Direct visual evidence for chemical mechanism of SERRS of the S-complex of pyrimidine molecule adsorbed on silver nanoparticle via charge transfer

Xin Zhang\textsuperscript{a}, Peijie Wang\textsuperscript{a,⇑}, Shaoxiang Sheng\textsuperscript{b}, Lisheng Zhang\textsuperscript{a}, Yan Fang\textsuperscript{a}

\textsuperscript{a}The Beijing Key Laboratory for Nano-Photonics and Nano-Structure, Department of Physics, Capital Normal University, Beijing 100048, China
\textsuperscript{b}Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603-146, Beijing 100190, China

Highlights

- Characteristics of the electronically excited state of pyrimidine–Ag\textsubscript{20} is calculated.
- SERRS of pyrimidine were obtained on Ag electrode with increase of the cathode potentials.
- Different incident wavelength regions are dominated via CHEM and EM mechanisms of SERRS.
- The trend of absorption spectrum of S-complex is similar to that of SERRS spectrum.

Abstract

In this paper, the S-complex of pyrimidine molecule absorbed on silver clusters was employed as a model molecule to study the enhancement mechanism in surface-enhanced resonance Raman scattering (SERRS). We described the chemical enhancement of SERRS through charge transfer (CT) from Ag\textsubscript{20} to pyrimidine on resonance excitation, and electromagnetic enhancement through intracluster charge redistribution (CR) on the electronic intracluster collective oscillation excitation. It is shown that SERRS process of the pyrimidine molecule absorbed on silver clusters with different incident wavelength are dominated by different enhancement mechanisms. Both experimental and theoretical works have been performed to understand the CT process in SERRS.

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Introduction

Surface-enhanced Raman scattering (SERS) has been playing an important role in identifying molecular structures adsorbed on the metal surface and it is also a powerful tool for probing the in situ chemical reaction mechanisms [1–4]. It has been generally accepted that the enormous enhancement in SERS occurs from two kinds of mechanisms [5–8]. One is called electromagnetic (EM) enhancement which dominates almost total enhancement in SERS and is caused by the strong surface plasmon resonance (SPR) of rough metal surfaces coupled to the incident light [4–9]. The other is chemical (CHEM) enhancement, which originates from the complex interaction among the adsorbed molecules and the metal. The CHEM enhancement is similar to a resonance Raman process between the ground electronic state of the molecule–metal complex and its new excited levels arisen from the CT between the adsorbed molecule and the metallic...
surface [12–15]. However, generally speaking, under most circumstances CHEM and EM mechanism will contribute to SERS enhancement together. Although rather minor contribution from the CHEM mechanism of the metal-adsorbate system was observed, it was often ignored due to its complexity in the electronic transitions at the surface which was very difficult to visualize. So, the understanding of the CT process is still very limited [16–21]. Recently, a great deal of theoretical studies have been carried out to reveal the mechanisms of SERS, but the time-dependent density functional theory (TD-DFT) method can reveal visually CT from metal to molecule or vice versa, and has been used in many theoretical studies [22]. Sun and his group have distinguished CHEM from the EM mechanism for SERRS by the TD-DFT method for the models of Au25-pyrazine–Au25 complex [23], pyridine–Ag20 complex [12], pyridine–Ag25 complex [24], and pyridine–Ag complex [25].

Pyrimidine has been a subject of great interest due to its direct derivatives which consists of RNA and DNA in combination with uracil and thymine respectively. In some natural products or synthetic compounds, such as vitamin B1 (thiamine), barbituric acid and veronal, the pyrimidine skeleton was also found there [25,26]. Thus, the pyrimidine has quickly become a model molecule to extend the understanding of absorption and orientation on surface by theoretical and experimental approaches. The pyrimidine molecule has C2v symmetry, with 24 (3N-6, N is its atom number, N = 10) vibrational normal modes, its Raman spectra under different experimental conditions have also been reported [27–33], and a variety of calculation methods have been used, such as semiempirical [34], Hartree–Fock, density functional theory levels. The vibrational assignments of pyrimidine were performed by correlating with that of the benzene [35,36]. Simmons and Innes proposed a new assignment for the A1, fundamentals from the infrared and Raman spectra [37]. Milani–Nejad and Stidham prepared several different deuterated pyrimidines of C2v symmetry and recorded their IR and Raman spectra [38]. Silvia and co-workers studied the vibrational spectroscopy of pyrimidine adsorbed on silver at different electrode potentials [21]. However, those previous works mentioned above have not revealed visually the CHEM and EM mechanism. It was shown that the CT from the metal to the molecule (vice versa) and the CR within the metal on the electronic intracluster collective oscillation excitation can directly interpret the CHEM enhancement to SERRS and EM enhancement by collective plasmons respectively [23]. Hence, the experimental and theoretical studies need further to be performed to interpret the CT process and CHEM enhancement in SERRS. These studies on the enhancement mechanisms for the local SERS is essential, since these are the precondition to understanding enhancement mechanism in the complex nanostructures, such as remote SERS [39] and Tip-enhanced Raman spectroscopy [40–42].

