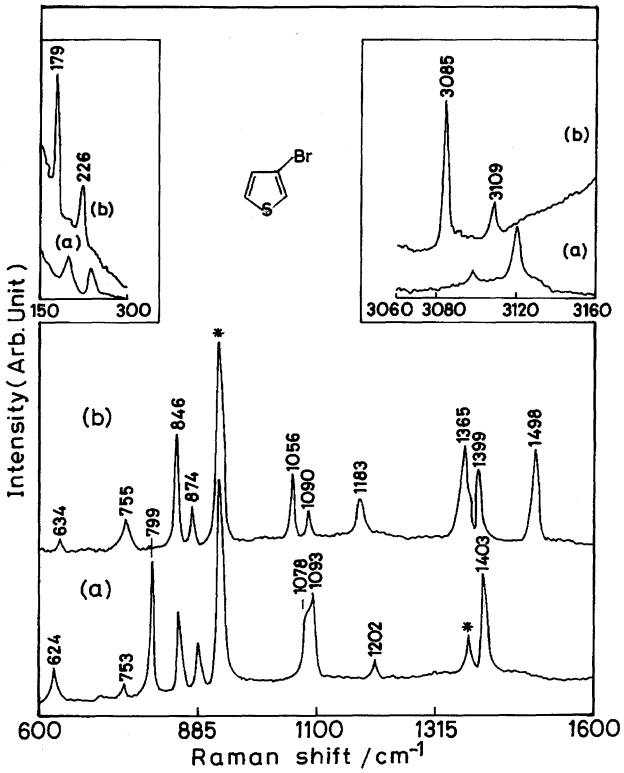

Fig. 2. (a) Raman spectrum of 3-bromothiophene in acetonitrile solvent (1 M): (b) SER spectrum of 3-bromothiophene adsorbed on silver sol (1×10^{-3} M). Left inset indicates the lower spectral range and the right inset is for higher spectral range. * denotes acetonitrile bands.

The strong adsorbate–metal interactions are indicated by the appearance of some Raman bands in the 150—300 cm^{-1} region. SER spectrum of 2-BrT shows two bands at 161 and 174 cm^{-1}, which are not observed in solutions. The 161 cm^{-1} band is assigned to ν(Ag–Br)[12] and the 174 cm^{-1} band is assigned to ν(Ag–S) stretching. Ag–S stretching is known to be in the 150—250 cm^{-1} range.[13—15] These results indicate that the molecule is adsorbed through both the sulfur and the bromine atoms. In the SER spectrum of 2-BrT, the stretching mode ν(Ag–Br) is more intense than the ν(Ag–S), whereas 3-BrT shows only ν(Ag–S) vibration at 179 cm^{-1}. The ν(C–Br) at 330 cm^{-1} mode shows large enhancement and red shift in 2-BrT, whereas this mode is absent in the SER spectrum of 3-BrT. This is understandable since in the 2-isomer the halogen atom is closer to the heteroatom and is involved in the adsorption process. The C–Br bond makes a larger projection on the surface normal in 2-BrT than in 3-BrT. Large enhancement of the in-plane ring breathing mode, the symmetric and asymmetric ring stretching ν(C=C) modes and ν(CH) modes in SER spectrum of 2-BrT indicate vertical orientation of the adsorbate ring plane on the metal surface, according to the surface selection rule given by Moskovits and co-workers.[16—18] Indeed except for π(C–Br) in 2-BrT and π(C=C) in 3-BrT which appear weakly, no other out-of-plane modes appear in the SER spectra. The $\nu(C_3–C_4)$ mode shows large enhancement in both the isomers. This suggests that the orientation of the molecules on the surface [Fig. 3] is such that the $C_3–C_4$ bond makes a large projection on the surface normal. The SER spectra show that both the symmetric and asymmetric ring stretching modes ν(C=C) appear at a higher wavenumber in 2-BrT than in 3-BrT. This can be attributed to a more strong conjugation of the substituent group with the ring in 3 position than in 2 position. The shoulder of $\nu(C_3–C_4)$ mode at 1360 cm^{-1} in each isomer is due to the presence of an adjacent acetonitrile band.

