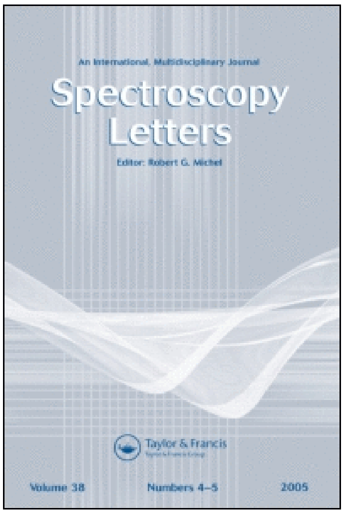

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Surface Enhanced Raman Scattering Studies of 1,4-Diaminoanthraquinone Dye in Ag Colloid

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SURFACE ENHANCED RAMAN SCATTERING STUDIES OF 1,4-DIAMINOANTHRAQUINONE DYE IN Ag COLLOID

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ABSTRACT

Surface enhanced Raman scattering studies are carried out for 1,4-diaminoanthraquinone dye [1,4-DAAQ] in Ag colloid in order to understand the enhancement effect and the nature of interaction between the dye molecule and Ag surface. Detailed analysis of the enhanced vibrational bands in the SERS spectrum shows that the 1,4-DAAQ molecule is not adsorbed through its coordinating sites, because of intramolecular hydrogen bond formation. The 1,4-DAAQ molecule is seen having 'flat on' orientation. Laser induced fluorescence measurements in different solvents and in different pH confirm the intramolecular hydrogen bond formation.

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INTRODUCTION

Investigations of Raman scattering of dye molecules adsorbed on metal colloids have a basic aim in understanding the enhancement effect .The major contribution to the intensity enhancement of the Raman scattered adsorbed molecules is mainly from two sources [1,2].Systematic SERS studies of structurally and chemically similar systems will help us to understand the enhancement mechanism through the dynamics of adsorbate-substrate interaction and relative orientation of the adsorbate molecule. Considering this aspect 1,4-diaminoanthraquinone (1,4-DAAQ), a member of α- aminoanthraquinone series, is chosen for the SERS studies on Ag surface. Also, the importance of anthraquinone dyes, widely used in textile chemistry for colouring textile materials, justifies the choice of this dye for the SERS study in order to investigate its optical properties [3]. Laser induced fluorescence measurements are also carried out for the 1,4-DAAQ dye in different solvents and in different pH to evaluate the nature of interaction between the solvent and the molecule and also its emission characteristics.

EXPERIMENTAL

All chemicals used in the experiment are analytical reagent grade and the solvents are HPLC/spectroscopic grade. Double distilled water is used throughout. Aqueous silver sol. is prepared according to the procedure given in (4). The experimental set up for Raman studies consists of a He-Ne laser (SPECTRA PHYSICS 125A) operating at 632.8 nm, single grating GCA-McPHERSON one meter scanning monochromator coupled with predispersing unit, a RCA C31034 PMT and a KEITHLEY picoammeter coupled with a strip chart recorder.

The laser power (λ= 632.8 nm) at the sample is set at 35 mW and the right angle geometry of the laser excitation and scattered radiation is employed. The concentration of methanolic 1,4-DAAQ mixture is approximately 1 x 10^{-5} M. For the SERS spectral observation the individual sample solution and Ag sol are mixed in the volume ratio 1:1. The excitation source employed for fluorescence measurements is a Spectra-Physics 2020-04s argon ion laser. A glass cuvette is used as the liquid cell. A CEL 0.25 m single grating monochromator is used to disperse the emitted radiation. A thermoelectrically cooled RCA C 31034 PMT is used as a detector.

