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SERS and DFT study of p-hydroxybenzoic acid adsorbed on colloidal silver particles

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Abstract

In this study, normal Raman spectra of p-hydroxybenzoic acid (PHBA) powder and its surface-enhanced Raman scattering (SERS) spectra in silver colloidal solutions were measured under near infrared excitation conditions. In theoretical calculation, two models of PHBA adsorbed on the surfaces of silver nanoparticles were established. The Raman frequencies of these two models using density functional theory (DFT) method were calculated, and compared with the experimental results. It was found that the calculated Raman frequencies were in good agreement with experimental values, which indicates that there are two enhanced mechanism physical (electromagnetic, EM) enhancement and chemical (charge-transfer, CT) enhancement, in silver colloidal solutions regarding SERS effect. Furthermore, from high-quality SERS spectrum of PHBA obtained in silver colloids, we inferred that PHBA molecules in silver colloids adsorb onto the metal surfaces through carboxyl at a perpendicular orientation. The combination of SERS spectra and DFT calculation is thus useful for studies of the adsorption-orientation of a molecule on a metal colloid.

Key words: p-hydroxybenzoic acid, SERS, DFT, colloidal silver particles.

Introduction

Since the first observation of surface-enhanced Raman scattering (SERS) by Fleischmann et al. in 1974 (1), this technology has opened up wide research fields in Raman spectroscopy and in physics and chemistry of interfaces (2). It is a powerful tool in surface chemistry and physics because of its high sensitivity and potential in providing useful information about the nature and orientation of adsorbed molecular species and the adsorbate metal interaction mechanism (3). SERS has the possibility of greatly increasing sensitivity of Raman spectroscopy, even to 10^5–10^{10} fold. The enhancement of the Raman signal induced by metal nanoparticles, which is the basis of SERS spectra, can be understood as a contribution from two different enhanced mechanisms: electromagnetic and charge-transfer mechanisms (4-6). Currently, SERS has been widely investigated in biomedical engineering, such as the detection of human tissue, cells and blood fluid, and so on (7-9).

Recently, DFT calculations as a post self-consistent field (SCF) method have been used extensively to calculate structures of molecules and their infrared adsorption and Raman scattering (10,11). The DFT method allows to calculate the electrostatic properties and Raman scattering intensities of molecules and to assign their Raman bands (12,13). But one of the important defects of density functional theory (DFT) is not widely used in electronic multi-state structure research.

Wu et al. (14) studied the adsorption behavior of PHBA on silver nanoparticles, using a simplified model, which is that employing one Ag atom instead of the Ag cluster. Fang et al., in particular, used PHBA extensively as a molecular probe for a number of different applications (15-18). Other studies of molecular adsorption on metal surface can be found in Refs. (19,20).

In the present work, silver aqueous colloid used as a substrate and high-quality SERS spectra of PHBA were obtained. Considering the two different enhancement mechanisms, we established two corresponding models of PHBA adsorption on the surfaces of silver nanoparticles and applied DFT-B3LYP (21,22) methods with 6-31+G**(C,H,O)/ lanl2dz(Ag) basis sets to calculating the Raman vibrational wave numbers based on the two models. The theoretical results were compared with the experimental values. We find that the two models lead to different vibration spectra, which correspond well to the experimental observation. In addition, based on the relative intensities of SERS signals, we investigate the adsorption orientation of a molecule, as known as surface selection rules by Moskovits et al. (23). It is found from the analysis of normal Raman and SERS spectra that, in silver aqueous colloids, PHBA stands perpendicularly on the surfaces of silver nanoparticles through the carboxyl groups.

Materials and methods

Experimental

The silver colloid used in the SERS experiments was prepared following the method of Munro et al. (24) by reduction of silver nitrate with sodium citrate. A weight of 90 mg of silver nitrate was suspended in 500 ML distilled water (45°C) and heated rapidly to boiling under stirring. Immediately after the silver nitrate solution started boiling, 10 ML of a 1.0% trisodium aqueous solution was added, while the solution was kept stirring gently and continuously during the process. After the mixture had boiled for 90 min, the heat source was removed and the solution was cooled naturally. The silver