Two intense bands at 1128 and 1317 cm^{-1} appear in the SER spectrum of 2-bromothiophene. Such bands are not

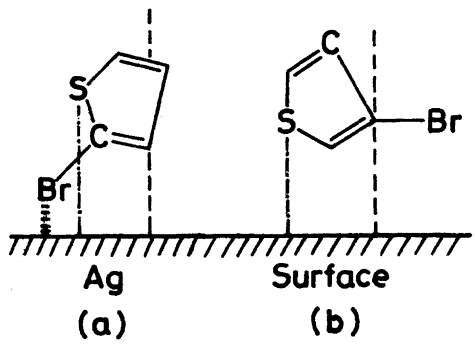

Fig. 3. Schematic diagram showing the possible orientation of (a): 2-bromothiophene and (b): 3-bromothiophene with respect to the metal surface.

observed in the neat liquid or in solution. In this spectral range, the thiophene ring stretching and the C–H in-plane-bending modes have been assigned to bands at 1368 cm^{-1} (1342 cm^{-1} in solution) and 1092 cm^{-1} (1087 cm^{-1} in solution) respectively. We attribute these two new bands to vibrations in the 2BrT–Ag complex. It has been pointed out that this isomer forms a complex with silver particles, through both the S and the Br atoms.

The absorption spectrum of the pure silver sol and that with added substituted thiophenes [1×10^{-3} M] are shown in Fig. 4. The silver hydrosol is stable for days. On addition of pyridine and substituted pyridines to silver hydrosol, a new band appears on the longer wavelength side of the sol absorption band (395 nm). This new band is stable for hours, which is sufficient to record the Raman signal. This has been attributed to the aggregation of the colloidal silver particles, which results in the shift of the plasmon resonance band.[6,19,20] Such a situation is not encountered with bromothiophenes in the present study. In each case, the spectra with added thiophenes show a lowering of the absorbance at 395 nm, but no new band or shoulder appear in the longer wavelength region. This indicates that the bromothiophene molecules do not influence coagulation of the silver particles in the sol. The Raman excitation profiles of the symmetric ν(C=C) mode of the halothiophenes [1×10^{-3} M] are shown in Fig. 5. It is observed that the profile follows the surface plasmon resonance peak within the limited wavelength range available for Ar^+ laser. This confirms that the classical electromagnetic contribution to the SERS is predominant in the case of halothiophenes.

Figure 6 shows the concentration dependence of the relative enhancement of the C=C symmetric stretching mode of 2-bromothiophene. 3-BrT also shows similar dependence. It is observed that the maximum enhancement occurs at a concentration of 1×10^{-3} M, indicating the first monolayer of 2-bromothiophene forms on the silver surface at this concentration. The enhancement due to the "first layer effect" has previously been reported on metal electrodes and cold

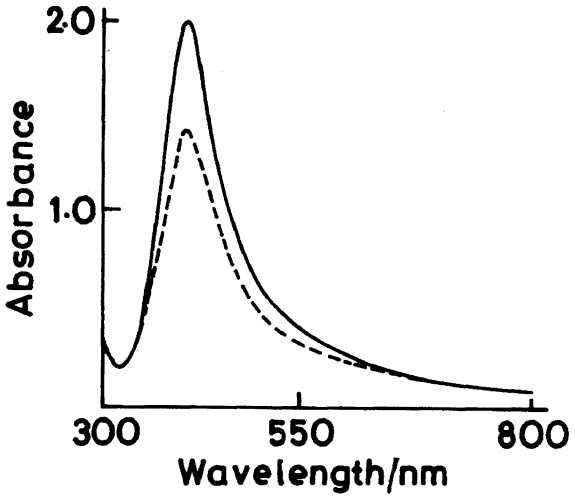

Fig. 4. Absorption spectra of Ag-sol without (——) and with (- - -) bromothiophenes [1×10^{-3} M].

