DFT study of adsorption site effect on surface-enhanced Raman scattering of neutral and charged pyridine–Ag\(_4\) complexes

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**Abstract**

Density functional theory (DFT) and time-dependent DFT (TDDFT) methods have been used to investigate the adsorption site effect of Raman scattering for neutral and charged pyridine–Ag\(_4\) complexes. The calculated results show that the SERS spectra are strongly dependent on adsorption site and the configuration of new complexes. The normal Raman spectra of neutral and charged pyridine–Ag\(_4\) complexes are similar with that of isolated pyridine but with an enhancement factor below 10 times. This enhancement is ascribed to ground state chemical enhancement. The pre-surface-enhanced Raman scattering (SERS) spectra were calculated at 1256 nm, 769 nm and 744.3 nm, which are nearly resonant with the charge transfer excited states \(S_2\) for neutral and charged pyridine–Ag\(_4\) complexes, respectively. We obtain the enhancement factor about \(10^3\) to \(10^5\) in pre-SERS spectra which is mainly caused by charge transfer resonance Raman enhancement. The three-dimensional cube representation is also applied to describe the photoinduced CT, which are considered as direct evidence of chemical enhancement, between pyridine and two isomers of Ag\(_4\) clusters.

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**1. Introduction**

The Raman intensity of pyridine was strongly enhanced when the molecular adsorbed on rough silver surface which was found by Albrecht et al. and Van Duyne et al. in 1977 [1–3]. This phenomenon was commonly said to be surface-enhanced Raman scattering (SERS) spectra which enhanced the Raman intensity by at least 14 orders of magnitude. Because of the significant contribution on the vibrational spectra, the mechanisms of such huge enhancement have been referred to in a large number of investigations [4–7]. Two kinds of mechanisms are mainly resulted in the huge enhancement of SERS spectra [5–10]. The electromagnetic (EM) enhancement mechanism results from the excitation of surface plasmon resonance with incident light [11–13]. On the other hand, the chemical mechanism (CM) enhancement is complicated and roughly divided into three parts: (1) ground state chemical enhancement is caused by the change of chemical environment around the molecular; (2) resonant Raman enhancement results from resonant between a molecule transition and the excitation wavelength. (3) Charge transfer (CT) resonance Raman enhancement is produced by the excitation wavelength resonant with new transition states between metal and adsorbed molecular [3,10,14–18].

Large numbers of theoretical studies have been carried out to elucidate the mechanism of SERS [10,16,19–24]. Tian and co-workers presented a computation of the differential Raman scattering cross-section of totally symmetric vibrational modes of pyridine and pyridine–metal clusters [25]. They found that due to the weak bonding for pyridine–silver complexes, the chemical interaction did not influence the relative intensities of the Raman peaks of modes \(\nu1\) and \(\nu12\). In 2006, pyridine–Ag\(_{20}\) model system was put forward by Schatz and co-workers, and they analyzed enhanced Raman scattering using time-dependent density functional theory (TDDFT) method in detail [14]. Results showed a strong dependence of the absolute and relative intensities on the adsorption site and incident light. They presented a general profile of different contributions to the enhancements, involving static chemical enhancements (factor of 10), charge-transfer enhancements (\(10^3\)) and EM enhancements (\(10^5\)). Recently, Cardini et al. [26] reported that an improvement of pyridine adsorbed on silver clusters with different charges and considered the coadsorption of chloride anions effect in SERS. They pointed out the strong CT effect between pyridine and silver clusters are closely related with the formation of both in the absence and presence of coadsorbed chloride anions. Those previous work mentioned above have provided some understandings of the enhancement mechanism of SERS, but the adsorption site effect on the Raman intensity of pyridine...
attached to silver clusters is neglected and there is a lack of direct and convenient method to show the important CT effect in CM. This problem calls for a great deal of further research effort in this area.

In this work, a new theoretical method charge different densities (CDDs) [27–29] was applied to visualize CT between pyridine and neutral or charged Ag4 clusters at different electronic excited states. We largely focused on the pure CT excited state of pyridine–Ag4X (X = L, S, V) complexes which is considered to be the most direct evidences of chemical enhancement. For calculating pre-SERS, we chose the approximation of transition energy of pure CT excited states at 1256 nm, 769 nm and 744.3 nm as incident light for py–Ag4X (X = L, S, V) complexes, respectively.

2. Method

Structures of pyridine and Ag4 clusters in ground state were optimized using density-functional theory (DFT) [30] with BP86 functional [31,32] at the level of 6-311++G (d, p) basis set and LanL2DZ, respectively [33]. Geometries of neutral and charged pyridine–Ag4 complexes were optimized using DFT with BP86 functional at the level of 6-311++G (d, p) basis set for C, N, O, H atoms and LanL2DZ for Ag atoms. The vibrational frequencies of all the structures were calculated without imaginary frequencies, which stood for energy minima. The optimized geometries of neutral and charged Ag4 clusters and metal–pyridine complexes were shown in Fig. 1. The calculations for adiabatic electronic state optical absorption of neutral and charged Ag4 cluster and pyridine–Ag4 clusters were carried out by the time-dependent DFT (TDDFT) method [34] using BP86 functional with the same basis set as ground state. In this work, we did not use any scale factors in calculation of Raman spectra. All these calculations were performed with GAUSSIAN03 program [35].