RESULTS AND DISCUSSIONS

(a) Raman Scattering Studies

Fig.1 compares the normal Raman spectrum (nRs) and SERS spectrum of 1,4-DAAQ. The observed Raman shifts for 1,4-DAAQ molecule are listed and assigned in Table1. Tentative vibrational assignments are made with reference to available data of 1-hydroxy 9,10-anthraquinone, 9,10-anthraquinone and α-aminoanthraquinones [2,4-6]. By assuming that all the atoms are lying on the same plane, the 1,4-DAAQ molecule belongs to the C_s point group and it has 78 normal modes. From the Fig.1 it is evident that not only enhancement in intensity of the bands (1466 and 3096 cm^{-1}) but new spectral bands are also observed in the SERS spectrum. The SERS spectrum contains 13 bands, whereas the nRs contains only three bands. It is interesting to note that there are a few number of low wavenumber bands in the SERS spectrum attributing to deformation vibrations.

The SERS spectral profile shows a very strong band at 3096 cm^{-1} , eight medium intensity bands at 1648, 1471, 1285, 988, 922, 877, 412 and 364 cm^{-1} and four weak bands at 182, 394, 594, and 1114 cm^{-1}. The bands due to methanol are subtracted.

The characteristic SERS spectral features of 1,4-DAAQ molecule (Fig. 1 and Table 1) are the following.

(i) The carbonyl stretching vibrations of various carbonyl groups occur in the region 1900-1600 cm^{-1}. But a more specific range is defined by the type of carbonyl group (alkyl, ketone etc.) and its position is further affected in a subtle manner by a variety of effects such as chelation, hydrogen bonding etc . Aminoquinones can be regarded as vinylogous amides and 2- aminoanthraquinone showed two bands at 1680 and 1625 cm^{-1} due to carbonyl stretching vibration [7]. The low frequency 1625 cm^{-1} band was assigned to the hydrogen bonded carbonyl group.

The strength of hydrogen bonding can be inferred from the shift in frequency of C=O stretching vibration. This can be also obtained by

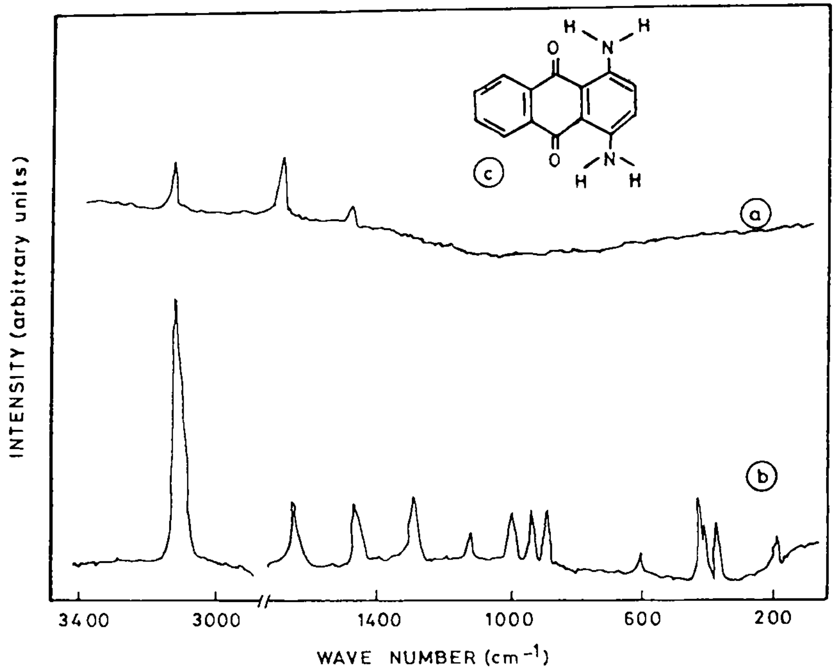

Fig. 1

(a) Raman spectra (nRs)of 1,4-diaminoanthraquinone (1,4-DAAQ).

(b) SERS spectrum of 1,4-DAAQ.

(c) Structure of 1,4-DAAQ.

comparing the frequency downshift of C=O vibration in conjunction with the lowering of OH stretching frequency for the hydroxyl derivatives and NH stretching frequency for the amino derivatives. Here SERS of 1,4-DAAQ shows a medium and broad band at 1648 cm^{-1} and it is assigned to C=O stretching mode. The broad and low frequency shift of this band led us to the conclusion that intramolecular hydrogen bonding has occurred as the carbonyl and amino groups in the dye molecule form a conjugate chelation and it is given in the Fig.2. In the nRs spectrum this band is observed at the same frequency.

