

## The mechanism research for the surface plasmon-catalysed reaction of the mercapto group substituted benzoic acid.

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**Abstract.** In this study, we experimentally investigated the substituent effect on benzoic acid where the mercapto group was located in different positions, namely as 2-mercaptobenzoic acid (2-MBA), 3-mercaptobenzoic acid (3-MBA) and 4-mercaptobenzoic acid (4-MBA). The substituent effect was found to have an influence on the surface plasmon-catalysed reaction on the surface of the Ag<sub>4</sub> atoms in the reaction of MBA with silver sol. In addition to the direct evidence from the surface-enhanced Raman scattering (SERS), the chemical enhancement mechanism for the generation of the MBA–Ag complex is presented. In contrast with the normal Raman scattering (NRS) spectra, new signals appeared in the SERS spectra of 2-MBA, 3-MBA and 4-MBA under the theoretical and experimental conditions. On investigation of the SERS spectra, the characteristic peaks of the C≡C bond have been demonstrated. The structural, atomic and chemical bond properties of the three types of MBAs indicate that the S atom of the mercapto group in the MBA molecules is the position site that attaches to the silver substrate through the bond of S···Ag, and under laser irradiation, “hot electrons” are generated between the surface of MBA and Ag<sub>4</sub> atoms. With the effect of “hot electrons”, the –COOH bond of the MBA molecules is broken, and then the two single carboxylate MBA molecules become dimerized thiophenol acetylene (TPA). To briefly consider the substituent effect, the SERS spectra of these three types of MBAs were specifically studied for the enhancement of the Raman signal intensity with a variational tendency evident. Therefore, the conclusion was reached that the substituent effect plays a vital role in the surface plasmon-catalysed reaction, where the changing of the surface-enhanced Raman intensity was demonstrated.

**Key words:** Surface plasmon-catalysed reaction, MBA, thiophenol acetylene (TPA), normal Raman scattering (NRS) spectra, surface-enhanced Raman scattering (SERS) spectra, hot electron, substituent effect.

### 1. Introduction

In addition to identifying types of material, Raman spectroscopy is mainly used to measure molecular vibration frequencies and quantitatively analyse the phenomena of intermolecular and intramolecular forces [1,2]. Thus, molecular symmetry, geometric structure formation and how atoms are arranged in molecules can be inferred using Raman spectroscopy. Since 1974, scientists have found that surface-enhanced Raman scattering (SERS) technology [3–5] (based on its high sensitivity, little interference by water, formal research of interface effect, and so on) has played a powerful role in interface features and ultrathin membrane material research; it has thrived both in theory and experiment due to its extensive applications in fingerprint detection, even at the single molecule level [6–9]. SERS is the most extensive spatial location technique involving the adsorption process at solid or liquid interfaces because of its simplicity and ability to recognize the material structures rapidly, along with its ability

to detect different types of supramolecular architectures as well as its ability to investigate distinct functional group adsorption phenomena [10–12]. As a potentially comprehensive application, many investigations have been presented on the mechanism of SERS [13,14].

The self-assembled monolayer, with organic small molecules that contain the mercapto group on the surface of the metal film, has been widely used in embellishing electrodes, biological sensors and other research fields [15–17]. Furthermore, thiol molecules along with some other molecules with specific functional groups were usually regarded as the superior substance for SERS recognition, as the formation of Au-MBA@SiO<sub>2</sub> nanoparticles was achieved on the basis of Stöber's method by the hydrolysis of TEOS. The thiol compounds with containing aromatic rings are noteworthy, especially in recent years [6].

Miriam C. Rodríguez González et al. conducted STM that the Au(111) surface after 2-MBA adsorption shows atomically smooth terraces separated by steps of monatomic height, without any evidence of vacancy island formation, through the detection of 2-MBA and 4-MBA that adsorbed on the surface of Au(111), showing atomically smooth terraces separated by steps of monatomic height [18]. These compounds revealed the favourable adsorption on the noble metal nanoclusters with rigid structure stability, and the monolayer film also had

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excellent electrical conductivity [19–21], showing potential application in the design of molecule-conducting wire [22].

At first, in the process of vigorous study using SERS, we explored the material properties just through its signal increasing by the adsorption between the substance and the metal surface, and then we explored an intensive chemical reaction arising spontaneously based on the SERS mechanism. Thus, in this study we used SERS as a starting point, and discuss the surface plasmon-catalysed reaction occurring for three types of MBA that adsorbed on the silver surface.