Absolute off and on resonance Raman intensities can be calculated as the differential Raman scattering cross-section. For Stokes scattering with an experimental setup of a 90° scattering angle and perpendicular planar-polarized light, the cross-section is written as [36]

$$d\sigma = \frac{\pi^2}{12} \left( \omega_{in} - \omega_p \right)^4 \frac{h}{8\pi^2 c \omega_p} S_p \left[ \frac{1}{45} - \exp \left( -\frac{hc\omega_p}{k_BT} \right) \right]$$

(1)

The $\omega_{in}$ and $\omega_p$ are the frequency of the incident light and of the $p$th vibrational mode, respectively, and $S_p$ is the Raman scattering factor (or Raman activity in unit Å⁴/amu),

$$S_p = 45 \left( \frac{\partial \alpha_p}{\partial \epsilon_p} \right)^2 + 7 \left( \frac{\gamma_p}{\partial \epsilon_p} \right)^2$$

(2)

which is a pure molecular property and independent of experimental setup. $\alpha_p$ and $\gamma_p$ are the isotropic and anisotropic polarizabilities. In this paper, $S_p$ were directly calculated by Gaussian 03 suite [35].

The photoinduced excited state properties of neutral and charged pyridine–Ag4 complexes were investigated by CDDs. The TDDFT calculations were used to construct the CDDs by

$$\Delta \rho_{\mu\lambda}(r) = \sum_{a, i, j} C_{\lambda a} C_{\mu b} \psi_i(r) \psi_j(r) - \sum_{a, b, i} C_{\mu a} C_{\lambda b} \psi_a(r) \psi_b(r)$$

(3)

where $C_{\mu a}$ reveals the $\mu$th eigenvector of the (singlet-CI) Hamiltonian in the basis of the occupied Hartree-Fock molecular orbital $\psi_i(r)$ and the unoccupied molecular orbital $\psi_a(r)$. The CDDs visualizes the difference in electron density upon electronic transition between ground state and a singlet excited state in our case [27–29,37–39].
Fig. 2. Charge difference densities for nine different singlet excitation states of neutral or charged pyridine–\(\text{Ag}_{\text{el}}\) (\(X=L, S, V\)) complexes (the green and red stand for holes and electrons, respectively, and the isovalue is \(4 \times 10^{-4}\) a.u.). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
3. Results and discussion

3.1. Geometries and the absorption properties

The structural, electronic and optical properties of small-sized silver clusters have been mentioned experimentally and theoretically in a large number of studies [40–44]. As the cluster size rises, the number of isomers also increases greatly. It is difficult to consider so many different adsorption sites in the calculations, when pyridine attaches to a large number of silver cluster isomers. In this work we adopt two small-sized Ag4 clusters as calculated model: neutral rhombic D2h Ag4 cluster and Td Ag4 cluster with two positive charges [43]. When pyridine adsorbed on neutral and charged Ag4 clusters, there are three different adsorption sites: pyridine binds to long axis (py–Ag4L) or short axis (py–Ag4S) of neutral rhombic Ag4 cluster which represent pyridine adsorbed on Ag (1 1 1) surface and pyridine attaches to the vertex (py–Ag4V) of charged Ag4 cluster which stands for hot-site effect (or binding site effect). All optimized geometries in ground state mentioned above are shown in Fig. 1.

In ground state, properties of three different pyridine–Ag4 complexes are listed in Table 1. Notice that, we adopting basis set superposition errors (BSSE) when calculate the binding energy: $E_{\text{binding energy}} = E_{\text{complex}} - (E_{\text{Ag4 cluster}} + E_{\text{pyridine}})$. It is found that Ag–N bond length of complexes decrease in the trend of py–Ag4L, py–Ag4S and py–Ag4V, which reveals that the interaction between molecule and metal increase. For this reason, charge transfer and binding energy increase in the same trend. It reveals that the interaction between pyridine and charged Ag4 cluster is stronger among these complexes. For py–Ag4V complex, the Ag–N bond length agrees well with the calculated Ag–N bond length of Py/(Ag4)2+ by Cardini et al. (2.167 Å) [26]. All these properties in ground state indicate that adsorption site has a strong influence on the properties of complexes, which includes the Raman scattering.

