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Adsorption of 2-aminobenzothiazole on nano-colloidal silver surface: A concentration and time dependent SERS study aided by density functional theory

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ABSTRACT

Concentration and time dependent SERS spectra of 2-aminobenzothiazole molecule adsorbed on nano-colloidal silver surface have been investigated. The experimental observations are aided by density functional theory. The general interpretation of the concentration dependent SERS spectra corroborates the predominant existence of the "N" specie of the molecule at 1.0×10^{-6} M adsorbate concentration which ensures the edge on adsorption of the molecule with its short axis (y-axis) almost normal to the nano-colloidal silver surface. The time dependent SERS spectra of the molecule are characterized by the increase in intensity of bands primarily representing the vibrational signatures emanating from the benzene ring moiety of the molecule. The possible rationale of the selective enhancement of the vibrational signatures emanating from the benzene ring moiety of the molecule with time has been envisaged.

1. Introduction

Surface enhanced Raman scattering (SERS) has opened up wide research fields in Raman spectroscopy and in physics and chemistry of interfaces [1]. It is a useful tool in surface chemistry because of its high sensitivity and potential in providing useful information regarding metal-adsorbate interactions [2]. The origin of SERS still remains a matter of controversy, though it is now widely accepted that there are two main contributions of the overall effect. One is the long range electromagnetic (EM) effect and the other is the short-range chemical (CHEM) effect, which is now thought to be simultaneously operative. The EM mechanism is based on the amplification of the electromagnetic field generated due to coupling of the radiation field with the surface plasmons of the metal nano-particles [3]. The CHEM mechanism is associated with the charge transfer (CT) interaction between the metal surface and the adsorbed molecule, resulting in the change of molecular polarizability [4]. Recently quantum chemical calculations are successfully utilized to model the experimentally observed SERS spectra and their results help one to understand the CHEM mechanism of SERS in particular [5–8].

2-Aminobenzothiazole (2-ABT) molecule is known for its local anesthetic action and has numerous applications in human and veterinary medicine [9]. The optimized structure of 2-ABT molecule is shown in Fig. 1. 2-ABT is a metabolite of methabenzthiazuron and is reported to form the main fraction of soil bound residues [10]. Considering the enormous biological importance, we present here a concentration and time dependent SERS study of 2-ABT molecule adsorbed on nano-colloidal silver surface. The concentration dependent SERS spectra of the molecule enable us to understand the adsorptive behavior of the probe molecule on the nano-colloidal silver surface at different adsorbate concentrations, close to that encountered under physiological conditions in living systems. The time dependent SERS spectra help us to comprehend the charge transfer contribution to SERS.

2. Materials and methods

2.1. Chemicals and procedure

2-ABT was purchased from Aldrich Chemical Co. and used without further purification. The molecule is readily soluble in acetonitrile solution. Stable silver sol was prepared by the process of Creighton et al. [11]. Mixing a specific volume of stock solution in acetonitrile with an appropriate volume of silver nano-colloid, the desired concentration of 2-ABT on the nano-colloidal surface has been attained.

2.2. Instrumentation

Raman spectra were recorded by a Spex double monochromator (Model 1403) fitted with a holographic grating of 1800

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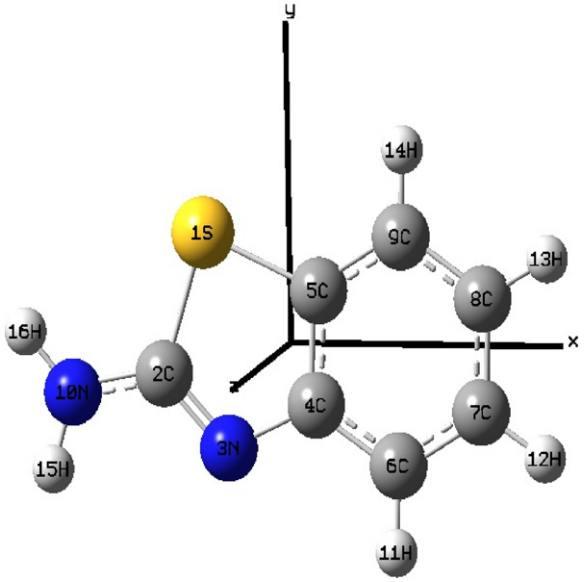

Fig. 1. The optimized molecular structure of 2-ABT molecule obtained from B3LYP/LANL2DZ level of theory.

grooves/mm and a cooled photomultiplier tube (Model R928/115) from Hamamatsu Photonics, Japan. The sample was taken in a quartz cell and was excited by 514.5 nm radiation from a Spectra Physics Ar^+ ion laser (Model 2020-05) at a power of 200 mW. Raman scattering was collected at a right angle to the excitation. The operation of the photon counter and data acquisition and analysis were controlled by Spex Datamate 1B. The acquisition time by the spectral element was 0.5 s. The scattered light was focused onto the entrance slit of width of 4 cm^{-1}.