In this paper, we studied the SERRS process of the pyrimidine molecule absorbed on silver clusters by changing the silver electrode voltage. By comparing the experimental results with the theoretical calculations, the CHEM mechanism of the SERRS has been visually revealed.

### Experimental

A three-electrode cell was used to perform the oxidation-reduction cycles (ORCs). The working electrode was a single-crystal silver rod of 99.9% purity and a platinum wire was used as the counter electrode. Ag/AgCl electrode was employed as the reference electrode. The applied voltage of the working electrode was controlled by a CHI660A electrochemical instrument. The Raman spectra were recorded by a microprobe Raman system RH13325 R-2000 spectrophotometer equipped with a high sensitivity CCD detector. The sample were excited with a 514.5 nm laser with an effective power of 100 mW. A 50X objective is used to perform a 180° backward scattering configuration.

Prior to the experiment, Ag electrode was polished with emery paper and cleaned with Milli-Q water in an ultrasonic bath. It was placed in a typical electrochemical cell containing 0.1 M KCl solution for roughening. A double potential step was used to roughen the surface by applying a voltage of +0.25 V for 8 s and then applying a voltage at −0.35 V. This roughening treatment is applied to strengthen rather steady-going Raman intensity for the convenience of our spectra recording.

After the roughing pretreatment, the electrode is placed in the electrochemical cell containing 0.1 M KCl and 0.1 M pyrimidine solutions. The SERS of pyrimidine is performed on the electrode with the voltage ranging between 0 and −1.2 V.

### Theoretical

All of the theoretical chemical calculations in our work were performed by using the Gaussian 09 suite [43]. By using density functional theory (DFT) [44] method, we could obtain the Fermi energy level as well as the energy of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of Ag20 cluster. Besides, the Fermi energy level of pyrimidine–Ag20 complexes was also acquired. The Perdew–Zunger parametrization (LDA–PZ) functional was used for the approximation in calculation. The geometry of pyrimidine was optimized by DFT with B3LYP functional and 6–31G basis and the LANL2DZ basis set was chosen for Ag20 metal cluster. We calculated directly the CT and CR between pyrimidine and the Ag20 cluster as well as within the Ag20 cluster on the EICOE respectively by using the method of charge difference density. In the process of SERS enhancement, the method of charge difference density has the visualization advantage that the direction and occurrence region of charges transfer in the pyrimidine–Ag20 complex can be visualized directly. On the other hand, we calculated the adsorption spectrum of pyrimidine–Ag20 complex by the TD-DFT method [45].

Here, from the differential Raman scattering cross section, the absolute Raman intensities are calculated. For Stokes scattering with an experimental set up of a 90° scattering angle and perpendicular plane-polarized light, the cross section of Raman scattering is given by [46]

\[
\frac{d\sigma}{d\Omega} = \frac{\pi\epsilon_0}{2\epsilon} \left(\omega_h - \omega_p\right)^4 \frac{\hbar}{8\pi^2 c \chi_0} S_p \frac{1}{45 \left[1 - \exp\left(k/\Delta\right)\right]} 
\]

The \(\omega_h\) and \(\omega_p\) are the frequencies of the incident light and the pth vibrational mode, respectively, and \(S_p\) is the Raman scattering factor (or Raman activity in unit A^4/amu).

\[
S_p = 45 \left(\frac{d\sigma_p}{d\Omega_p}\right)^2 + 7 \left(\frac{d\sigma_p}{d\Omega_p}\right)^2
\]

which is a pure molecular property and independent of experimental setup. \(\chi_0\) and \(\chi_p\) are the isotropic and anisotropic polarizabilities [43]. In this paper, \(S_p\) values were directly calculated by Gaussian 09 suite.