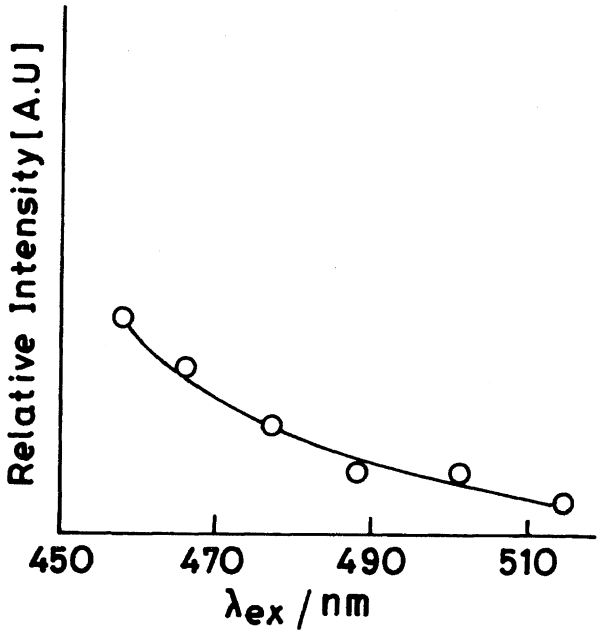

Fig. 5. Excitation profile of ν_{sym}(C=C) mode of 3-bromothiophene [1×10^{-3} M] in adsorbed state.

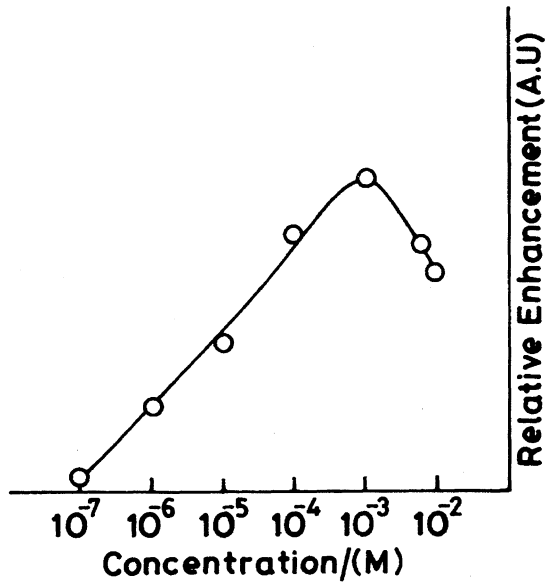

Fig. 6. Dependence of relative enhancement of C=C symmetric stretching of 2-bromothiophene on concentration.

deposited film surfaces.[21,22] Maximum enhancement at optimum concentration is attributed to monolayer formation on the surface[23] and also to a favorable orientation of the polarizability of the adsorbed molecule. When a monomolecular layer is formed on the substrate, the adsorbate molecules come into direct contact with the silver atoms and chemisorption may take place by transferring charge from adsorbate to substrate or vice versa. At higher concentrations, alignment becomes progressively random due to multilayer formation, which also results in reduced proximity of the molecules to the surface. At a lower concentration, relative enhancement decreases due to a lower number of available scattering

centers.

Conclusion

Thus we conclude that the 2-bromothiophene molecule is adsorbed on the metal surface through both the S and the Br atoms, whereas the 3-isomer is adsorbed only through the S atom. The orientation of the molecule on adsorption is such that the thiophene ring plane is nearly normal to the metal surface, with the C_3–C_4 bond making a large projection on the surface normal. The ring plane of the 3-isomer is, however, more inclined to the surface than that of 2-isomer.

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