INSIGHT INTO ADSORPTION BEHAVIORS OF M-AMINOBENZOIC ACID ON DRIED SILVER-COATED FILTER PAPER
A Combined Experimental and Theoretical Exploration

by

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In this study, we present a comprehensive investigation into the surface-enhanced Raman scattering spectra of M-aminobenzoic acid adsorbed on silver nanoparticles on dried silver-coated filter paper. In order to gain in-depth insights into the adsorption behaviors of M-aminobenzoic acid, five distinct models were meticulously established. The Raman spectra of these models were calculated using the density functional theory - B3PW91 method with the LANL2DZ basis set. A comparison of the theoretical values with the experimental results revealed a remarkable degree of agreement. This finding serves to validate the rationality of employing a simplified model to depict the surface-enhanced Raman scattering phenomenon. The results indicate that on the dried silver-coated filter paper, M-aminobenzoic acid molecules predominantly adsorb onto the surfaces of silver particles via carboxyl and amidogen groups, with the benzene ring plane being vertical or nearly vertical to the silver particle surface. Indeed, a multitude of adsorption models coexist for M-aminobenzoic acid on silver nanoparticles, among which model c has a relatively higher probability of occurrence. This research offers valuable insights into the interaction mechanism between M-aminobenzoic acid and silver nanoparticles, providing a theoretical basis for related applications in surface-enhanced Raman scatterning-based detection and surface science.

Key words: *adsorption mode, M-aminobenzoic acid, density functional theory, surface-enhanced Raman scatterning, silver nanoparticles*

Introduction

Surface-enhanced Raman scattering (SERS) is a highly sensitive and powerful analytical technique. The device utilizes substrates composed of silver, gold, or other noble metals, and has found extensive applications in diverse fields [1-3]. The unique properties of these noble metal substrates can be leveraged to enhance the Raman scattering signals of adsorbed molecules by a significant margin. This enhancement has two primary functions. First, it enables the detection of trace-level substances. Second, it provides in-depth information about the adsorption behavior of molecules on substrates. For instance, it can precisely reveal

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the orientation of molecules and the underlying mechanisms of interactions between molecules and substrate surfaces [1-3].

The SERS is widely regarded as a versatile surface analysis technology. It offers the fingerprint vibration spectra of molecules, which act as unique identifiers for chemical substances. These spectra can be used to accurately identify and analyze the components of complex mixtures. Furthermore, SERS has been demonstrated to facilitate the elucidation of molecular interactions with substrates, a process that is imperative for comprehending surface-related chemical processes [4, 5]. In the domain of security, SERS based substrates have facilitated the detection of gas-phase VX and HD by hand-held Raman spectrometers, thereby serving a pivotal function in the context of chemical warfare and environmental safety monitoring [6]. In the food industry, SERS has emerged as a powerful tool for detecting trace elements in food, ensuring food safety and quality control [7, 8].

The adsorption behavior of molecules on substrate surfaces is a complex phenomenon that is primarily determined by two key factors. The initial factor is the surface characteristics of the SERS-active substrates, including surface roughness, morphology, and the nature of the metal atoms. It has been demonstrated that these properties can exert a significant influence on the strength and mode of molecule-substrate interactions. The second factor is the surface configuration of the adsorbed molecules themselves. This phenomenon is further compounded by the observation that even allotropes composed of the same elements but with different configurations exhibit significant variations in their adsorption behaviors on a given substrate [9, 10].

It is imperative to acknowledge that experimental studies, in isolation, are inadequate for comprehending the intricacies of molecular adsorption behavior on substrates. While experiments can provide direct observations and data, they often face challenges in precisely determining the detailed interaction mechanisms and molecular orientations. Consequently, it is highly advantageous to integrate experimental studies with theoretical models. Theoretical calculations can offer insights into the electronic structures and energy changes during adsorption, thereby providing a more comprehensive understanding of the adsorption process.

Density functional theory (DFT) based calculations have found wide applications in various scientific fields [11, 12]. When calculating the vibration frequencies of molecules, DFT based methods have demonstrated excellent agreement with experimental results. This renders them a reliable approach for studying the adsorption behavior of molecules on substrates.

Previous studies have employed experimental and theoretical methods to investigate the adsorption modes of p-hydroxybenzoic acid (PHBA) in silver colloidal solution [13]. Subsequent studies were conducted on m-hydroxybenzoic acid (MHBA) and P-aminobenzoic acid (PABA) in silver colloidal solution [14, 15]. However, the adsorption behavior of M-aminobenzoic acid (MABA) on dried silver-coated filter paper remains relatively unexplored.

