# SERS studies of 1-butylaminoanthraquinone in silver sol

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**Abstract.** SERS studies of 1-butylaminoanthraquinone in silver sol have been made to understand the nature of adsorption. The enhancement mechanism is explained on the basis of charge transfer process. The molecule is adsorbed through the binding sites but not flat on to the surface.

**Keywords.** SERS spectrum; adsorption; charge transfer.

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## 1. Introduction

Surface enhanced Raman scattering (SERS) has been established as a powerful method for elucidating the structure of molecules adsorbed on metal-electrolyte, metal-vacuum and metal–solid interfaces (Fleischmann *et al* 1974; Jeanmire and Van Duyme 1977; Jeanne E Pemberton 1985; Tai Ha Joo *et al* 1984). It is a sensitive technique because of the large surface enhancement effect and the small sample volume required. The richness of the spectroscopic information, surface selectivity and sensitivity of SERS greatly help to solve problems in analytical chemistry. The theoretical understanding of the mechanisms for surface enhancement is not yet complete. The large enhancement may be either due to the change in molecular polarizability or due to the high electric field experienced by the molecule or due to both the effects acting simultaneously on a molecule (Kneipp *et al* 1983; Li Xia li *et al* 1988). The present SERS studies have been made for understanding the enhancing effect and also the interaction between the molecule and the metal.

For visible wavelength Raman excitation sources, the primary requirement implies that only the noble metals and alkali metals will be very good surface enhancing substrates. However, it has been shown theoretically that other metals will provide a high enhancement in other regions of the spectrum (Robin L Garrel 1989). Investigations by SERS from dye molecules adsorbed on a Ag metal surface have been undertaken to understand the photographic process and spectral sensitization also (Kneipp *et al* 1983).

Recently our group has investigated SERS studies of some α-aminoanthraquinones in silver sol (Ramakrishnan *et al* 1990). It is found that the carbonyl oxygen which

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is charged partially negative (9th position) and lone pair electrons of nitrogen atom form good binding sites for surface adsorption. Our group has also studied SERS of 1–4 dihydroxyanthraquinone (DHAQ) in silver/gold sol (Ramakrishnan *et al* 1992), in which it is found that the DHAQ molecule is lying with its molecular plane on the top of the metal surface and is chemisorbed. Here, we have undertaken an investigation of SERS studies of 1-butylaminoanthraquinone (hereinafter called BAAQ) adsorbed on colloidal silver particles.

## 2. Experimental details

Since various SERS studies have established Ag as the most effective substrate, we have used it in the form of colloids. 10 ml of 1 mM $AgNO_3$ solution was added to 30 ml of 2 mM $NaBH_4$ solution dropwise whilst stirring the solution so as to obtain Ag sol which has a very strong and sharp absorption band at 390 nm. The concentration of methanolic BAAQ is $10^{-4}$ mol/litre. The sample solution and silver sol are mixed in the ratio 1:1 and it consists of large assemblies of individual colloidal particles satisfying the condition for SERS regarding the particle size and the incident wave-length. The experimental set-up for Raman studies consists of a He–Ne laser (60 mW. Spectra Physics 125 A) operating at 632·8 nm, a single grating GCA/Mcpherson one meter monochromator coupled with a predispersing unit, a RCA C31034 PM tube and a Keithley picoammeter coupled with a strip chart recorder. The scattered light is collected at 90° to the incident laser beam. The sample solution has sufficient stability so that the intensity of the scattered light remains constant.

## 3. Results and discussion

BAAQ belongs to $C_s$ point group and has 108 normal modes (figure 1). The complete interpretation of different vibrational modes of this adsorbed molecule can only be made qualitatively. For our study, it is essential to compare the normal Raman spectrum with SERS spectrum. The observed SERS spectrum has 18 lines, whereas the normal Raman spectrum gives only 13 lines (figure 2). The frequencies are tabulated in table 1.

