

Experimental Identification of Chemical Effects in Surface Enhanced Raman Scattering of 4-Aminothiophenol[†]

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We report on the experimental identification of Raman modes that are enhanced through the chemical effect in surface enhanced Raman spectroscopy of 4-aminothiophenol (also known as *p*-mercaptoaniline) adsorbed on gold substrate. Introduction of a thin spacer layer between the metal and the sample can prevent any possible chemical bonding between metal atoms and sample molecules, hence such a sample shows only those Raman modes that are enhanced through the electromagnetic effect. Alternatively, a significant increase in the chemical effect could be observed in the presence of halide ions as compared to their absence. This result provides another way to experimentally identify those Raman modes that undergo chemical enhancement. In addition, apart from the electromagnetic-based resonance in SERS, chemical enhancement also shows a resonance with varying wavelength of the excitation light, which provides yet another way to experimentally identify chemically enhanced Raman modes in SERS. Some new chemically enhanced modes could be observed when the sample molecules were sandwiched between gold substrate and a gold nanopip.

Introduction

Raman spectroscopy has always been a preferred technique for the optical characterization of physical, chemical, and electronic properties of a sample, because this method is based on a nondestructive technique that can deal simultaneously with the electronic and vibrational energies of the sample, fetching rich information related to the intrinsic properties of the sample. However, since the optical efficiency of this technique is extremely low, it becomes difficult to study nanosized samples which usually have very small scattering volumes, because Raman scattered signals from such samples are too weak for practical observation. The discovery of surface enhanced Raman scattering (SERS)¹ in 1974 came with a breakthrough where researchers showed that when a small volume of Raman active molecules are deposited on an electrochemically roughened metallic surface a huge enhancement in Raman scattering could be observed. Ever since then, SERS has attracted tremendous interest,^{2–10} because it has proved handy for several interesting and important applications in molecular identification, sensors, nanosciences, and biosciences. An excellent early review on this subject was published by Moskovits in 1985.¹¹ In the later years, it was also shown that even a single molecule could be measured through SERS,^{12,13} which implied that an overall enhancement of as high as 10^{14} was possible in SERS.

The current understanding of signal enhancement in SERS is that there are two separate mechanisms responsible for the enhancement of Raman scattering, namely the electromagnetic (EM) effect and the chemical (CM) or the charge-transfer effect.^{14,15} The EM effect is based on the excitation of localized surface plasmon polaritons (SPPs) of the roughened metallic

surface. Since the roughness of the surface essentially creates metallic nanoparticles on the surface, the SPPs could be localized and hence could be excited with a propagating light to result in the enhancement of the light field in the close vicinity of the surface.¹⁶ In fact, after the first demonstration of SERS on an electrochemically roughened metallic surface, there has been an extensive amount of research on optimizing the rough surface by utilizing metallic colloids or dispersed metallic nanoparticles.^{17–20} The spatial extent of this enhanced field on the roughened surface is typically on the order of a few tens of nanometers. If two or more metallic nanoparticles on the surface are close enough, the enhanced light fields associated with them could overlap and interact together to result in huge enhancement of the light field at the space between the nanoparticles.^{21–23} Such spots on the metallic surface are usually referred to as the hot spots, and if a sample molecule migrates into one of these hot spots, Raman scattered light could be enhanced to the extent that even a single molecule detection becomes possible through SERS.

While the EM effect can extend up to a few tens of nanometers, the CM effect is extremely localized in nature. When sample molecules come very close to the metal atoms, typically at molecular distances, the sample molecules may get adsorbed on the metal and make chemical bondings with metal atoms. This usually happens with a transfer of charge from the metal to the sample molecule. This chemical bonding on one hand restricts the natural vibration of free molecules resulting in a modified vibrational frequency of the adsorbed molecules, and on the other hand, the charge transfer results in resonance effects, enhancing the overall Raman scattering from the adsorbed molecules. In fact, the charge transfer serves as the intermediate stage of the resonance Raman process in the CM effect.⁹ Thus, the CM effect adds up in enhancement and results in shifts of the vibrational frequencies. The enhancement through the CM effect is generally lower in comparison with the

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enhancement through the EM effect; however, they usually exist together to form the SERS spectrum.

