Surface enhanced Raman scattering of 2,2′-biphenyl dicarboxylic acid on silver surfaces: Structure and orientation upon adsorption

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ABSTRACT

The SERS spectrum of 2,2′-biphenyl dicarboxylic acid (22-BPDC) adsorbed on Ag nanoparticles has been measured and the observed bands are identified and assigned referred to the ordinary Raman spectrum and to the previously measured SERS spectrum of 4,4′-biphenyl dicarboxylic acid (44-BPDC). [J. Mol. Struct. **1050**, 2013, 128] As in the case of 44-BPDC, quantum chemical density functional theory calculations have also been performed to figure out structures and to calculate vibrational wavenumbers and eigenvectors in 22-BPDC. The observed SERS spectra could successfully be simulated from the models for adsorption of 22-BPDC to Ag and three Ag atom clusters. As opposed to 44-BPDC adsorbed flat on the Ag surfaces through both the COO—Ag and phenyl π-electron-metal interactions, the two phenyl rings remain twisted in 22-BPDC upon adsorption on the Ag surfaces with less π-electron-metal interaction because of small space allowances for the two closely located carboxyl groups compared to 44-BPDC.

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1. Introduction

Recently, the surface enhanced Raman scattering (SERS) spectrum of 4,4′-biphenyl dicarboxylic acid (44-BPDC) in Ag colloidal solution has been reported employing a newly developed systematic method of preparing effective Ag substrates for SERS [1]. Dramatic enhancement of SERS signals were achieved when three or four prepared Ag nanoparticles of about 25 nm size were found to be aggregated forming islands in solution. This enhancement was realized as the electromagnetic enhancement mechanism by excitation of localized surface plasmon resonance of a nanostructured metal surface resulting in enhanced local electromagnetic field. Although another enhancement has been known as the chemical enhancement mechanism by electronic resonance between the metal and a molecular state, the actual SERS signal enhancement would result from either one of the two or both [2–4]. Taking advantage of these signal enhancements, SERS has widely been used to measure spectra of trace amounts of chemicals such as 4,4′-bis(mercaptomethyl)biphenyl (44-BMBP) in solution [5].

Vibrational transitions in the Raman spectra of certain molecules adsorbed on metal surfaces should be governed by the surface selection rules. According to this surface selection rule, Raman scattering tensor elements along the surface normal should be larger relative to the ordinary tensor elements when the molecules are adsorbed on the metal surfaces [6,7]. Intensities of certain vibrational transitions thus should be increased in the SERS spectra compared to those in the ordinary Raman spectra depending upon orientation of the molecules relative to the metal surfaces. In this regards, vibrational bands in the SERS spectra in the region of phenyl C—H stretch are especially recognized to indicate relative orientation of the phenyl rings with respect to the surface normal in benzene and biphenyl derivatives adsorbed on the metal surfaces since the C—H stretching motions are mostly confined in the plane. For example, benzenedithiols have been known to be adsorbed in general through a single S—Au linkage on Au but two S—Ag linkages on the Ag surfaces although the adsorption behavior depends upon surface coverage [8–10]. The orientation of the phenyl ring relative to the surface depends upon the characteristics of the molecules (numbers and relative positions of different adsorption sites) in solution and upon the substrates as well such as for 1,2-benzenedithiol, the tilt angles with respect to the surface normal being ~51° on Au and ~38° on Ag, respectively [11].

Structures of biphenyl derivatives adsorbed on the metal surfaces have recently been focused on because the relative orientation of the two phenyl rings, twisted or parallel, could be responsible for molecular switches through interaction of π-electron systems on molecular electronic devices when the molecules are bridged between metal junctions [12,13]. Thus, the structure

and orientation of such molecules on the metal surfaces have to be firstly characterized for application. As in the case of benzenedithiol, it was suggested from the SERS spectra with an aid of quantum chemical calculations that 4,4′-biphenyldithiol (44-BPDT) should be adsorbed on the surface through the two S—Ag linkages with slightly tilted orientation of the two phenyl rings [14]. When this molecule was bridged between the two Au crystal surfaces, the relative orientation of the two phenyl rings could be controlled by applying the electric field between the metal junctions [15]. 4,4′-Biphenyl dicyanide and diisocyanide on the Au and Ag surfaces of nanoparticles were also studied by SERS [16,17]. Flat orientation of both phenyl rings through the interaction between the π-electron systems and the metal surfaces was suggested for 4,4′-biphenyl dicyanide on both the Au and Ag surfaces whereas the bridged structure between the Au particles was found at low concentration and the vertical structure adsorbed via one of the isocyanide groups on the Au surface was shown at high concentration for 4,4′-biphenyl diisocyanide.

The SERS spectra of benzoic acid and 4-biphenyl carboxylic acid were obtained and analyzed to study adsorption characteristics on the Au colloidal surfaces where the phenyl rings are parallel to the surface due to adsorption through both carboxylates and π-electron systems of the phenyl rings on the surfaces [18]. In order to analyze the SERS spectra and to determine the relative orientation of the adsorbed molecules by applying the surface selection rules, vibrational assignments of the observed peaks in the spectra should first be accomplished. This could be done employing spectral correlations between the target molecule and its derivatives observed in ordinary IR and the Raman spectra. However, there should be a large number of normal modes in biphenyl derivatives such as biphenyl carboxylic acid (69 normal modes), which makes the peak assignments in the spectra a very formidable task. Recently, the SERS spectra of 44-BPDC adsorbed on the Ag nanoparticle surfaces were obtained. The observed Raman bands were identified and successfully assigned with an aid of model calculations under the B3LYP/DGDZVP density functional theory level comparing with the spectra of the sample in basic condition [19]. The peaks were assigned adopting the Mulliken notation referred to the calculated frequencies and to the mode characteristics [20]. It was suggested that 44-BPDC should be adsorbed through both carboxylate groups and that the two phenyl rings should be parallel to the metal surface opposed to the twist configuration of the phenyl rings in free molecules in the gas phase.

