Interaction of anthranilic acid with silver nanoparticles: A Raman, surface-enhanced Raman scattering and density functional theoretical study

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HIGHLIGHTS

- SERS technique is used to study the surface adsorption properties of anthranilic acid.
- Strong enhancement and red shift is observed for CO_2 sym. stretch in SERS.
- Chemisorption takes place directly through the carboxylate group with perpendicular ring orientation.
- Wavelength-dependent SERS illustrates augmented binding through the phenyl ring.

GRAPHICAL ABSTRACT
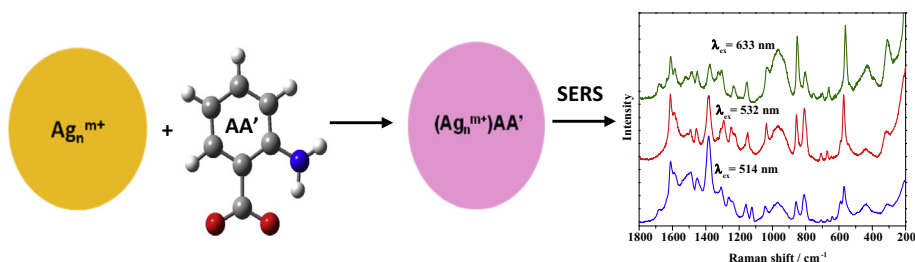
ABSTRACT

Raman and surface-enhanced Raman scattering (SERS) studies of anthranilic acid have been investigated in solid, aqueous solution and on silver colloid. Anthranilic acid plays a key role in the brain in the production of quinolinic acid which is a powerful excitant and convulsant substance. Due to its medicinal importance, the surface adsorption properties of anthranilic acid have been studied. The experimental Raman and SERS data is supported with DFT calculations using B3LYP functional with aug-cc-pvdz and LANL2DZ basis sets. The comparison of experimental and theoretical results infers that anthranilate is chemisorbed to the silver surface directly through the carboxylate group with a perpendicular orientation. The time-dependent SERS spectrum of anthranilate showed no observable change indicating no structural transformation with time. The SERS spectrum recorded at different excitation wavelengths helped in understanding the origin of the SERS mechanism.

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Introduction

Surface Enhanced Raman Scattering (SERS) is a technique that provides greatly enhanced Raman signal [1,2] from Raman-active analyte molecules that have been adsorbed onto certain specially prepared nanometer-sized metal nanostructures. SERS, thus, facilitates the low level detection of analytes due to its high sensitivity and selectivity for the molecules adsorbed over the surface of

metal nanostructures. Hence, it is widely exploited in identifying biomolecules, drugs and proteins as it provides the information about the interaction of the analyte with the metal surface i.e. the binding sites and the orientation over the metal surfaces [3–21]. The combination of electromagnetic (EM) and chemical or charge transfer (CT) effect is believed to explain the mechanism of SERS. The contribution from EM effect in SERS is much more prominent as compared to CT effect [22]. Noble metal nanostructures have been exploited for producing substrates for SERS because of their unique property of showing local plasmon resonance. The SERS signal intensity has been found to depend on the properties of the substrate used. Application of the surface

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selection rules [23,24] in combination with the observed shifts or enhancements in the SERS spectra provides information on the sites of binding and the molecular orientation on the metal surface [25–27].

In recent times, metal nanoparticles have been exploited for the delivery of drugs [28,29]. It is therefore, important to study the physicochemical characteristics of various pharmacologically important drugs and to investigate their surface adsorption characteristics. Here, we have carried out a detailed structural analysis of anthranilic acid (AA) in solid state, aqueous solution and on silver nanoparticle surface. AA is the biochemical precursor to the amino acid tryptophan. It is used as an intermediate in the manufacture of dyes (as indigo), pharmaceuticals, and perfumes. It also plays a key role in the production of quinolinic acid which is a powerful excitant and convulsant substance [30]. Therefore, the levels of AA in the body have to be in check. The chemistry of AA is of importance in medicinal and biological science. We have earlier shown that AA acid reacts with free radicals and acts as an antioxidant [31]. It is also the key ingredient for the synthesis of methaqualone which is a highly addictive, illegal, drug. Consequently, there is a critical need to rapidly identify the compound. SERS is being exploited for the detection of compounds as biomarker in harmful products. One typical example is of the detection of dipicolinate in anthrax [32]. Infrared and Raman studies of AA have been reported in the literature [33]. SERS spectrum of AA was only reported in an article discussing eye lens pigments [34] without giving any details regarding its vibrational structure. Due to the lack of any detailed understanding on the vibrational structure of AA, in this article, we have carried out a comprehensive investigation of the Raman and SERS studies of AA in the solid state, in aqueous solution and on colloidal silver surface. AA contains both carboxylic group and amino group. It can bind to the colloidal silver surface via either the carboxylic or the amino group. SERS studies were carried out to understand the nature of binding of AA to the metal and its probable orientation on the surface. DFT (B3LYP functional with aug-cc-pvdz and LANL2DZ basis set) calculations were carried out for a detailed interpretation of the Raman and SERS spectra. From the SERS spectra, and theoretical calculations it has been inferred that AA is chemisorbed to the silver surface through the carboxylate group with a perpendicular orientation. Time-dependent (TD) SERS spectra of AA was investigated to see whether the molecule undergo any structural change over the silver surface with increasing time. The wavelength-dependent SERS spectra were also recorded to understand the origin of the SERS mechanism.