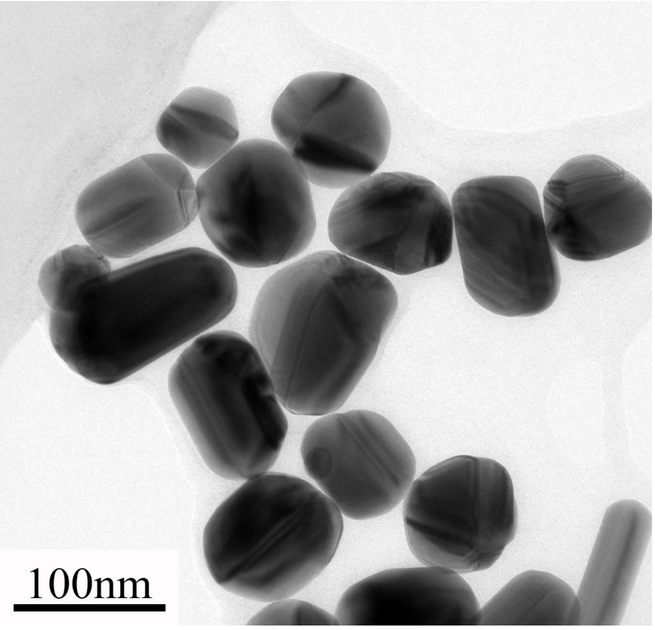

Figure 1. TEM micrograph of colloidal silver.

colloids were rinsed by centrifugation at 10000 rpm for 20 min and then were kept in dark at room temperate. The solution could be stable for several weeks.

The transmission electron microscopy (TEM) observation of silver nanoparticles was performed on a Hitachi model H-800 transmission electron microscope with an accelerating voltage of 200 kV. The samples were prepared by pipetting a drop of the silver colloids solution onto 230 mesh copper grids coated with carbon and allowing the sample to air-dry before measurement. Figure 1 shows a TEM photograph of the prepared silver colloid. The TEM photograph revealed that the diameter of spherical-like and club-shaped silver nanoparticles is in the range of 60–70 nm. A 10^{-2} mol/L PHBA aqueous solution was added to the silver colloid to obtain the sample for SERS measurements.

Raman and SERS spectra were recorded with a confocal Raman micro-spectrometer (Renishaw, Great Britain) in the range of 300–1800 cm^{-1}. The operating wavelength was 785 nm. Typically, the incident laser power was attenuated to 1–3mW. The spectra were collected in backscattering geometry using a microscope equipped with a Leica 20× objective with a spectral resolution of 2 cm^{-1}; the detection of Raman signal was carried out with a Peltier cooled charge-coupled device (CCD) camera. The software package WIRE 2.0 (Renishaw) was employed for spectral acquisition and analysis. The spectra were acquired with a 10 s integration time.

Calculations

The molecular geometry optimization and vibrational spectra calculations for the optimized equilibrium structures were performed with the Gaussian 03W software package (25) on the personal computer using DFT. The geometries were constructed by GaussView 5.0, which was also applied to observe the calculated Raman-active vibrational modes. DFT calculations were carried out with B3LYP (26) functional in combination with the 6-31+G**(C, H, O)/lanl2dz(Ag) basis sets. The basis sets (6-31+G** for the O, C and H atoms and lanl2dz for the Ag atom) have some advantages, particularly as regards basis set completeness (27). The computations were converged upon a true energy minimum, which was supported by the lack of imaginary frequencies. Satisfactory agreement between calculated and observed vibrational frequencies was obtained, without using any scaling factor. The assignment of the signals for the spectra is aided by the Gaussian view program, which gives a visual presentation of the vibrational modes. Therefore, the calculated wave numbers assignments were created with a high degree of confidence.

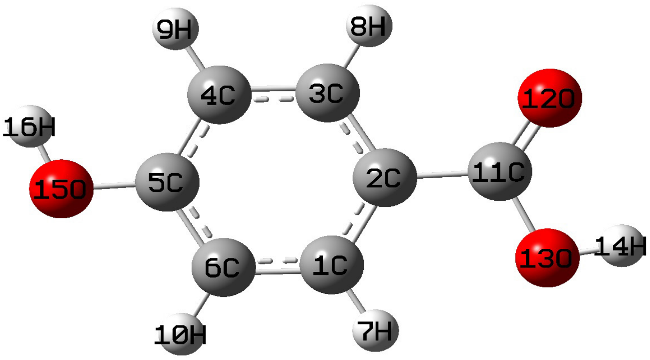

Figure 2. The optimized molecular structure of PHBA along with numbering of atoms.

Results and Discussion

The DFT optimized structure of PHBA molecule is presented in Figure 2 with numbering of the atoms.

The calculated (DFT) and the experimental normal Raman spectra of PHBA are shown in Figure 3(a) and (b), respectively. It was found that the calculated Raman frequencies were in good agreement with experimental values. We can see from Figure 3 that modes such as those at 504, 649, 694, 850, 1106, 1299 cm^{-1} were in good agreement with the experimental values. The results prove that our calculated model was reasonable.