Even though the basic mechanism is well understood, the CM effect is less explored in SERS than the EM effect. One of the reasons is that the CM effect is weaker than the EM effect and that it is usually difficult to separate out these two coexisting effects in a SERS spectrum. Within a given SERS spectrum, usually there are several Raman modes that are enhanced only through the EM mechanism, some modes are enhanced only through the CM mechanism, while there are some modes which are enhanced through both mechanisms together. In this article, we demonstrate the identification of those modes which are enhanced through different mechanisms, separating out the chemically enhanced modes from the electromagnetically enhanced modes in SERS of 4-aminothiophenol (4-ATP), which is also known as *p*-mercaptoaniline (*p*-MA). While it is practically impossible to block the EM effect in SERS, it is possible to do so with the CM effect, because the CM effect originates from adsorption or the physical/chemical contact between the metal atoms and the sample molecules. A very thin spacer layer between the sample and the metallic surface could block the CM effect completely, while the EM effect could still exist through this thin spacer layer. Thus, by utilizing a spacer layer, it could be possible to identify those modes which are enhanced only through the CM effect. Another way to separate out the two effects is to selectively further enhance one of them. Again, it is possible to do so with CM effect by including halide ions in the sample. It has been recently demonstrated that chemical bonding between metal and sample can be increased in the presence of halide ions.^{24–27} Further, since the enhancement mechanism of the CM effect is based on the resonance Raman scattering, it can show a dependence on the wavelength of the excitation light. Indeed, we demonstrate in our experiments that as the excitation wavelength is scanned the CM enhancement passes through a resonance peak. This selective resonance of chemically enhanced modes can clearly differentiate between the two mechanisms behind the enhancement process in SERS. In addition, we also demonstrate that, when sample molecules are sandwiched between gold substrate and the apex of a gold nanotip, some new chemically enhanced modes show up in the SERS spectrum.

Experimental Section

The sample for normal Raman scattering experiments was the bulk 4-ATP material, prepared by dropping and drying 1 mM ethanol solution of 4-ATP molecules on a cover glass slip. This sample served as a bulk for sample reference measurements. The 4-ATP sample used in present study was purchased from Aldrich Chemical Co., which was used without further treatment or purification.

The substrate for SERS measurement was prepared by evaporating gold metal on a cover glass slip under high vacuum. The evaporation conditions were carefully controlled so that a thin layer of gold with an average thickness of 8 nm and an average surface roughness of about 1 nm was deposited on the cover glass slip. A small amount of 1 mM ethanol solution of 4-ATP was adsorbed onto the evaporated metallic surfaces by immersing the substrate into the solution for a few hours, which led to the formation of a self-assembled-monolayer (SAM) of 4-ATP on the substrate. The excess 4-ATP molecules were removed from SAM by carefully washing the adsorbed metal surfaces with pure ethanol. While most experiments discussed in this article were performed on gold substrate, some experiments were also performed on silver substrate. The average

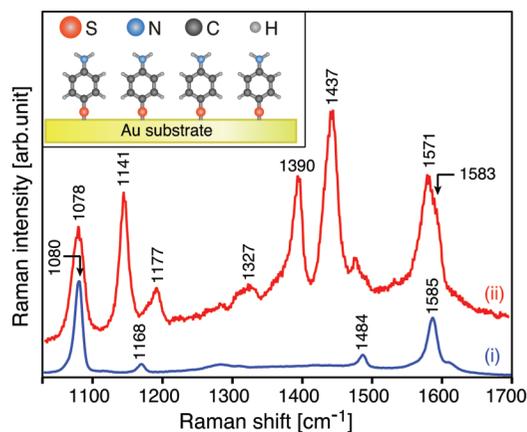


Figure 1. (i) Raman spectrum of 4-ATP measured with 532 nm excitation wavelength and (ii) SERS spectrum of 4-ATP adsorbed on 8-nm-thick Au substrate measured with 633 nm excitation wavelength. Inset shows a schematic of 4-ATP SAM on gold substrate where S atoms are attached to the gold atoms.

thickness and surface roughness of the silver substrate were the same as those of the gold substrate.

