Vibrational Spectroscopy 81 (2015) 22–31

Contents lists available at ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec

Significance of chemical enhancement effects in surface-enhanced Raman scattering (SERS) signals of aniline and aminobiphenyl isomers

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ARTICLE INFO

Article history:
Received 18 May 2015
Received in revised form 7 September 2015
Accepted 7 September 2015
Available online 9 September 2015

Keywords:
Aminobiphenyl
Aromatic amines
Surface-enhanced Raman scattering (SERS)
SERS enhancement factors
Raman spectroscopy
Density functional theory
Chemisorption on silver nanoparticles
Silver colloids

ABSTRACT

Surface-enhanced Raman scattering is a useful technique for detecting low levels of aromatic amines as environmental contaminants because it can be used to detect and distinguish among their isomers based on their distinctive SERS spectra. This paper demonstrates the feasibility of measuring the concentrations of aminobiphenyls (ABPs) including 4-ABP, 3-ABP, and 2-ABP down to the levels of about 5, 50, and 250 μg/mL, respectively. The SERS signal intensities of ABPs are dependent on the pH values of the samples and colloidal media. The optimal sample pH values were found to be 6.86, 7.83, and 7.36, for 2-ABP, 3-ABP, and 4-ABP, respectively, whereas the optimum silver colloidal pH ranges from 5.0 to 6.5. A detailed analysis of the different vibrational modes of aniline and the ABP isomers was carried out using computational modeling based on the density functional theory (DFT). Compared to aniline, the ABPs produced greater SERS enhancement of the intensities for the biphenyl ring-breathing mode. The SERS signal for the NH_2 wagging band shows the order of enhancement as given by 4-ABP > 2-ABP > 3-ABP, which correlates well with the HOMO-LUMO energy gap based on the DFT modeling of the amines adsorbed on the silver cluster.

1. Introduction

The surface-enhanced Raman scattering (SERS) technique was first reported by Fleischmann and co-workers in 1974 [1] whereby pyridine adsorbed onto the roughened silver electrode surface gave rise to a Raman signal that was enhanced significantly relative to the normal Raman signal of pyridine. The overall signal enhancement of adsorbed molecules has been attributed to two factors commonly known as the chemical enhancement and the electromagnetic enhancement mechanisms. Chemical enhancement mechanism, which requires molecule-metal interactions as a prerequisite is due to the charge transfer between energy levels of the adsorbate molecules and the metal nanoparticles. This interaction causes the formation of an adsorbate-metal complex with a larger Raman scattering cross-section relative to the free molecules. It is also possible that the resonance Raman effect becomes operative due to the shifted and broadened electronic levels of the adsorbate molecules [2]. This charge transfer can occur from the metal state near the Fermi level to the lowest unoccupied molecular orbital (LUMO) of the adsorbed molecules in the case of *p*-aminothiophenol on silver [3] or from the highest occupied molecular orbital (HOMO) of adsorbed molecules to the LUMO level of the metal clusters in modeled aniline-metal interactions [4]. Chemical enhancement is also closely associated with the bond strength between analyte molecules and the metal atoms at the surface active sites. In order for the chemical enhancement to occur, the molecule must be directly adsorbed onto a roughened metal surface, and the molecular interactions must occur between that surface and the adsorbate. Hence, analyte species with stronger affinity for chemisorption onto the metal surface will be preferentially adsorbed and will have greater enhancement.

The electromagnetic enhancement is due to the strong electromagnetic (EM) field that arises from the enormous localized surface plasmon resonances (SPR) at roughened nanostructure surfaces. The roughened metal surface provides SERS-active sites for the substrates to interact with the light and undergoes surface plasmon resonance to yield signal enhancement. The magnitude of the electromagnetic enhancement effect and its dependence on the interfacial distance of adsorbed aromatic analytes, including benzene and tertiary butylbenzene, was demonstrated by using self-assembled monolayers of alkanethiols with various alkane chain lengths on a modified SERS substrate [5]. SPR depends on the metal nanoparticle morphology such as size, shape, geometry, and aggregation [6–8]. The overall intensity of SERS is determined by the interaction of laser excitation beam with the metallic nanostructure, analyte adsorption, and scattering.

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http://dx.doi.org/10.1016/j.vibspec.2015.09.002

Research indicates that SERS enhancement is possible in metals with high optical reflectivity such as silver (Ag), gold (Au), copper (Cu), aluminum (Al), and even nickel (Ni). Among all these, Ag and Au nanoparticles are ideal substrates for SERS enhancement because they yield large SERS enhancement factors and are relatively easy to prepare. The procedure has also been extended to include the use of non-metallic materials like germanium, silicon, and quartz [9]. Commonly employed SERS substrates are metal colloids of Ag, Au, and Cu, as well as roughened electrodes [10], nanoprobes [11,12], and silver-coated mica [13].

Although both the electromagnetic and chemical enhancement mechanisms are important in SERS, previous studies [14–16] have estimated signal enhancement can reach as high as 10^{14}–10^{15} and the typical enhancement magnitude of 10^{11} can be attributed to the electromagnetic effect. The magnitude of contribution from the chemical effect is highly variable with reported estimates ranging from 10^2–10^3 to as high as 10^6 [17–20]. In general, the electromagnetic component due to the excitation of the surface plasmons in the metal nanoparticles contributes to a greater extent to the SERS enhancement effect whereas the chemical component, which results from the molecular interactions between the metal surface and the adsorbate, accounts for a smaller magnitude of the overall SERS enhancement. This article investigates the SERS experimental variables and the dependence of the chemical enhancement effects on the structural characteristics for selected aromatic amines.