Table 1

Vibrational frequency bands of 1,4-DAAQ

Frequency (cm^{-1}) nRs	SERS,	Assignments
	182	skeletal deformation
	364	skeletal deformation
	394	skeletal deformation
	412	β-C=O
	594	Ring deformation
	877	γ- CH
	922	γ- CH
	988	Ring breathing
	1114	β-CH
	1285	C-N stretching
1466	1471	Ring stretching
1648	1648	C=O stretching
3096	3096	CH stretching

β -in plane bending

γ - Out of plane bending

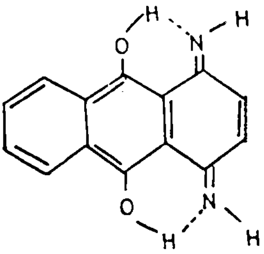

Fig.2

Chelated form of 1,4- DAAQ.

(ii) The very strong and broad band at 3096 cm^{-1} in the SERS spectrum is assigned to stretching vibration of the CH group.

(iii) The band due to carbonyl inplane bending mode usually occurs around 485 cm^{-1}. A shift to a lower frequency region arises when the C=O group is involved in an intramolecular hydrogen bonding [8]. Here in the SERS spectrum the band at 412 cm^{-1} is assigned to carbonyl in plane bending vibration.

(iv) A strong band due to C-N stretching vibration was observed for 2-aminoanthraquinone at 1340 cm^{-1} [7]. The nR spectrum of the1,4 DAAQ molecule does not contain any bands for this vibration, while the SERS spectrum contains a band at 1285 cm^{-1}.

(v) Ring stretching vibration is found to occur at 1466 cm^{-1} in nRs and at 1471 cm^{-1} in SERS, but the intensity of this stretching band is very weak in nRs. The ring breathing vibration normally gets downshifted depending upon the substituents in the ring and here this vibration is downshifted and observed at 988 cm^{-1}.

(vi) In the SERS spectrum the out of plane bending CH vibrations are observed at 922 and 877 cm^{-1} and these are medium intensity bands. Apart from this, there is also another weak band due to in plane bending vibration, which occurs at 1114 cm^{-1} . The bands at 182, 364, 394 and 594 cm^{-1} are assigned as ring deformation vibrations.

(b)Orientation determination

Shifts in vibrational frequencies and relative intensities in the spectra of molecules adsorbed on the metal surface in comparison with the same molecule in solution will provide information about the relative proximity of different parts of the adsorbate molecules with the substrate and also the strength of adsorbate- substrate interactions. Now, in order to determine the orientation of the 1,4-DAAQ molecule on the Ag surface, let us compare the relative intensities of various vibrational bands of both SERS and nR spectra.

The enhancement of weak bands at 1466 and 3096 cm^{-1} in nRs and also the appearance of new bands in SERS clearly indicate the possibility of adsorbate-substrate interaction. But we need to find out the group through which the adsorbate molecule interacts with the Ag surface and how the molecule is anchored on it. According to surface selection rules for SERS [9] the vibrational modes possessing polarizability components in the direction of the surface normal should commonly experience greater intensity enhancement. Now coming to the enhanced bands in SERS spectrum, the CH stretching vibration is rather broad and intense. Further the shift towards low frequency region for both C=O stretching and bending modes confirm our suspicion of intramolecular hydrogen bond formation between the amino and carbonyl groups. The distinct possibility of hydrogen bond formation is evident from the proximity of the hydrogen in the amino groups to the carbonyl groups.

One possibility for the interaction of the adsorbed 1,4-DAAQ molecule on the Ag surface is through its coordinating sites (C=O and amino groups). If that is the case, then very strong bands are expected for carbonyl and CN stretching modes in the SERS spectrum. But here, these characteristic bands are either weak or of medium intensity type. Hence, it rules out the possibility of adsorption through these sites.