The objective of this paper is to address the existing research gap by presenting high-quality Raman spectra of MABA on dried silver-coated filter paper under infrared excitation. In order to achieve a more profound comprehension of the adsorption modes of MABA, five models have been established. The Raman frequencies of these models are calculated using DFT with the B3PW91 functional and LANL2DZ basis sets [16]. A comparison of the theoretical results with the experimental values is conducted to assess the reliability of the models and the calculation methods. It is hypothesized that this research will contribute to a more profound understanding of the adsorption behavior of MABA on silver-coated filter

paper. This enhanced understanding may have implications for improving SERS based detection techniques and for furthering the understanding of the fundamental principles of molecule-substrate interactions.

Experimental section

The preparation of silver colloid is carried out in accordance with the method established by Lee and Meisel [17]. A quantity of 90 mg of silver nitrate is dissolved in 500 mL of deionized water. Following the heating of the solution to its boiling point, a 1% trisodium citrate aqueous solution of 10 mL is introduced into the solution in a dropwise manner, accompanied by vigorous stirring. The mixture is then subjected to a boiling process for approximately 10 minutes. Subsequently, a green-gray silver colloidal solution is obtained, which demonstrates stability for a period of several weeks.

The procedure entails the addition of 1 mL of silver colloidal solution to double layers of quantitative and slow-speed filter papers, which are then allowed to dry for approximately 10 minutes. These procedures are repeated to obtain a series of filter papers with different coverage density of silver nanoparticles. Subsequently, 1 mL of MABA aqueous solution is added to the silver-coated filter papers. This results in the acquisition of a series of dried samples for SERS measurement, whose proportions between silver nanoparticles and MABA molecules differ.

The RFS 100/s Brukernear-infrared Fourier transform spectrophotometer is employed to obtain the Raman spectra. The operating wavelength of the spectrophotometer is 1064 nanometers, and the resolution is 3 Å. The laser output power that is incapable of inducing a change in the adsorbate-substrate system is 200 mW.

Theoretical calculations and models

The construction of five models is predicated on the interaction between MABA molecules and silver nanoparticles on silver-coated filter paper, as evidenced by the following observations. The MABA molecule has been observed to interact with one silver atom through the carboxyl group. A similar interaction has been observed between the MABA molecule and one silver atom through the amidogen group. Furthermore, the MABA molecule has been shown to interact with two silver atoms through the carboxyl and amidogen groups. In addition, the MABA molecule has been observed to interact with two silver atoms through the carboxyl group. Finally, the MABA molecule has been observed to interact with three silver atoms through the carboxyl and amidogen groups in a parallel orientation. As illustrated in fig. 1, the models are presented.

Obtaining Raman spectra for a significant number of atoms in the interaction of MABA molecules with silver nanoparticles is a formidable task. Given the substantial mass of an Ag atom, it is reasonable to hypothesize that a model comprising some Ag atoms, rather than the entirety of silver nanoparticles, could serve as the *substrate*. The DFT-B3PW91 with lanl2dz is employed to calculate the Raman frequencies of five models. The findings indicate that the calculated Raman frequencies align with the experimental values.

Results and discussion

As demonstrated in fig. 2, the graphs at 675 cm^{-1} and 1120 cm^{-1} exhibit a high degree of congruence with the experimental values. At 796 cm^{-1}, the fig. 2(b) demonstrate a strong correlation with the experimental values. Figure 2(c) are in accordance with the experimental values at 428 cm^{-1}, 675 cm^{-1}, 1120 cm^{-1}, and between 1166 cm^{-1} and 1590 cm^{-1}.