Experimental

AA, AgNO₃, and sodium borohydride used for the Raman measurements as well as preparation of silver colloid were from Aldrich chemicals, and S. D. fine chemicals, India and were used without further purification. Silver colloid was prepared by the chemical reduction of AgNO₃ with NaBH₄ using the method of Creighton et al. [35]. In brief, 10 ml AgNO₃ (10^{-3} M) solution was added drop wise to 30 ml of 2×10^{-3} M ice-cold NaBH₄ with slow stirring. The silver colloid was yellow in color and was stable at room temperature for several weeks. The pH of the silver colloid was ∼9. AA was added to the silver colloid and characterized using UV–Vis absorption and Raman technique. UV–Vis absorption spectra were recorded using a Jasco V-650 spectrophotometer. Raman and SERS spectra of AA were recorded at room temperature using the 514 nm line from the Argon ion laser (35-LAP-431-230, Melles Griot), 532 nm line, from a diode pumped solid state Nd^{3+}:YAG laser (Cobolt Samba 0532-01-0500-500) M/s Cobolt AB, Sweden and 633 nm line, from a HeNe laser. The laser power used to record

the Raman spectrum was ∼10 mW, and the spot size on the sample was ∼ 50μ. For the Raman measurements, the sample solution as well as silver colloid was taken in a standard $1 \times 1\ cm^2$ cuvette and the Raman scattered light was collected at 90° scattering geometry and detected using a CCD (Synapse, Horiba Jobin Yvon) based monochromator (Triax550, Horiba Jobin Yvon, France) together with a notch filter, covering a spectral range of 200–1700 cm^{-1}.

Computational details

The pK_a of AA is known to be 4.95 [36]. Hence, it exists mainly as anthranilate (carboxylate ion form, $AACO_2^-$ referred to as AA′) in aqueous solution at pH 9. In order to get an insight into the experimental results, the geometry optimization was performed for AA, its carboxylate ion and its neutral and charged silver complexes using the Density Functional Theory (DFT) with B3LYP functional [37] and aug-cc-pvdz (for AA and AA′) and LANL2DZ (for Ag) basis set using Gaussian 03 program [38]. No symmetry restriction was applied during geometry optimization. The vibrational frequencies for AA, AA′ and its silver complexes were computed at the optimized geometry to ensure that it corresponds to a local minimum on the potential energy surface and not to a saddle point. The computed vibrations at the optimized geometry were compared with the normal Raman and the SERS spectra.

Results and discussion

Molecular structure of AA, AA′ and its silver complexes

The optimized structures of AA and AA′ are shown in Fig. 1(a) and (b), respectively along with their atom numbering. The optimized structures indicate that the COOH and carboxylate as well as the amino groups lie in the plane of the phenyl ring in AA and AA′. The calculated frequencies of AA and AA′ at the optimized geometry were tabulated in Table 1. For a one to one correspondence of the calculated frequencies with the observed Raman vibrations in solid and in aqueous solution (pH ∼ 9), the computed Raman intensities were also taken into account.

The charged and neutral silver complexes of AA′, viz. AA′-Ag⁺, AA′-Ag⁰, AA′-Ag₄⁺ and AA′-Ag₄⁰ were optimized using B3LYP functional with aug-cc-pvdz (for AA′) and LANL2DZ (for Ag) basis sets. The net charge of AA′ bound to the neutral and charged silver atom(s) is −1 and 0 respectively. The optimized structures of AA′-Ag⁺, AA′-Ag⁰, AA′-Ag₄⁺ and AA′-Ag₄⁰ are shown in Fig. 2(a–d), respectively. As shown in the figure, the neutral and charged silver are mainly bound to the carboxylate oxygen (O_8) and (O_9) atoms leading to a change in C_7O_8 and C_7O_9 bond distances. It is observed from the figure that both in the charged and neutral silver complexes, the C_7O_8 and C_7O_9 bond distances are elongated, with the bond lengthening being more prominent in the former. Moreover, it is observed that in the charged silver complex both the O–Ag bond distances are ∼2.3 Å and in the neutral silver complex, the O_9Ag bond distance is 2.3 Å whereas, the O_8Ag bond distance is 3.2 Å. In the charged and neutral complex, the O_8AgO_9 bond angles are 58.3° and 45.8°, respectively. The O_8O_9AgAg dihedral angle in the charged AA′-Ag₄⁺ and neutral AA′-Ag₄⁰ complexes are −0.01° and 110.2°, respectively. The dihedral angle values as well as the optimized structures of AA′-Ag₄⁺ and AA′-Ag₄⁰ in Fig. 2(c) and (d), suggests that the AA′ molecule lies in the same plane as the Ag₄⁺ whereas, it lies almost perpendicular to the Ag₄⁰ plane. The binding energies (BE) of the silver complexes of AA′ were calculated taking the Basis Set Superposition Error (BSSE) [39] into consideration. The BE for AA′-Ag⁺, AA′-Ag⁰, AA′-Ag₄⁺ and AA′-Ag₄⁰ were found to be 166.2, 20.5, 144.1 and 45.1 kcal mole^{-1}. The higher BE values