### Results and discussion

It is known that the pyrimidine molecule adsorbed on silver nanoparticles is aligned in a vertical manner with the N group being located in the top of benzene ring [21]. Fig. 1 shows the SERRS spectra of the pyrimidine molecule adsorbed on ORC-roughened silver electrode in KCl aqueous solution. When the applied voltage was −0.5 V, it was observed that the spectral
are applied, the contribution of the CT states to the SERS and is the optical absorption energy, and cluster. Previous work will shift with the changing of the incident photon + ¼ metal = 33x334 resulted from the CT of CHEM mechanism[47].

The optical absorption energy in the absorption spectrum and the shift of electrode potential can be estimated with:

\[ E_{\text{optical}} = E_{\text{optical} \rightarrow 0} - e\Delta V \] (3)

The \( E_{\text{optical}} \) is the optical absorption energy, and \( \Delta V \) is the variation of the electrode potential, \( e \) is the electron charge, and the coefficient \( \beta \leq 1 \). In the system of pyrimidine molecule adsorbed on silver nanoparticles, the coefficient \( \beta \) can be taken as 0.75 [24]. For example, if we choose the incident laser wavelength as 514.5 nm (\( E_{\text{optical} \rightarrow 0} = 514.5 \) nm), the voltage applied to the electrode potential is \(-0.1\) V, according to Eq. (3) a new incident excitation of 2.51 eV (494 nm) can be obtained.

For convenience, Eq. (3) is rewritten as

\[ E_{\text{optical} \rightarrow 0} = E_{\text{optical}} + e\beta\Delta V \] (4)

where the \( \Delta V \) is the increased value of the electrode potential. It is clearly seen that the increase of the cathodic potential is not tuned to the energy of the incident light, but shifted the optical absorption from higher energy (eV) toward 514.5 nm.

From Eqs. (3) and (4), the Raman spectra of pyrimidine molecule adsorbed on silver nanoparticles obtained by changing the potential of electrode can be regarded as the spectra excited by different wavelength incident light. The corresponding different wavelength incident lights are demonstrated in the right side of Fig. 1.

In the followings, the enhancement mechanisms of pyrimidine molecule adsorbed on silver nanoparticles with different incident light were theoretically analyzed. Thus, the S-complex of pyrimidine as the chemical model system was built to calculate the SERS spectra by DFT method. It is well known that the local EM field enhancement (collective plasmon) of small clusters is the förster excitation [12] and the plasmon excitation in large clusters is electromagnetic enhancement. However, both effects are almost similar for larger clusters. For example \( R > 10 \) nm (the clusters is regarded larger), the two mechanisms of the förster excitation and electromagnetic enhancement are the same [12]. So the complex of the pyrimidine molecule adsorbed on \( \text{Ag}_{20} \) becomes the first choice to imitate a part of larger nanoparticles. On the other hand, the S-complex can replace V-complex as nanoparticles of a much larger size than the \( \text{Ag}_{20} \) cluster. Previous work has shown that the S-complex is better in agreement with the experimental outcome [22,24,25,50–52]. So, we choose the S-complex of pyrimidine molecule adsorbed on silver nanoparticles as our theoretical model. In the followings, we just used the DFT method to calculated the properties of S-complex.

When the pyrimidine molecules are adsorbed on \( \text{Ag}_{20} \) metal nanoparticles, the CT between molecule and nanoparticles will takes place [44], this directly changes the static polarizability.

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**Fig. 1.** The SERS spectra of pyrimidine adsorbed on Ag electrode with applied voltage from 0 V to \(-1.2\) V vs. Ag/AgCl electrode.

**Fig. 2.** (a) The conceptual model of the energy levels changes with the electrode potential in the charge transfer process. (b) The relevant energy states involved in the electronic levels and the vibrational levels in the charge transfer process.