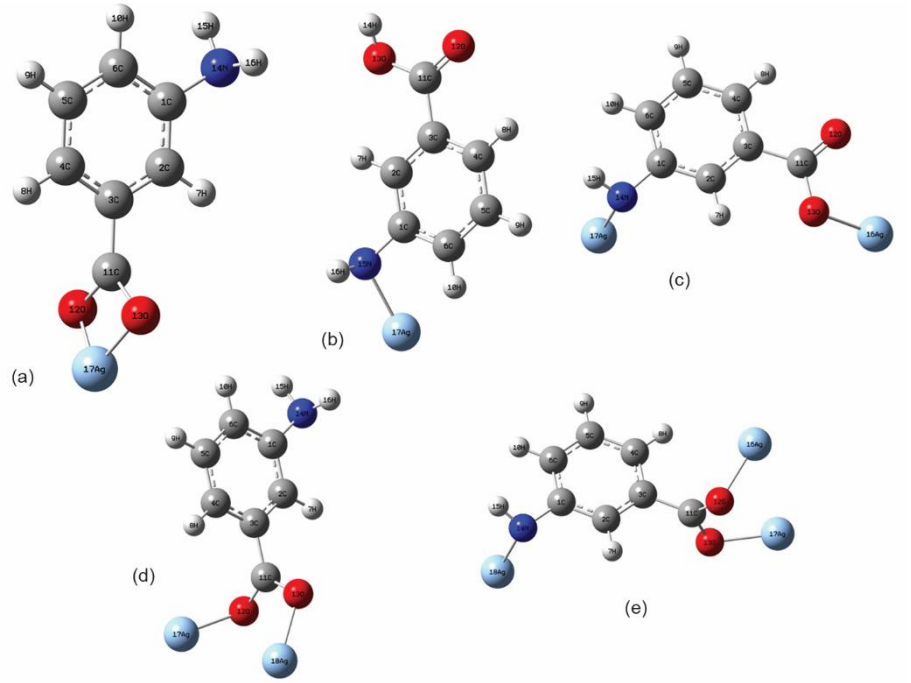

Figure 1. Adsorption models of MABA molecule on Ag atoms; (a) the MABA molecule is adsorbed on one Ag atom on the surface of the silver nanoparticle through the carboxyl group; (b) the MABA molecule is adsorbed on one Ag atom on the surface of the silver nanoparticle through the amidogen group; (c) the MABA molecule is adsorbed on two Ag atoms on the surface of the silver nanoparticle through the carboxyl and amidogen groups; (d) the MABA molecule is adsorbed on two Ag atoms on the surface of the silver nanoparticle through the carboxyl group, and (e) the MABA molecule is adsorbed on three Ag atoms on the surface of the silver nanoparticle through the carboxyl and amidogen groups in a parallel orientation

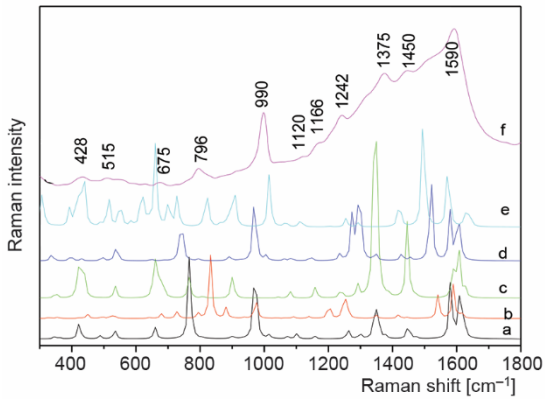

Figure 2. Calculated Raman spectra based on (a) model a, (b) model b, (c) model c, (d) model d, (e) model e, and (f) experimental spectra of MABA on the silver-coated filter paper

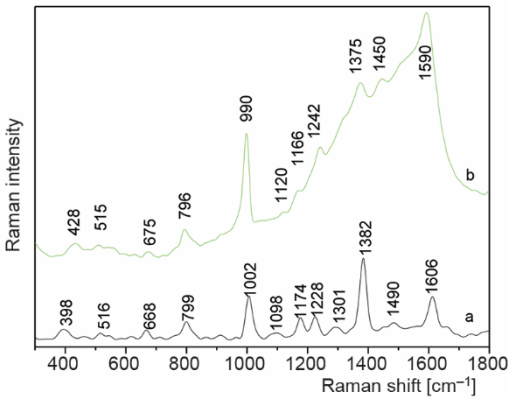

Figure 3. Comparison of SERS Spectra of solid MABA and MABA on silver-coated filter paper; (a) below: SERS spectra of solid MABA and (b) above: SERS spectra of MABA on the silver-coated filter paper

Figure 2(d), with wavenumbers of 990 cm^{-1} and 1120 cm^{-1}, demonstrate a strong correlation with the experimental values. Figure 2(e) demonstrate a high degree of congruence with the experimental values, with a concurrence of 428 cm^{-1}, 515 cm^{-1}, 675 cm^{-1}, 796 cm^{-1}, and 990 cm^{-1}. As demonstrated in the preceding analysis, fig. 3(c) demonstrates a high degree of concordance with the experimental values.