In order to prevent the chemical adsorption of 4-ATP molecules on the metal surface for some of the experiments, a thin spacer layer was deposited on the metal surface before depositing the 4-ATP molecules. This spacer layer was formed by immersing the metal-coated substrate into a 1% ethanol solution of polyvinylpyridine (PVP) for about 8 h. Since PVP does not have any observable Raman mode in the spectral region of 1000–1600 cm^{-1} , it was a good choice as a Raman-inactive spacer. The average thickness of the spacer layer could be controlled by the solution concentration and immersion time and could be measured by ellipsometry. In the present case, the average spacer thickness was around 4 nm. Also, we found through AFM imaging that the PVP layer contains some holes, however, with reasonably low density. The average distance between such holes was several micrometers; hence, it was always possible to select a surface area avoiding the holes. After drying the substrate, 4-ATP molecules were deposited on the PVP-coated metallic substrate.

All Raman measurements were performed under usual confocal backscattering geometry. Most experiments were performed utilizing the 633 nm laser line, however, in some experiments, various other wavelengths were also used. The excitation light was focused on the sample through a high-NA objective lens, and the scattered signal was collected back through the same objective, which was then dispersed through a polychromator and Raman spectra were recorded by a cooled CCD detector.

Results and Discussion

Identification of Chemically Enhanced Modes. A typical far-field Raman spectrum measured from bulk 4-ATP sample excited with 532 nm laser line and measured in the spectral range of 1000–1700 cm^{-1} is shown as spectrum (i) in Figure 1. As one can see, there are two prominent peaks at 1080 and 1585 cm^{-1} , which could be assigned to the C–S stretching and C–C stretching modes, respectively. Spectrum (i) in Figure 1 also shows two comparatively weak peaks at 1168 and 1484 cm^{-1} , which could be assigned to pure C–H bending and a combination of C–C stretching and C–H bending, respectively. All these peaks are associated with the characteristic vibrational modes of 4-ATP, as summarized in Table 1.^{15,28,29} Spectrum (ii) in Figure 1, on the other hand, shows SERS spectrum excited

TABLE 1: Peak Positions (in cm^{-1}) for 4-ATP in Normal Raman and 4-ATP SAM on Au Film from Figure 1 and Their Assignments^{15,28,29a}

normal Raman	SERS on Au	assignments
1585	1583	νCC , 8a (a_1)
	1572	νCC , 8b (b_2)
1484		$\nu\text{CC} + \delta\text{CH}$, 19a (a_1)
	1438	$\nu\text{CC} + \delta\text{CH}$, 19b (b_2)
	1390	$\nu\text{CC} + \delta\text{CH}$, 3 (b_2)
	1327	
1168	1177	δCH , 9a (a_1)
	1141	δCH , 9b (b_2)
1080	1078	νCS , 7a (a_1)

^a The notations ν and δ indicate stretching and bending modes, respectively.

with 633 nm laser line from 4-ATP SAM adsorbed on Au substrate, where one can notice several prominent peaks. The two prominent modes appearing at 1080 and 1585 cm^{-1} in spectrum (i) can also be found in spectrum (ii). There is a slight shift in the frequency positions of these modes, however within the limits of experimental errors. The weak mode originally observed at 1168 cm^{-1} is shifted to 1177 cm^{-1} in spectrum (ii). The other weak mode observed at 1485 cm^{-1} in spectrum (i) cannot be seen clearly in spectrum (ii) anymore, indicating that this mode might have been buried under the luminescence background originating from the Au substrate. In addition, there are several new peaks found in spectrum (ii), which appear due to the enhancement in SERS. These new peaks can also be assigned to various vibrational modes of 4-ATP; however, they are too weak in spectrum (i) to be observed without any enhancements. Here, it should be noted that spectra (i) and (ii) are measured with different excitation wavelengths. The reason is that normal Raman scattering from the present 4-ATP sample, when excited with 633 nm laser line, is extremely weak, and hence, one could add no information by presenting that spectrum here. We therefore chose the Raman spectrum excited with 532 nm laser line to show how the relative intensities of various Raman modes in normal Raman spectrum of 4-ATP look like. However, by taking care of all the experimental conditions, it is possible to calculate the enhancement factor in spectrum (ii), which is estimated to be about 6.0×10^3 .