Surface plasmons (SPs) are collective electron oscillations confined evanescently along the interface between a conductor and a dielectric [23,24]. It is often assumed that the material adsorbed on the silver surface, and the silver atoms exist under this relationship. It is well known that the electrons on the surface of a metal can absorb a certain energy of an electric field (such as photons, etc.), then they would be excited, and these electrons are called “hot electrons” in the excited states [25–28]. Under the effects of surface plasmons and “hot electrons”, the surface plasmon-catalysed reaction would take place.

In physical chemistry, the substituent effect has tremendous significance in understanding and quantitatively analysing the performance activity relations of molecular structures [28]. In this article, we use the centrifuge to mixed mercaptobenzoic acid (2-MBA, 3-MBA and 4-MBA)  $10^{-5}$  mol/L sample solution and silver sol solution sufficiently to obtained the centrifugal sedimentation of the mixture. Herein, comparison of SERS signals of the MBAs indicated a changing tendency, with a remarkable discovery of the substituent effect playing a crucial role in the surface plasmon-catalysed reaction and demonstrated in detail.

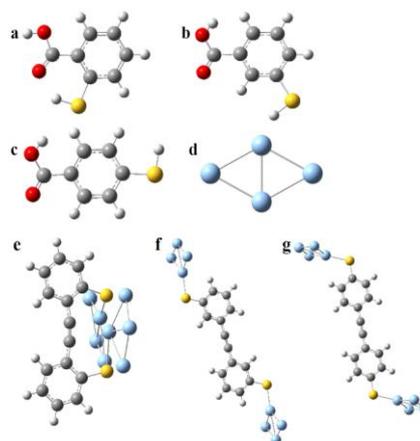
## 2. Experimental section

In order to measure SERS, the silver sol was prepared under high vacuum using a vacuum electron beam evaporator. Silver sol was generated by a silver nitrate and trisodium citrate reduction reaction. As follows, silver nitrate solution was heated until boiling, and then the silver nitrate solution was poured into trisodium citrate (10 mL). The mixture was heated for an hour with stirring, and then cooling the heated mixture. In our experiment the anhydrous ethanol was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. (China). The three types of MBA solid powder samples were 2-mercaptobenzoic acid (2-MBA), 3-mercaptobenzoic acid (3-MBA) and 4-mercaptobenzoic acid (4-MBA) that obtained from AR, Aladdin Reagent Co., Ltd. Then these MBA powder samples were mixed with anhydrous ethanol to gain solution that the concentrations of  $10^{-5}$  mol/L. Next, the solution of the 2-MBA was mixed in silver sol (with the proportion of 1 to 5) that add the silver sol of 5ml and 2-MBA solution of 1ml. Finally, the mixture was placed into the ultracentrifuge with centrifuging 8000 rad/min for 15 mins. After this process, the supernatant and sediment were separated. The sediment was placed on a washed, dust-free microslide and dried naturally. These preparation steps were followed for the two other MBA

samples. Then these dried sediment samples were exposed under the laser with the wavelength of 532 nm, the intensity of 0.1%. All the Raman spectra records were drawn by Renishaw in Via.

## 3. Theoretical methods

The ground-state geometry of 2-MBA, 3-MBA and 4-MBA were all optimized with density functional theory (DFT), using the B3PW91 functional, 6-31G(d) basis set for C, H, O and S atoms and the LANL2DZ basis set for Ag4 atoms (Figure 1). All models have almost little imaginary frequency on these optimizations. The normal Raman scattering (NRS) spectra calculations indicate the same features and infrastructure in the ground state geometry optimization. All calculations were performed use the Gaussian 09 package for optimization.



**Figure 1:** Optimized structures: a. 2-MBA, b. 3-MBA, c. 4-MBA, d. Ag4 atoms, e. Ag 2-MBA, f. Ag 3-MBA, g. Ag 4-MBA.

## 4. Results and discussion

First, the absorption spectra of 2-MBA, silver sol and 2-MBA in silver sol were experimentally measured in the range of 200–400 nm (see Figure 2). It can be seen from Figure 2 that the absorption peak at around 257 nm in the UV spectra is the absorption peak of 2-MBA itself (black line), and it seems to be similar to the peaks of the 2-MBA with silver sol solution (blue line) and the pure 2-MBA solution (black line) at around 200 nm, respectively. In Figure 2, the obvious peaks (shown in the black and blue lines) appear at around 225 nm and 250 nm for 2-MBA, but there are no similar peaks for the silver sol solution. This indicates that resonance oscillation was not taking place between these two species upon photoexcitation due to their different optical energy levels. Significantly, a weak absorption peak is found at around 203 nm and 205 nm (1.24 eV) for 2-MBA in silver sol (see the blue line in Figure 2). This suggests the formation of a new compound which is likely to be a 2-MBA with silver sol complex caused by the interactions between 2-MBA and silver.

Second, we compared the 2-MBA NRS spectra from the experiment and the calculations, the specific vibration