In a simple molecule like benzene, the relative SERS intensities of symmetric ring breathing mode ν_1 and aromatic CH-stretching mode ν_2 provide useful information about its orientation. Considering 'flat on' adsorption of benzene, the molecular and surface planes are coincident, so that the surface normal will be in the z-direction and the contribution is mostly from α_{zz}. Both (ν_1 and ν_2) modes contain the polarizability component α_{zz}. However, the magnitude of α_{zz} is substantial for ν_1 than ν_2 (10). The ν_2 mode upon surface binding shows a considerable intensity loss, whereas a high intensity along with frequency downshift and line broadening is observed for the ν_1 band and thus provides an evidence for the flat orientation of adsorbed benzene [11].

However, the orientation determination of 1,4-DAAQ from the relative intensities of the ring breathing and CH stretching modes is not a straight forward one as in the case of benzene, because of fused ring formation and heavy atom substitution. Moreover the 1,4-DAAQ molecule is of very low symmetry type (C_s point group) where all the vibrations of the adsorbed molecules have a component perpendicular to the surface in all orientations. We find significant intensity enhancement only for the CH stretching mode in the observed SERS spectrum. The ring breathing mode is observed as a medium intensity one. So, the orientation determination from the relative intensities of ring breathing and CH stretching vibration is quite difficult to predict here.

SERS studies of certain aromatic species at colloidal and electrochemical surface environments [9,12] showed that, the adsorbate orientation is sensitive to some out and in plane bending modes. Out of plane vibrations especially due to CH bending mode play a dominant role in the SERS spectra of planar molecules for flat orientation on metal surfaces even if they are absent in nRs [13,14]. Thus, based on the above detailed discussion on possible orientation for the DAAQ molecule, one arrives at a conclusion that the molecule assumes 'flat on' configuration, which is further confirmed by the appearance of few skeletal deformation bands and also a few out of plane CH bending vibrations in the SERS spectrum [13,14].

(c)Laser induced fluorescence studies

The brightness of colour in α-aminoanthraquinones is due to the presence of absorption bands in the visible region. This character is due to the intramolecular charge transfer from the electron donor (amino groups) to the anthraquinone nucleus. The stronger the electron donating property of the donor, the longer the wavelength position of the absorption band [15]. The laser induced fluorescence measurements are carried out to understand the emission characteristics of the 1,4-DAAQ molecule and its nature of interaction it interacts with the solvent. These studies are done in different solvents (from polar to non-polar) and in different pH. The emission bands are at 610 and 630 nm. The influence of solvents differing in polarity on the emission bands can give useful information on the nature of hydrogen bond formation. Here, no wavelength shift is observed, thereby indicating the absence of any dipole-dipole interaction. This enables us to infer that the carbonyl and amino groups are intramolecularly hydrogen bonded and are not free. The amino derivatives of anthraquinone belong to the group of compounds in which the S_1 and T_1 states are of charge transfer (CT) type [16]. The observation of long wavelength fluorescence bands for DAAQ molecule indicates that the transition is intramolecular charge transfer (ICT) type and is assigned to n, π^* transition. The energy of this transition in 1-aminoanthraquinone is 18,500 cm^{-1} [17], but an addition of a second amino group lowers the energy and gives an increase in intensity of ICT band. This effect is more pronounced for 1,4-DAAQ molecule, because two electron donor substituents are added to one benzene fragment.

Polarization measurements are made to deduce the relative orientation between absorption and emission dipoles. When a molecule is excited by a polarized light, the intrinsic polarization (P_o) will have values $-1/3 < P_o < 1/2$. The limiting value for $P_o = 1/2$ indicates that emission and absorption dipoles are parallel to each other, whereas $P_o = -1/3$ shows that they are perpendicular to each other. Here, for the 1,4-DAAQ molecule, the calculated value of P_o is found to be around -0.30, which means that the emission dipole is almost perpendicular to the absorption dipole.

CONCLUSION

Altogether the evidences gathered in the present study clearly show that the adsorption of the DAAQ molecule is through its pi-orbital system i.e.

the molecule is adsorbed flat on the silver colloidal surface. The intramolecular hydrogen bond formation between carbonyl and amino groups is found to be the main reason against the 'stand on' orientation since it prevents the molecule from getting adsorbed through the substituents.

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