In order to experimentally confirm the nature of enhancement in Figure 1, another sample was prepared, which was exactly the same as the one used in Figure 1, except that there was a thin PVP layer between the Au layer and 4-ATP molecules. In this sample, any possibility of chemical bonding between Au atoms and 4-ATP molecules was completely eliminated and hence enhancement through the CM effect is not expected. The enhancement through EM mechanism still persists, however, it is expected to reduce slightly due to the increased distance between the Au atoms and 4-ATP molecules caused by the presence of the spacer layer. The black curve in Figure 2 shows SERS spectrum for the new sample with PVP spacer layer. For a comparison, SERS spectrum from Figure 1 is also included as the red curve. In order to compensate the slight decrease in EM enhancement due to the introduction of the PVP layer, the two spectra are normalized for the mode at 1078 cm^{-1} . As it can be seen from Figure 2, some of the modes remain unchanged, while others decrease significantly by the introduction of PVP spacer layer. The modes which remain almost unchanged by the introduction of PVP spacer layer are dominantly enhanced through the EM effect, and the modes which are drastically decreased with the introduction of PVP spacer layer are dominantly enhanced through the CM effect.

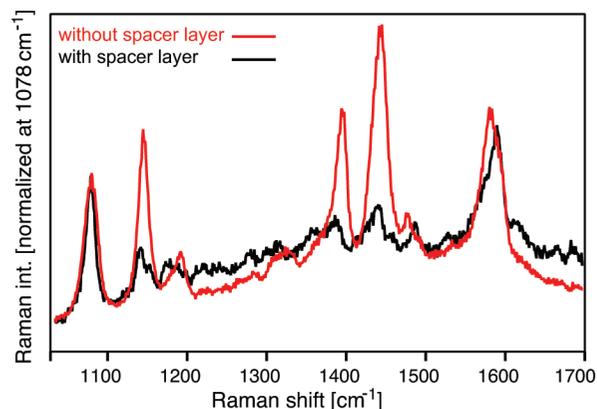


Figure 2. SERS spectra of 4-ATP adsorbed on Au film (red) and deposited on PVP spacer layer over Au film (black), excited with 633 nm laser line. The thickness of PVP layer is estimated to be around 4 nm.

The structure around 1580 cm^{-1} is formed by two modes, as indicated in Figure 1. One of them is dominantly enhanced through the CM effect, and hence, its intensity is reduced in the sample that contains spacer, whereas the other mode which is enhanced through the EM effect remains almost unchanged. The modes enhanced through the EM effect are the so-called a_1 -type vibrational modes, whereas the modes enhanced through the CM effect are the b_2 -type vibrational modes. One can notice that the b_2 -type modes are still observed in the black spectrum, albeit with extremely weak intensities. This is because, even though the prominent mechanism for the enhancement for these modes is CM effect, they also have slight contribution through the EM effect.

The introduction of a spacer layer between the metal and the sample provides a practical way to distinguish between the modes that are dominantly enhanced by either EM or CM mechanism. Another evidence of chemical enhancement could be found by the introduction of halide ions in the sample, which are supposed to increase the number of chemical bondings between metal atoms and sample molecules. There have been several recent reports on SERS as well as surface-enhanced hyper Raman scattering, where introduction of halide ions increased the overall enhancement.^{24–27} The authors argued that the additional enhancement with the introduction of halide ions was due to the increase in the enhancement through the CM effect. Which means it should be possible to identify the Raman modes that are dominantly enhanced through the CM effect by introducing some halide ions and then observing the mode that are further enhanced. For this purpose, we prepared a sample which was identical to the one used in spectrum (ii) of Figure 1, except that the sample was also immersed into diluted NaBr solution for a short time. It was observed that the intensities of all b_2 -type modes increased with the introduction of NaBr solution, while the intensities of the a_1 -type modes remained unchanged. As an example, the intensity ratio between the modes at 1141 cm^{-1} (enhanced through CM effect) and at 1078 cm^{-1} (enhanced through EM effect) are plotted in Figure 3. The experimental data points in green are taken from Figure 1, which corresponds to the usual SERS on Au surface. The data for the sample with PVP spacer layer are shown by blue colors, where one can see the decrease of intensity ratio, confirming that the CM effect is drastically reduced. On the other hand, the data points in red correspond to the sample where NaBr solution was included. As one can see, the intensity ratio is increased, confirming again that the mode at 1141 cm^{-1} is enhanced through the CM effect. Several data points were collected over