2. Materials and methods

2.1. Chemical standards and Raman instrumentation

Aromatic amines including 2-aminobiphenyl (2-ABP; 97% purity), 3-aminobiphenyl (3-ABP; 97% purity), and 4-aminobiphenyl (4-ABP; 97.9% purity) were purchased from Alfa Aesar (Ward Hill, MA, USA), TCI (Portland, OR, USA) and Sigma Aldrich (St. Louis, MO, USA), respectively. The normal Raman signals for the ABP isomers were acquired for the powder samples with integration times ranging from 5 to 30 s. For aniline of 99.5% purity (Sigma Aldrich, St. Louis, MO), the normal Raman signal was acquired with 5 s of signal integration time. The EnWave ProRaman-L spectrometer (EnWave Optronics Inc, Irvine, CA) was equipped with a fiber-optic probe and a laser with an excitation wavelength of 785 nm and line width of 0.04 nm.

2.2. Colloidal preparation and SERS analysis

Silver colloid was prepared using the Leopold-Lendl method [21] with minor modifications in which, 450 mL of 1.11×10^{-3} M silver nitrate solution (Fisher Scientific, Fair Lawn, NJ) was rapidly mixed with 50 mL of a solution containing 1.5×10^{-2} M hydroxylamine hydrochloride (Baker Chemical Co., Phillipsburg, NJ) and 3.0×10^{-2} M sodium hydroxide (Fisher Scientific, Fair Lawn, NJ). These freshly prepared silver colloids were centrifuged using a Beckman Coulter™ Allegra™ 64R centrifuge at 5000 rpm at 12 °C for fifteen minutes and pre-concentrated to fivefold and tenfold. The tenfold pre-concentrated colloids prepared by centrifugation at 5000 rpm was buffered to the desired pH using a series of phosphate buffers described previously [22]. The pH of each buffered colloid was recorded after mixing the silver colloid with the phosphate buffer at 1:1 ratio. The buffered colloid maintained a pH similar to that of the buffer used.

The aniline sample for SERS analysis was prepared by mixing the 30 mg/mL standard dissolved in deionized water with fivefold pre-concentrated silver colloid at 1:9 volume ratio and the SERS signal collected at 5 s integration time. The effect of silver colloid pH on SERS signals were studied by mixing each stock solution of 200 mg/L 4-ABP (pH 5.97), 1000 mg/L 3-ABP (pH 7.18), and 6000 mg/L 2-ABP (pH 6.08) prepared in ethanol with silver colloids buffered at different pH values at a 1:9 volume ratio. The SERS measurements were collected with signal integration times of 5, 5, and 10 s, respectively, for the three ABP isomers. The ABP analyte solutions at different pH were prepared by mixing each of the above ABP stock solutions with different phosphate buffers at a 1:1 volume ratio. The pH values of the buffered analytes were in the range of pH 2.53–pH 10.88. Each buffered analyte of 4-ABP, 3-ABP, and 2-ABP was then mixed with fivefold pre-concentrated silver colloid at a 1:9 volume ratio and the SERS signals were collected at integration times of 3, 5 and 5 s, respectively.

2.3. Transmission electron microscopy (TEM) analysis

Silver colloids buffered at different pH were converted into aerosol, using Plumo Aide nebulizer (Devilbiss, Somerset, PA), for deposition onto a carbon-coated 200 mesh TEM grid. These grids were placed at a fixed distance of 1.5 cm from the nebulizer nozzle and the nebulization time for each sample was 75 s. The size and shape of the silver nanoparticles were analyzed using a Hitachi H-7650 transmission electron microscope. The instrument was operated at 80 kV or 100 kV at a magnification of 25,000–120,000 times. The images were processed and analyzed using the Image J software (NIH, Bethesda, Maryland) to determine the particle size distribution.

2.4. Computational analysis

A molecule-metal cluster complex model similar to that described by Zhao et al. [4] was adopted to compute the surface adsorption parameters of the aromatic amines on silver as well as to model the Raman spectra of the amine-metal interactions. A silver cluster size of four metal atoms was used for the computational modeling of the adsorption of the aromatic amines on the colloidal silver nanoparticles based on results reported by Zhao et al. [4].

Density functional calculations were performed using the B3LYP hybrid functional [23,24]. The 6-311+G(d,p) basis sets, which include polarization functions for all four atom types and diffuse functions for the C, N, and O atoms, were used to describe the C, N, O, and H atoms [25,26]. The LANL2DZ basis set, which includes the corresponding relativistic effective core potentials, was used for all Ag atoms [27,28]. Geometry optimizations and Raman vibrational frequency calculations were performed using the Gaussian 09 package (Gaussian, Inc., Wallingford, CT). Vibrational mode assignment for Raman peaks was made by viewing visual animations of the vibrational modes using GaussView05 (Semichem Inc., Shawnee Mission, KS). Deconvolution of the spectral peaks was done using Origin 8.1 (OriginLab, Northampton, MA).

Both analytical enhancement factors (AEF) based on analyte concentrations in the colloidal sample mixtures and surface enhancement factors (SEF) based on the concentrations of analyte molecules adsorbed on the silver nanoparticles were calculated. The relationship between AEF and SEF are expressed as follows,

$$\frac{SEF}{C_s} = \frac{\Lambda EF}{C_b}$$

where C_s and C_b refer to concentration of analyte molecules on the silver nanoparticle surfaces and in the bulk solution, respectively [29]. An assumption is made that 70% of analyte molecules are adsorbed onto the colloidal silver particles based on a prior study of residual analyte concentration after the removal of silver nanoparticles by ultracentrifugation. The surface enhancement