The characteristic skeletal stretching vibrations of benzene ring lead to the appearance of a group of bands between 1400–1600 $cm^{-1}$ (Bellamy 1975). There is a considerable
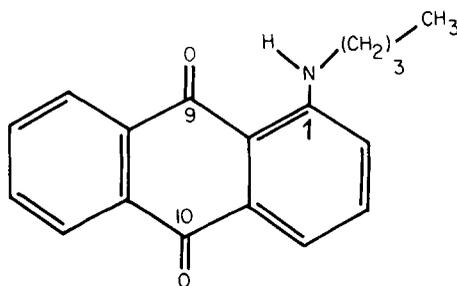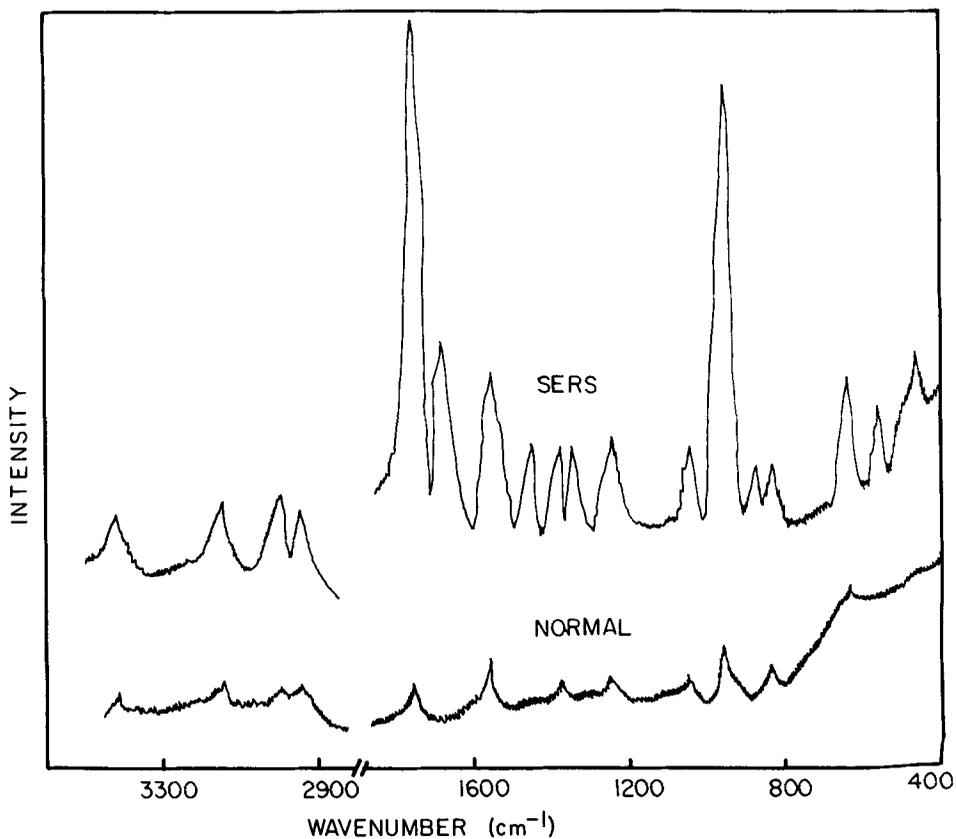


Figure 1.  Structure of BAAQ.

**Figure 2.** SERS and normal Raman spectra of BAAQ.

**Table 1.** Spectral data and assignments.

| Normal Raman spectrum (BAAQ + methanol) cm$^{-1}$ | SERS spectrum (BAAQ + methanol + silver sol.) cm$^{-1}$ | Assignments |
|---|---|---|
| 460 | 460 | Ring deform |
| | 549 | Ring deform |
| 632 | 632 | Ring deform |
| 830 | 830 | $\gamma_{C-H}$ |
| | 870 | $\gamma_{C-H}$ |
| 954 | 954 | Ring breathing |
| 1042 | 1042 | $\beta_{C-H}$ |
| 1246 | 1246 | CH$_2$ Wagging |
| | 1347 | $\nu_{C-N}$ |
| 1372 | 1372 | CH$_3$ deformation |
| | 1443 | CH$_2$ deformation |
| 1557 | 1557 | Ring stretching |
| | 1678 | |
| 1751 | 1751 | $\nu_{C=O}$ |
| 2942 | 2942 | CH$_2$ stretching |
| 2998 | 2998 | CH$_3$ stretching |
| 3146 | 3146 | $\nu_{C-H}$ |
| 3416 | 3416 | $\nu_{N-H}$ |

$\nu$ – Stretching; $\beta$ – in plane bend; $\gamma$ – out of plane bend

variation in the relative intensities of these bands with changes in substitution. However, the actual positions of these bands are influenced to some extent by the nature of substituent groups (Colthup 1950; Cannon and Sutherland 1951). In the Raman spectrum, the most characteristic band of a number of substitution patterns is due to the ring breathing vibration (Bellamy 1975). In this vibration each carbon atom of the ring is expanding or contracting in the opposite direction to each of its immediate neighbours. So, the position and intensity of the band due to this mode largely depends on the nature of the substituents.