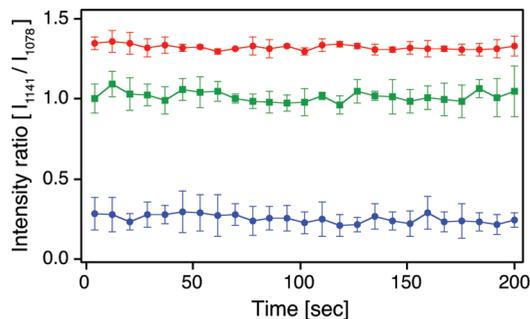


Figure 3. Time dependence of SERS intensity ratio between the modes at 1141 and 1078 cm^{-1} . The green data points correspond to the SERS experiments discussed in Figure 1, the blue data points represent SERS with PVP spacer layer and the red data points represent SERS with inclusion of NaBr.

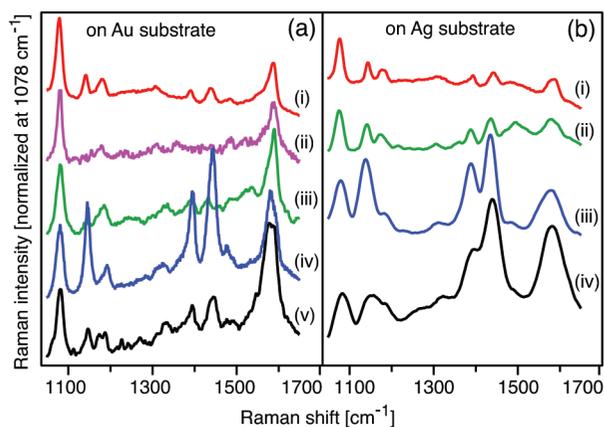


Figure 4. (a) SERS spectra of 4-ATP adsorbed on Au substrate, normalized at 1078 cm^{-1} . The excitation wavelengths for the spectra (i) through (v) were 785, 658, 642, 633, and 532 nm, respectively. (b) SERS spectra of 4-ATP adsorbed on Ag substrate, normalized at 1078 cm^{-1} . The excitation wavelengths for the spectra (i) through (iv) were 785, 642, 514.5, and 458 nm, respectively.

a long period, and it was found that the difference in the intensity ratio for the three samples remains consistent. Similar results were observed for the other b_2 -type modes as well. Both techniques presented here can help us in experimental identification of the enhancement mechanisms for various Raman modes.

Resonance in Chemical Enhancement. It is well-known that enhancement in SERS shows a resonance effect with the excitation laser energy. This is usually interpreted in term of the resonance of the localized SPPs of the metallic nanoparticles on the surface. When the excitation energy matches the natural oscillation frequency of the SPPs, the SPPs can couple with the excitation light and can be resonantly excited, resulting in huge enhancement of the light field in the close vicinity of the metallic surface. This resonance effect is related to the EM enhancement and is well-known. However, when SERS spectra are normalized at one of the a_1 -type modes, it is interesting to see that SERS enhancement goes through another resonance and this time only b_2 -type modes are enhanced. This indicates that the second resonance is related to the CM effect. Figure 4a shows a series of SERS spectra measured from 4-ATP on Au, excited with indicated wavelengths. These spectra are normalized for the mode at 1078 cm^{-1} , so that one can focus attention on the modes that are enhanced through the CM effect. The increased intensities b_2 -type modes in spectrum (iv) shows the chemical resonance in SERS. Similar results were also obtained for silver substrate, which are shown in Figure 4b, where b_2 -