For studying the enhancement mechanism of PHBA molecules adsorbed on the surfaces of silver nanoparticles, two models were established as can be seen Figure 4(a) and (b). The 'Mod A' shows that ionized PHBA molecules (deprotonation in solution) can adsorb on the silver atom in silver colloidal solutions, which indicates charge transfer enhancement mechanism. 'Mod B' shows the PHBA molecules neighboring silver atoms are enhanced, for which an electromagnetic field enhancement is expected. The calculated Raman spectrum based on 'Mod A', the calculated Raman spectrum

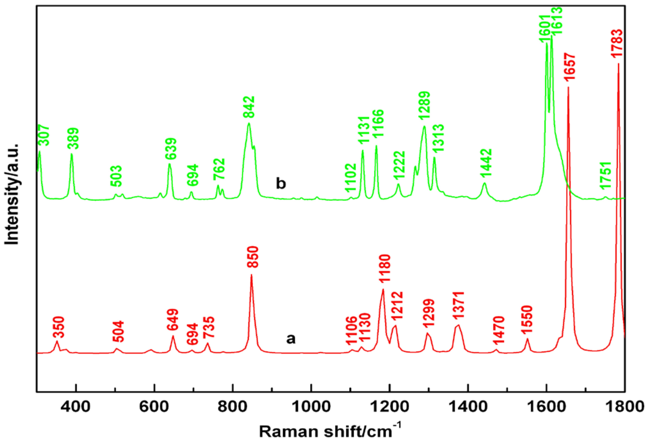

Figure 3. The calculated normal Raman spectra (a) and the experimental Raman spectra of PHBA solid powder (b).

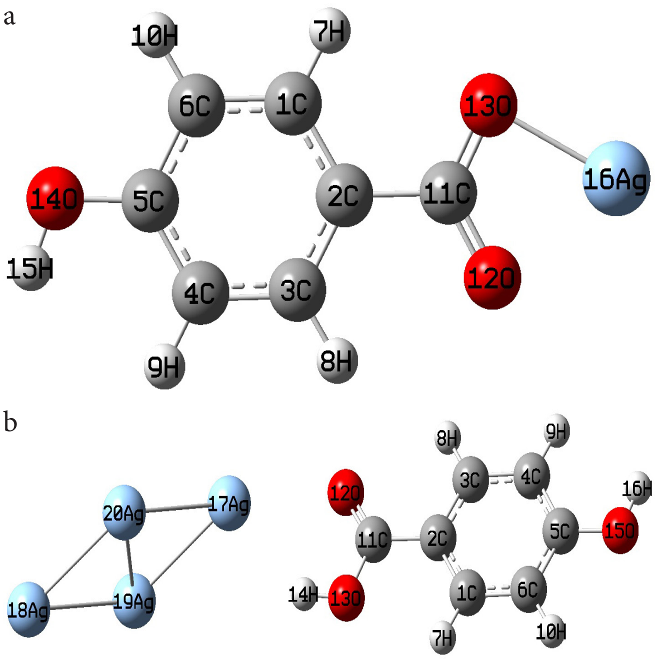

Figure 4. Two models of PHBA molecule on the surfaces of silver nanoparticles: (a) the 'Mod A' of charge transfer enhancement and (b) the 'Mod B' of electromagnetic enhancement effect.

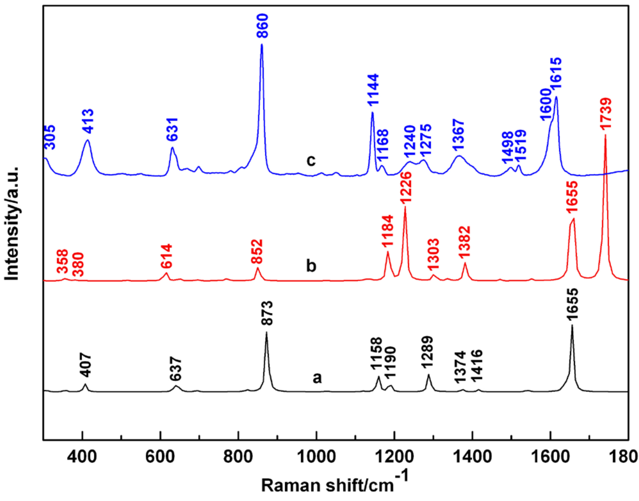

Figure 5. (a) The calculated SERS spectra based on 'Mod A', (b) the calculated SERS spectra based on 'Mod B', and (c) the experimental SERS spectra of PHBA adsorbed on silver colloids.

based on 'Mod B', and the experimental SERS spectrum of PHBA on the silver nanoparticles are shown in Figure 5(a), (b) and (c), respectively. Figure 5(b) and (c) are the original spectra, while Figure 5(a) is five times the original spectrum. Table 1 summarizes the positions and the intensities of the calculated and experimental Raman and SERS bands together with their vibrational assignments for PHBA.