The band at $1557 \, cm^{-1}$ observed with appreciable intensity in SERS and normal Raman spectra arises due to ring stretching vibrations. The ring-breathing mode occurs around $1000 \, cm^{-1}$ for benzene derivatives (Gyn Senng Shin and Long Jean Kim 1985). Here, in SERS spectrum this band is observed at $954 \, cm^{-1}$. The downward shift in the frequency of the ring-breathing mode is due to the fused rings formation and substitution. The ring-breathing mode is observed as an intense band in the SERS spectrum, whereas in the normal Raman spectrum it appears as a weak one. In the SERS spectrum the ring deformation vibrations appear as medium intensity bands at 460, 549 and $632 \, cm^{-1}$. The ring deformation vibration at $549 \, cm^{-1}$ is not observed in the normal Raman spectrum. Both the spectra show a band at $3146 \, cm^{-1}$ due to C–H stretching vibration. The band at $1042 \, cm^{-1}$ in both SERS and normal Raman spectra is assigned to C–H in plane bending mode. The band at $870 \, cm^{-1}$ due to C–H out of plane bending vibration appeared only after adsorption. Normally this band is very weak and is not observed in normal Raman spectrum.

Two bands observed both in SERS and normal Raman spectra at 2942 and $2998 \, cm^{-1}$ are due to stretching vibration of $CH_2$ and $CH_3$ groups. These two bands are intense in SERS than the normal Raman spectrum. Since the solvent used also has a methyl group, there is a probability for overlapping of bands. SERS bands at 1372 and $1443 \, cm^{-1}$ are due to $CH_3$ and $CH_2$ deformations respectively. The band at $1443 \, cm^{-1}$ is not observed in normal Raman spectrum. The $CH_2$ Wagging mode is observed both in SERS and normal Raman spectra at $1246 \, cm^{-1}$. This band is very weak in normal Raman spectrum, whereas it is intense in SERS spectrum.

Both spectra show a band at $3416 \, cm^{-1}$ due to the asymmetric stretching mode of $NH_2$ group. Generally in aromatic amines, the C–N band occurs around $1340 \, cm^{-1}$. The medium intensity band at $1347 \, cm^{-1}$ in SERS is assigned to C–N stretching vibration. This band is not observed in normal Raman spectrum. The lone pair electrons in the nitrogen atom may be a good binding site and the process of adsorption through this might have enhanced the Raman scattering cross-section for C–N stretching vibration.

Two bands at 1678 and $1751 \, cm^{-1}$ in SERS have been observed due to the stretching vibration of carbonyl group. The medium intensity band at $1678 \, cm^{-1}$ is not observed in normal Raman spectrum. The existence of two carbonyl groups with different bond strengths seems to be the more reasonable cause for the presence of two bands. Due to the charge transfer between the amino and the carbonyl groups, the carbonyl oxygen acquires partial negative charge. The lone pair electrons of nitrogen atom form good binding sites for the surface adsorption over the silver surface. After adsorption $C_9=O$ bond gets weakened as this gives a new band at $1678 \, cm^{-1}$. Thus, the bands at 1751 and $1678 \, cm^{-1}$ are assigned to the stretching vibration of $C_{10}=O$ and $C_9=O$ groups respectively. There is a probability in the change of charge transfer character between aminoanthraquinones on the basis of substituents.

The butyl group being more electron donating, there will be an enhancement in the charge transfer of $C_9$=O in BAAQ (compared to 1-methylaminoanthraquinone) which leads to the more single bond character for this $C_9$=O bond.

## 4. Conclusion

Out of all bands in SERS, the intensities of carbonyl stretching and ring breathing modes are more pronounced. During these vibrations the molecule does not alter the link with the surface, so the interaction between the metal and adsorbed molecule are strengthened. A molecule is being adsorbed on a metal surface through a coordinating site. Through this coordinating site, transfer of electrons from metal to molecule and molecule to metal are taking place. Due to the charge transfer between the amino and carbonyl oxygen (9th position), the lone pair electrons in the nitrogen atom and $C_9$=O form a good binding site. The adsorption of BAAQ molecule on silver gives rise to a large change in molecular polarizability and this causes enhancement in intensity. The presence of two bands for the stretching vibration of carbonyl group suggests that the adsorption has taken place through this site. Also, the new band at $1347 \, cm^{-1}$ due to the stretching vibration of C–N confirms that the molecule is being adsorbed through this site. Thus, from the above analysis we infer that the BAAQ molecules are getting adsorbed through the above mentioned binding sites but not flat on to the surface.

## Acknowledgements

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