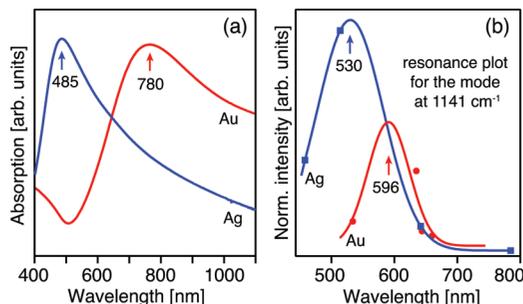


Figure 5. (a) Absorption curves for Au and Ag substrates used in the present study. (b) Resonance curves plotted from the intensity of the mode at 1141 cm^{-1} , after normalizing the SERS spectra at 1078 cm^{-1} .

type modes drastically increased in spectra (iii) and (iv). In fact, in the case of silver substrate, b_2 -type modes become even stronger than the a_1 -type modes at the resonance.

A careful observation of Figure 4a reveals that the b_2 -type modes are once again slightly enhanced in spectrum (i). This is because the excitation wavelength in this spectrum was 785 nm, which is close to the SPP resonance of 8-nm-thick gold substrate. Therefore, the EM effect is greatly enhanced at this wavelength. As mentioned earlier, the enhancement of the b_2 -type modes also has slight contribution from the EM effect. Thus, after passing through the resonance in CM effect, the b_2 -type modes are once again slightly enhanced near the SPP resonance. One way to find the SPP resonance is to look at the absorption curve of the metallic substrate. The peak position of the absorption curve corresponds to the SPP resonance. The red and blue curves in Figure 5a represent the absorption curves for the gold and the silver substrates, respectively. The absorption curves show maxima at around 780 and 485 nm, respectively, for the gold and the silver substrates. It should be noted that the absorption curves were measured for bare metal substrates without 4-ATP molecules. However, it was confirmed that the presence of 4-ATP SAM did not change the absorption curves significantly. As expected, our wavelength-dependent SERS measurements also show strongest enhancements, particularly for the a_1 -type modes, when excitation wavelengths are close to the absorption peaks.

In order to have a comparison between the EM and CM resonances in SERS, the resonance curves obtained from the intensity of the mode at 1141 cm^{-1} in Figure 4, are plotted in Figure 5b. The experimental data show a reasonably good fitting with Gaussian curves. The fitting indicates that the resonance for CM effect in SERS are obtained at around 596 and 530 nm, respectively, for gold and silver substrates. As one can notice, the resonance in SERS related to the EM and CM effects are distinctly different. Also, as evident from different resonance peak positions for gold and silver in Figure 5b, the amount of charge transfer for the two metals are not the same. This is caused by the difference of the Fermi levels of the two metals. These results show yet another way to experimentally identify the chemically enhanced modes. Further, comparing the relative intensities of chemically enhanced modes for gold and silver substrates, the enhancement for silver was much larger than that for gold. This implies that silver is more chemically reactive than gold, and that 4-ATP makes better chemical bondings with silver than with gold.

Finally, we show some interesting observation of chemically enhanced modes of 4-ATP in a sample where 4-ATP molecules were sandwiched between Au substrate and the apex of an Au nanopip. For this experiment, an Au-coated nanopip was prepared

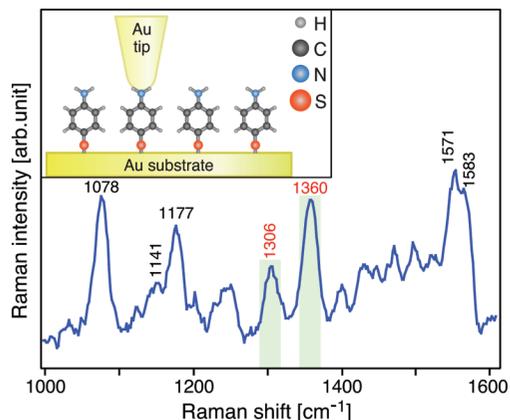


Figure 6. Raman spectrum of 4-ATP molecules sandwiched between Au substrate and Au tip, as illustrated in the inset. In order to remove the background signal from those 4-ATP molecules which were not under the tip apex, the spectrum here is presented after subtracting SERS signal obtained in the absence of the tip. The appearance of two new peaks at 1306 and 1360 cm^{-1} is due to chemical enhancement invoked by the bonding between Au atom of the tip and the N atom of the sample molecule.