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Table 1 shows the static polarizability of the S-complex and pyrimidine. It is a evident phenomenon that the polarizability of the static S-complex is higher compared to isolated pyrimidine molecule. The calculated SERS spectrum can be seen from Fig. 3, which is contributed by the static chemical (SC) enhancement. There are five evident enhanced modes (comparing with its normal Raman spectrum (NRS)), 1044 cm\(^{-1}\) (ring breathing with N moving toward silver), 1127 cm\(^{-1}\) (ring breathing) and 1403 cm\(^{-1}\) (C–H bending), 1565 cm\(^{-1}\) (C–H twisting in the plane) and 1576 cm\(^{-1}\) (C–H twisting in-plane normal modes) relative to isolated pyrimidine, they are symmetric vibrational modes perpendicular to the metal surface (as shown in Fig. 3) that is the orientation of CR between pyrimidine and the Ag\(_{20}\) cluster. So the selection rule for the SC enhancement is that the orientation of CT in the ground state is the same as that of molecular vibrations in the ground state. It is noted that, in the experimental SERS spectra as shown in Fig. 1, the intensities of these five peaks are enhanced obviously when the electrode potential is changed.

Fig. 4 shows the Fermi energy level of the S-complex and Ag\(_{20}\) clusters. The Fermi energy level of the S-complex is 0.027 eV higher than that of Ag\(_{20}\) clusters. When the pyrimidine molecules absorbed on Ag\(_{20}\) metal nanoparticle, the increasing Fermi energy level can be calculated by \[\Delta E_{\text{Fermi}} = E_{\text{Fermi (S-complex)}} - E_{\text{Fermi (Ag\(_{20}\))}}\] (5)

The energy levels of HOMO and LUMO of the Ag\(_{20}\) cluster is also shown in Fig. 4. The minimum energy of electronic intracluster collective oscillation excitation is 725 nm for the Ag\(_{20}\) cluster, which was calculated by:

\[\Delta E_{\text{(Ag\(_{20}\))}} = E_{\text{HOMO (Ag\(_{20}\))}} - E_{\text{LUMO (Ag\(_{20}\))}}\] (6)

The energy gap for Fermi energy level of Ag\(_{20}\) to the LUMO of pyrimidine is 590 nm, it is the minimum energy for transiting from the CR to CT, which can be estimated by:

\[\Delta E_{\text{CR-CT}} = E_{\text{Fermi (pyrimidine)}} - E_{\text{Fermi (Ag\(_{20}\))}}\]
\[= E_{\text{Fermi (pyrimidine)}} - E_{\text{HOMO (Ag\(_{20}\))}}\]

\[= E_{\text{Fermi (pyrimidine)}} - E_{\text{LUMO (Ag\(_{20}\))}}\]

The following formula leads to the outcome as:

\[\Delta E_{\text{CR-CT}} = E_{\text{Fermi (pyrimidine)}} - E_{\text{CT min}}\]

\[= E_{\text{Fermi (pyrimidine)}} - E_{\text{LUMO (Ag\(_{20}\))}}\]

The largest oscillator strength of the CT can be obtained at 427 nm. It would be easy to get a conclusion about different enhancement mechanisms of SERS with different wavelength incident laser by the DFT method above. A apparent separation of these enhancement mechanisms are as follows:

(a) When energy of the incident light is smaller than 1.71 eV (725 nm), the resonant electronic state transition cannot happen. Thus the SERS are involved in neither CHEM nor EM enhancement mechanisms, it just comes from the static chemical enhancement mechanisms.

(b) When the energy of the incident light is between 725 and 590 nm, the phenomenon of resonant electronic state transitions could happen, its major SERS enhancement contributions is the EM enhancement by plasmon excitation just in electronic intracluster collective oscillation excitation. The energy of the incident light is insufficient to produce the CT states, thus, only the CR can occur.

(c) When the energy of the incident light is larger than 590 nm, the SERS spectra is dominated by resonant electronic state transitions, in another word, the CT can occur from the Ag metal cluster to the pyrimidine molecule. This process results in CHEM enhancement. Beside, the resonant electronic state transitions energy 427 nm is the largest oscillator strength for the CT.

Above conclusions are based on the calculation results by DFT method on the S-complex model. However, this method cannot calculate the charge difference densities for the intracluster excitation and CT excitation (charge transfer from Ag\(_{20}\) cluster to pyridine), respectively. Hence, another advanced TD-DFT method can be used to study the S-complex model with different incident light. By observing the charge difference densities with different incident wavelength light, the CHEM mechanism of the SERS process of the pyrimidine molecule absorbed on silver clusters could be visually revealed.