In this study, the SERS spectra of 2,2′-biphenyl dicarboxylic acid (22-BPDC) adsorbed on the Ag nanoparticle surfaces have been obtained in silver sol. Compared to 4,4′-biphenyl dicarboxylic acid (44-BPDC), a different geometry and hence different adsorption behavior and orientation on Ag surfaces would be expected because the two carboxyl groups are close to one another in 22-BPDC. The observed Raman bands are assigned through comparison with those in the ordinary Raman spectra under neutral and basic conditions with the quantum chemical calculations and the adsorption characteristics and orientation of the adsorbed molecules are discussed.

2. Experiments

Preparation and characteristics of the silver nanoparticles for the most effective SERS substrates have previously been described in detail [1]. Briefly, the 30 mL of 2×10^{-3} M $NaBH_4$ solution at ice temperature was prepared and with a dispenser, the 8×10^{-3} M $AgNO_3$ solution at ambient temperature was added drop by drop to the prepared $NaBH_4$ solution with stirring at 1500 rpm. As reduction in the solution proceeded, its color turned yellow and afterwards the solution became turbid with precipitates. The reduction

was terminated by addition of 1 mL $NaBH_4$ solution for stabilization. The addition rate of the $AgNO_3$ solution was controlled by varying the number of droplets per second with the droplet volume of 50 μL. The optimum rate for the maximum SERS signal was determined to be 0.4 μmol/s and the substrate thus generated consisted of aggregates of the two or three Ag nanoparticles of about 30 nm sizes, providing hot-spots for the largest enhancement of the Raman signal. A sample to measure the SERS spectra was prepared by adding 22-BPDC (2×10^{-3} M, 20 μL) and PVP (2×10^{-4} M, 20 μL) as a stabilizer to the prepared 1 mL Ag solution. 22-BPDC was purchased from Aldrich and used without further purification. All other chemicals were of the reagent grade and deionized water was used all throughout the experiment.

Raman scattering was measured by utilizing a triple grating imaging monochromator (Princeton Instruments, SP-2500i) equipped with a back-illuminated CCD (Princeton Instruments, 100B_eXcelon). The excitation source was the 632.8 nm line of a He—Ne laser (Melles Griot, R54-168). A typical laser power at the sample position was 10 mW. The Raman scattering signals were collected at a right angle through a holographic Notch filter (Edmund Optics) set in front of the entrance slit of the spectrometer. The holographic grating of 1200 grooves/mm and the slit opening of 100 μm allowed the spectral resolution of 1 cm⁻¹. The spectrometer was calibrated with emission lines from a mercury lamp as references. The typical data acquisition times for ordinary Raman (OR) in neutral, in basic conditions, and for the SERS experiments were 30 s, 5 s, and 10 s, respectively.

Quantum chemical density functional theory (DFT) calculations were performed employing the GAUSSIAN 09 program packages under the B3LYP/6-311+G (d,p) level for spectral simulation of the OR spectra in neutral and in basic conditions [21]. The SERS spectrum was simulated for 2,2′-biphenyl dicarboxylate bound to either Ag atom (Ag) or a cluster of three Ag atoms (Ag₃) at both ends at the B3LYP/DGDZVP level.

3. Results and discussion

An ordinary Raman (OR) spectrum of 22-BPDC was obtained and presented in Fig. 1(a) in order to identify the chemical species adsorbed on the Ag nanoparticles and to help identifying the peaks observed in the SERS spectrum. Instead of the characteristic C═O stretching band at 1728 cm⁻¹ shown in the calculated spectrum of 22-BPDC monomer (Fig. 1) (b) and in other aromatic acids, the C═O stretching band in the measured spectrum seems downshifted to 1635 cm⁻¹. Since the solubility of 22-BPDC is extremely low in water, a small amount of the solid sample was dissolved in methanol and dried to form a solid film to measure the Raman spectrum. Since in solid, 22-BPDC might form hydrogen-bonded dimers like benzoic acid, the Raman spectra of the 22-BPDC dimer and trimer were hence calculated for comparison. The calculations were performed employing the GAUSSIAN 09 program packages under the B3LYP/6-311+G (d,p) level. In the simulated spectrum for the dimer shown in Fig. 1 (c), the two distinct peaks related to the C═O stretching modes were observed at 1629 and 1727 cm⁻¹ for the hydrogen-bonded and free COOH, respectively, while these two peaks were upshifted for the trimer but the peak intensity from the free COOH was remarkably decreased. From these calculations, the observed peak at 1635 cm⁻¹ in the OR spectrum could be assigned as the hydrogen-bonded C═O stretching mode. Therefore, it was suggested that 22-BPDC should be in the form of hydrogen-bonded clusters in solid because of no appreciable peaks observed in the region of free COOH. The observed peaks in the Raman spectra could then be assigned based upon the calculated normal modes and frequencies of the dimer. Among the observed peaks, the peaks at 1596, and 1576 cm⁻¹ are the characteristic C—C stretching