2.3. Theoretical calculations

The DFT calculations were carried out using Gaussian 03 software [12]. Optimization of 2-ABT molecule and calculations of the models for Ag_2-molecule complexes were performed using the combination of Becke three hybrid exchange Lee-Yang-Par B3LYP functional and LANL2DZ basis set. In the process of geometry optimization for the fully relaxed method, convergence of all the calculations and the absence of imaginary values in the wave numbers confirmed the attainment of local minima on the potential energy surface. The vibrational frequencies of Ag_2-molecule complexes as obtained from the B3LYP/LANL2DZ level of DFT calculations are presented without using any scaling factor.

3. Results and discussion

3.1. Concentration and time dependent SERS spectra of 2-ABT

The vibrational assignment and the concentration dependent SERS spectra of 2-ABT molecule adsorbed on silver nano-colloids were reported by our research group in our earlier communication [13]. The normalized SERS spectra of the 2-ABT molecule recorded at various adsorbate concentrations in the specific wave number range of interest is shown in Fig. 2. Each of the SERS spectra of 2-ABT molecule in the range of 1.0×10^{-6}–1.0×10^{-3} M adsorbate concentrations was monitored after 1 h from the preparation of the nano-colloid molecule mixture. For each reduction of concentration of molecules in the silver nano-colloid, the concentration of acetonitrile (ACN) was kept constant; facilitating the normalization of the SERS spectra. The normalization was done with respect to 921 cm^{-1} band of ACN. The concentration dependent

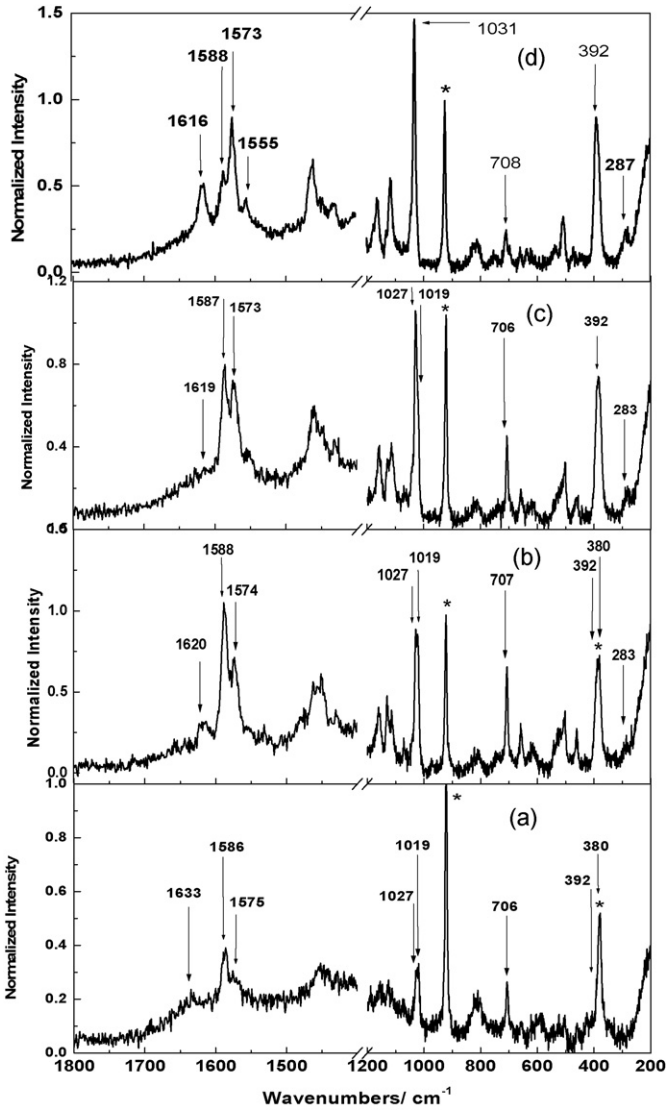

Fig. 2. Normalized SERS spectra of 2-ABT molecule adsorbed on silver nano-colloid at concentrations (a) 1.0×10^{-3} M, (b) 1.0×10^{-4} M, (c) 1.0×10^{-5} M, (d) 1.0×10^{-6} M for λ_{exc} = 514.5 nm (*denotes the solvent band of acetonitrile).

SERS spectral features, in general, reveal the existence of two types of vertically adsorbed species namely "M" and "N" on nano-colloidal silver surface whose relative population varies with the adsorbate concentrations. At lower adsorbate concentration (ca. $\sim 1.0 \times 10^{-6}$ M) only "N" type species were reported to be preponderant [13] while both the "M" and the "N" species coexist at higher adsorbate concentrations. The adsorption of the "M" species of 2-ABT molecule involves insignificant or no interaction of the benzene ring moiety in the adsorption process. The "N" species on the other hand involve strong interaction of the benzene ring in the adsorption mechanism. However, the concentration dependent SERS spectral profile of the molecule further divulge some interesting aspects concerning the orientation of both the species in general and the "M" species in particular on the nano-colloidal surface. Hence the spectral interpretation of the concentration dependent SERS spectra of 2-ABT molecule has been revisited.

The concentration dependent SERS spectra (as shown in Fig. 2) are mainly characterized by the increase in intensity of 392 cm^{-1} band with the decrease in adsorbate concentrations. This band has been ascribed to α(C–C–C) [ν_{6b}] mode originating from the