As illustrated in tab. 1, the wavenumber of Raman bands on the silver-coated filter paper is documented, along with the band assignments for MABA. The assignments are acquired by comparing SERS spectra of MABA on the silver-coated filter paper and referencing [18, 19]. In order to further analyze the results, please refer to figs. 3(a) and 3(b). The presence of a peak at 1375 cm^{-1}, which is attributed to the stretching vibration of carbon dioxide (CO_2^-), suggests a direct interaction between the carboxyl group of MABA and the surfaces of silver nanoparticles. However, the presence of the βs, CO_2, band at approximately 852 cm^{-1} is not observed, indicating that the C-COO surface is likely not perpendicular to the surfaces of the silver nanoparticle. The appearance of a peak at 1590 cm^{-1}, which is attributed to the symmetric stretching mode of the benzene ring [ν(CC)], suggests that the benzene ring is in close proximity to the silver base surface. The significant enhancement of benzene ring breathing vibration at 990 cm^{-1} indicates that the benzene ring plane is still perpendicular to the silver surface. The weaker wide peak near 515 cm^{-1} corresponds to the region of γs, NH_2, vibration. The presence of a wide peak suggests that the amidogen group is likely to adsorb on the silver surface through the lone pair electrons on nitrogen atoms. According to the SERS selection rule [20, 21], the MABA molecule on the silver-coated filter paper may adsorb on the surfaces of silver particles through the carboxyl and amidogen groups. The plane of the benzene ring is vertical or nearly vertical to the surface of the silver particles. The attribution of these vibration modes can also be detected by Gaussian view. In accordance with the aforementioned analysis, it is posited that model C is the most reasonable.

Table 1. Wavenumber and band assignments of MABA Raman and SERS bands [18, 19]

In aqueous colloid [cm^{-1}]	Band assignment
1590	υ(CC)
1442	υ(CC)
1375	$\upsilon_s(CO_2^-)$
1242	υ(CC)
1166	β(C-H)
990	Ring breathing
796	Symmetric ring breathing
672	Ring out-of-plane skeletal vibration
515	$\gamma_s(NH_2)$
428	Ring in-plane breathing

To further elucidate the issue, please refer to tab. 2. The aforementioned results are observed with the exception of 990 cm^{-1} and 1120 cm^{-1}. The discrepancy between the other values and the experimental values is less than 30 cm^{-1}. The mean relative deviation (MRD) is 1.67%, indicating that the theoretical values are in good agreement with the experimental values. The result aligns with our expectations, thereby substantiating the rationality of model C.

Table 2. Comparison of experimental values with calculated Raman frequencies of MABA based on model C using DFT-B3PW91

Experimental [cm^{-1}]	Theoretical [cm^{-1}]	$\triangle V$ [cm^{-1}]	Relative deviation [%]	MRD [%]
428	427	1	0.23	1.67
515	535	–20	3.88	
675	660	15	2.22	
796	796	0	0	
990	1035	–45	4.54	
1120	1080	40	3.57	
1166	1161	5	0.43	
1242	1236	6	0.48	
1375	1350	25	1.82	
1450	1447	3	0.21	
1590	1606	–16	1.01	

Conclusions

In summary, our experimental and theoretical study on the adsorption behavior of MABA molecules on silver nanoparticles of the dried silver-coated filter paper has revealed a complex yet systematic picture. The adsorption of MABA on silver nanoparticles does not conform to a single model; instead, multiple models coexist. Each model has a certain probability of existence, and through comprehensive analysis of experimental Raman spectra and theoretical calculations, we find that mode c is the most representative, and the geometrical potential theory [22, 23] is another promising tool to explanation of the absorption behavior

In mode C, the MABA molecule engages in interaction with two silver atoms through the carboxyl and amidogen groups. This mode demonstrates a remarkable congruence with experimental values across a substantial range of wavenumbers, including 428 cm^{-1}, 675 cm^{-1}, 1120 cm^{-1}, and the region of 1166 cm^{-1} to 1590 cm^{-1}. The MRD between the experimental and theoretical values for model C is a mere 1.67%, suggesting a high degree of consistency.

This predominant adsorption mode suggests that the carboxyl and amidogen groups of MABA play crucial roles in the adsorption process on the silver-coated filter paper. The benzene ring of MABA is oriented either vertically or nearly vertically with respect to the surface of the silver particles. This conclusion is supported by the appearance and enhancement of specific Raman peaks, including the peak at 1590 cm^{-1}, which is assigned to the ν(CC) mode. This finding indicates the proximity of the benzene ring to the silver base surface. Additionally, a significant enhancement of the benzene ring breathing vibration is observed at 990 cm^{-1}.

The present findings contribute to a fundamental understanding of the adsorption mechanism of MABA on silver-coated substrates. Moreover, these findings have potential implications for practical applications. For instance, in the development of SERS based sensors, a comprehensive understanding of the adsorption behavior of MABA is imperative. This understanding facilitates the optimization of substrate design, thereby enhancing the sensitivi-

ty and selectivity of sensors in detecting MABA like molecules. In subsequent research, it would be worthwhile to investigate how factors such as temperature, pH, and the presence of other co-adsorbed molecules influence the adsorption behavior of MABA on silver nanoparticles. Furthermore, extending the present study to include diverse types of silver-based substrates or other noble-metal substrates has the potential to further expand our knowledge of molecule-substrate interactions.

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