The comparison of Figure 5(a) and (b) with (c), shows that the calculated SERS spectra based on 'Mod A' and 'Mod B' were in good agreement with the experimental SERS spectra of PHBA adsorbed on silver colloids, which indicates that both enhancing mechanisms (EM and CT enhancement) are present for PHBA adsorbed on colloidal silver. These PHBA molecules adsorbed on the silver atoms were enhanced mainly by CT mechanism. It was shown in 'Mod A'. And these PHBA molecules untouched silver atoms were enhanced by EM enhancement mechanism basically which was shown in 'Mod B'.

From Figure 3 and 5, a summary table with relevant modes has been created (Table 1). We can see that SERS spectra were enhanced with some bands up or down shifting, and some new ones appearing. In the SERS spectra of PHBA in silver colloidal solution, the 1612 cm^{-1} band and the 1600 cm^{-1} band, attributed to the C–C stretching mode of benzene, are enhanced greatly, showing that the interaction between benzene rings of PHBA molecules and the surfaces of silver nanoparticles is strong. The relatively weak enhancement of 1275 cm^{-1}, assigned to the C–OH stretching, indicates that the interaction between hydroxyl and the silver nanoparticles is relatively small. The appearance of the broad band at 1367 cm^{-1} assigned to the COO$^-$ symmetric stretching shows that PHBA molecules interact with the silver nanoparticles through the carboxyl group. Furthermore, the 860 cm^{-1} band assigned to the C–COO$^-$ stretching, which is very sharp, indicates that the C–CO$_2^-$ group is perpendicularly adsorbed onto the surface of the silver nanoparticles. According to the SERS selection rules (23), the great enhancement of the 1144 cm^{-1}, assigned to C–H in-plane bending and some in-plane ring vibration bands (1615, 1498, 860 cm^{-1}), also can support this conclusion. From the above discussion, PHBA molecules stand perpendicularly on the surfaces of the silver nanoparticles through their carboxyls in the silver colloidal solution, which is in accordance with that of Refs. (28,29). The assignments are made according to Refs. (15,29). The assignments of these vibrational modes can be also examined in the Gaussian view program.

Conclusions

We have obtained a high quality Surface-enhanced Raman scattering (SERS) spectrum of p-hydroxybenzoic acid (PHBA) in silver colloidal solutions. The Raman vibrational frequencies and SERS spectra of PHBA were calculated using DFT-B3LYP methods with 6-31+G**(C,H,O)/lanl2dz(Ag) basis sets of two models, and compared with the experimental spectra. It was found that calculated frequencies were in good agreement with experimental values, which testified that there were two enhancement mechanisms (EM and CT enhancement). Moreover, from the information obtained from high-quality SERS of PHBA in silver colloidal solutions, we could derive that PHBA molecules adsorb onto the surfaces of the silver nano-particles through carboxyl groups at a perpendicular orientation.

Acknowledgments

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Table 1. Raman and SERS bands of observed and calculated, Raman scattering activity and assignments for PHBA.

Raman		**SERS**			**Assignments**
		Cal			
Cal(Raman Intensity)	***Exp***	***Mod A (Raman Intensity)***	***Mod B (Raman Intensity)***	***Exp***	
	307ms			305w	C–H out-of-plane bending
350(4.65)			358(9.61)		Ring skeletal vibration
373(2.12)	389ms		380(3.06)		O–H out-of-plane bending
		407(11.5)		413mw	In-plane ring deformation
504(1.46)	503w	515(0.23)		504vw	Ring breathing
649(6.78)	639ms	637(11.3)	614(32.2)	631mw	C=O bending
694(1.33)	694w	692(2.47)		698vw	Ring out-of-plane bending
735(4.24)	762w				C–H bending
	842s	821(2.94)		809vw	Ring breathing
850(40.2)	854ms	873(109)	852(53.8)	860vs	C–COO^- stretching
1106(1.78)	1102w				C–H in-plane bending
1130(2.79)	1131ms	1158(28.7)		1144s	C–H in-plane bending
1180(43.7)	1166ms	1190(8.83)	1184(116)	1168w	C–H in-plane bending
1212(20.4)	1222mw		1226(283)	1240w	O–H in-plane bending
1299(15.1)	1289s	1289(35.0)	1303(31.4)	1275w	C–OH stretching
	1313ms				C–C stretching of benzene
1371(20.4)		1416(3.97)	1382(61.3)	1367w	COO^- symmetric stretching
1470(2.05)	1442mw			1498w	In-plane ring deformation
1550(7.07)		1538(1.57)		1519w	COO^- antisymmetric stretching
	1601s			1600s	C–C stretching of benzene
1657(136)	1613s	1655(131)	1655(500)	1615vs	C–C stretching of benzene
1783(138)	1751vw		1739(675)		C=O stretching

Note: w, weak; vw, very weak; mw, medium weak; s, strong; vs, very strong; ms, medium strong.

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