Fig. 5 presents the calculated electronic absorption spectrum by TD-DFT method. Also the attributions of different levels are demonstrated. The intracluster and CT on resonant electronic transitions at lowest 100 singlet excited states have been shown. There the blue dot and red cross stand for charge transfer and charge redistribution electronic states, respectively. It shows that...
the different wavelength incident light can excite corresponding resonant electronic transitions.

So, it can be concluded that the enhancement mechanisms of SERRS process for the S-complex with different wavelength incident light by TD-DFT method are shown in Fig. 6: (a) at 456–332 nm region, almost all the excited states are CT, which is direct visual evidence for the CHEM enhancement. The largest oscillator strength of the CT transition can be obtained at 353 nm (which is corresponding to the maximum absorption shown in Fig. 5). (b) From 456 nm to 651 nm, and from 301 to 332 nm, the excited states are corresponding to the electronic intracluster collective oscillation excitation, where charge redistribution (CR) would occur, this is served as direct evidence for the EM enhancement. (c) When the incident light is above 651 nm, there the excitations cannot induce any transitions, the enhanced mechanism of Raman spectra should be static chemical enhancement, both CHEM and EM enhanced mechanism cannot occur. So, the CT could be possible to identify from the CR for SERS enhancement mechanism by visually observing the charge difference densities in our system.

Now, comparing the two results by two different methods (DFT method and the TD-DFT method) discussed above, one can see that the maximum oscillator strength is at 427 nm for the CT transition by DFT. As a result, we would expect that the largest oscillator strength of the CT transition by TD-DFT is also at 353 nm when we take the blue-shifted 74 nm into consideration. Generally, it can be viewed as a deviation by different ways of calculations, but the outcomes by the two methods are almost similar.

A further in-depth comparison and analysis for experimental and theoretical outcome based on the above discussing are shown in Fig. 7. Fig. 7(a) showed the SERRS of pyrimidine molecule adsorbed on silver electrode with the changing voltages. Fig. 7(b) showed the relationship between the changed electrode voltages and the corresponding excitation levels of the absorption spectra. For convenient discussing, Fig. 7(c) gave the calculated electronic absorption spectrum by TD-DFT method again as Fig. 5. From Fig. 7(a), it is clearly seen that the spectra profiles were varied drastically with the changing of the applied electrode voltages by globally viewing. The more prominent changing of the peaks are at 1004 cm$^{-1}$ (ring breathing with N moving toward silver) and 1562 cm$^{-1}$ (C–H twisting in the plane) which were very sensitive to the changing of the electrode voltages.
When the applied electrode voltage is 0 V and −0.1 V, the incident light is equivalent to 514 and 494 nm, the enhancement of SERRS is WEM enhancement which can be clearly seen from Fig. 7(b) where the excitations are in the CR region. Thus, their profile of SERRS are very similar. With the further increase of the voltage, the intensities of the normal modes at 1004 cm⁻¹ and 1562 cm⁻¹ are gradually enhanced, and when the applied electrode voltage is −0.5 V, the of two modes got the maximum enhancement where the excitations are in the CT region as demonstrated in Fig. 7(b). Then the enhancement of SERRS now becomes CHEM enhancement. In another word, it is sufficient to produce the CHEM enhancement. In electrochemical experiment, the maximum intensity of Raman peaks would decrease just as the tendency shown in Fig. 7(a) for electrochemical experiment. In SERRS experiment of Fig. 7(a), the maximum intensity of Raman peaks are at the −0.5 V corresponding to 426 nm wavelength incident light. This value is almost same as the resonant electronic state transitions energy 427 nm which the largest oscillator strength for the CT by DFT method.

Conclusions

In our work, we studied the CHEM and EM enhancement mechanism of pyrimidine adsorbed on the metal cluster by changing the electrode voltages. We revealed the CHEM mechanism and EM mechanism by the DFT method and TD-DFT method. Both experimental and theoretical works have been performed to understand the CT process. The mechanism of the CT was visualized with TD-DFT which provides a further insight on the understanding the CHEM enhancement of SERRS.

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