by evaporating gold on a commercially available atomic force microscopy cantilever tip. After gold evaporation, the diameter of the tip apex was about 30 nm. This Au-coated tip was brought in contact with the SERS sample used in spectrum (ii) of Figure 1, and Raman scattering was then excited with 642 nm laser line. A schematic of the sample arrangement is shown in the inset of Figure 6. This experimental situation is somewhat similar to the SERS measurements of 4-ATP molecules sandwiched between metal substrate and metal nanoparticles.³⁰ The authors observe selective enhancement of the b_2 -type modes and suggested that this selective enhancement could be interpreted in terms of a metal–molecule–metal charge-transfer theory due to the new chemical bonding between Au atoms on the nanoparticles and 4-ATP molecules. When a SAM of 4-ATP is prepared on gold substrate, the sulfur end of 4-ATP molecule aligns itself toward the gold substrate, and a chemical bonding is formed between S atom of the sample and Au atom of the substrate. This chemical bonding gives rise to the chemically enhanced modes observed in spectrum (ii) of Figure 1. Now when an additional gold-coated nanotip is brought close to the sample, as illustrated in the inset of Figure 6, the gold atoms on the tip make additional chemical bondings with 4-ATP molecules, however, this time though the nitrogen atoms, because the upper end of 4-ATP molecules in SAM contains NH_2 . This leads to a slightly different chemical structure compared to SAM of 4-ATP on Au substrate and hence one expects to see some new chemically enhanced modes for 4-ATP SAM sandwiched between Au layer and Au tip. The experimental result for such a sample is presented in Figure 6. The spectrum shown in Figure 6 was obtained by subtracting the SERS spectrum (such as spectrum (iii) of Figure 4a) from the spectrum obtained under the combination of the SERS substrate and the gold-coated tip. The subtraction essentially removes the background signal coming from those 4-ATP molecules which are not under the tip apex, and hence the subtracted spectrum represents only those modes which are enhanced from the molecules under the tip. Apart from the selective enhancement of the b_2 -type modes, one can notice that two new modes at 1306 and 1360 cm^{-1} are strongly enhanced in this spectrum, whereas both these modes were missing in Figure 1. We anticipate that one of the reasons for these two modes to appear is the new chemical bonding between Au atoms

and 4-ATP molecules through the nitrogen atom. The other possible reason could be a local structural deformation of the sample molecules under the tip, because such a tip often applies a small amount of local pressure on the sample. The deformation can give rise to a modified chemical bonding. In either case, we conclude that these two new modes are chemically enhanced modes. In fact, these modes could be found in the density functional theory analysis,³¹ where the mode at 1306 cm^{-1} is assigned to the C–C stretching and the mode at 1360 cm^{-1} is assigned to the C–H bending, both with b_2 -type vibrations. This method provides experimental observation of some new chemically enhanced modes, which are predicted by the theory, but are usually not observed in SERS.

Conclusions

This article has provided a couple of practical methods for identifying Raman modes that are enhanced through the EM or the CM effects in SERS measurements of 4-ATP sample. One method is to introduce a thin spacer layer of PVP between the metal and the sample, which prevents any possible chemical bonding between the metal atoms and sample molecules, hence selectively reducing the intensities of only those Raman modes that are enhanced through the CM effects. Another way is to include halide ions in the SERS sample, which selectively increase the intensity of those Raman mode that are enhanced through CM effects. In addition, we have also demonstrated that, apart from the SPP-based EM resonance, SERS also goes through another resonance that is based on the CM effect, which provided yet another way to identify chemically enhanced modes in SERS. In general, the chemical effects are stronger for silver substrates, in comparison with gold. Further, we have shown the appearance of some new chemically enhanced modes when the sample molecules are sandwiched between a gold substrate and a gold nanotip.

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