Fig. 2 shows nine lowest singlet–singlet excitations and CDDs of each complex. It is found that the strongest transitions occur in S5 (433.25 nm f = 0.5869) for py–Ag4L, and S6 (420.72 nm f = 0.8134) for py–Ag4S which are both CT excited states; however, py–Ag4V possesses the largest oscillator strengths at S6 (347.32 nm f = 0.2213) which is pure CT transition (all holes are localized on molecular and electrons are localized on silver cluster). Hereinto, the oscillator strength f represents the degree of the vertical absorption. It is clear to see that excited properties of py–Ag4L and py–Ag4S are similar, however, py–Ag4V owns less oscillator strengths and more blue-shift wavelength. For pyridine attached to D2h Ag4 cluster, the differences of excitation property is, not so evident, caused by adsorbed on long or short axis of silver cluster. But the vertical excitations are obviously blue shift for first three excitations when pyridine binding to Td Ag4 cluster and last four excitations are a bit red shift compared with pyridine binding to D2h Ag4 cluster. From the phenomena referred above, we conclude that configurations of Ag4 cluster are a significant point in the vertical excitation of pyridine–Ag4 complexes. In addition, absorption sites have a weaker effect on transition properties when pyridine adsorbed on the same configuration.

3.2. The ground state chemical enhancement and charge-transfer resonance enhancement

Properties in ground state indicate that adsorption site has a strong influence on the properties of complexes, which is mentioned hereinabove. In Table 2, we pay attention to changes in static polarizabilities of these complexes. The data show that static polarizabilities of three complexes decrease obviously following the trend of py–Ag4L, py–Ag4S and py–Ag4V. The static polarizabilities are one of decisive factors of the ground state chemical enhancement which is not associated with any excitation of the metal–molecule system.

Normal Raman spectra (NRS) and SERS of three complexes are shown in Fig. 3. The profile of NRS for three complexes accords with the observed SERS data (1008 cm−1) obtained from pyridine in Ag colloids. But the peaks at 1058 cm−1 is much red shift compared with the experiment data (1036 cm−1).

### Table 1

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For py–Ag$_{4L}$ the Raman shifts of these two symmetry modes are both blue shift, and for py–Ag$_{4S}$ one mode at 997 cm$^{-1}$ is blue shift and the other mode at 1054 cm$^{-1}$ is red shift. Our results of Raman shift accord with the experiment data as a whole [26]. The NRS intensities (presenting in square brackets) of modes at 991 cm$^{-1}$ and 1001 cm$^{-1}$ for py–Ag$_{4L}$ and py–Ag$_{4V}$ are smaller than modes at 1017 cm$^{-1}$ and 1058 cm$^{-1}$, respectively; whereas the intensity of corresponding two modes is reverse for py–Ag$_{4S}$ in NRS. Notice that two intense peaks at 1001 cm$^{-1}$ and 1058 cm$^{-1}$ for py–Ag$_{4V}$ are identical with the results performed by Cardini et al. [26]. Compared to the Raman spectra of single pyridine, the changes in NRS for complexes are mainly resulted from the modifications of the chemical environment around pyridine. The enhancement of NRS for complexes can be ascribed to ground state chemical enhancement. We focus on the SERS of three complexes contributed by CT resonance Raman enhancement. When pyridine binds to long axis (py–Ag$_{4L}$) or short axis (py–Ag$_{4S}$) of neutral rhombic Ag$_4$ cluster, these two geometries represent pyridine adsorbed on Ag (111) surface and when pyridine attaches to the vertex (py–Ag$_{4V}$) of charged Ag$_4$ cluster, it stands for hot-site effect (or binding site effect). From the data in Table 3, we obtain the CT resonance Raman enhancement factors which are equal to the proportion of intensity$_{SERS}$/intensity$_{NRS}$. For py–Ag$_{4L}$ and py–Ag$_{4S}$, the maximal enhancement factors are close to the order of $10^4$. For example, the enhancement factor of B$_2$ mode at 1199 cm$^{-1}$ for py–Ag$_{4L}$ is about $4 \times 10^3$ and the enhancement factor of A$_1$ mode at 1586 cm$^{-1}$ reaches to $1.1 \times 10^4$ for py–Ag$_{4S}$. However, the enhancement of py–Ag$_{4V}$ is quite different from those mentioned above, although the profile of the SERS is alike. Obviously, the enhancement factors of py–Ag$_{4V}$ are 10–100 times larger than those of py–Ag$_{4L}$ and py–Ag$_{4S}$ in most vibrational modes. For instance, the A$_1$ mode at 1067 cm$^{-1}$ is increased by a factor of $2.6 \times 10^4$ for py–Ag$_{4V}$, whereas the enhancement factors are $3.5 \times 10^2$ and $4 \times 10^3$ for the corresponding modes of py–Ag$_{4L}$ and py–Ag$_{4S}$, respectively. These discrepancies in enhancement factor are mainly attributed to the hot-site effect of $T_d$ Ag$_4$ cluster.

4. Conclusion

We adopt quantum chemistry methods to study the pyridine–Ag$_x$ (X=L, S, V) complexes for adsorption site effect on the CT resonance Raman enhancement. When the incident light is close to the energy of the CT excitation states, the pre-SERS spectra of three complexes are calculated and compared with those NRS spectra. These results indicate that the adsorption site has strong influence on the intensity of SERS spectra, and also the CT resonance Raman enhancement is one of indispensable ingredients in SERS enhancement. The order of enhancement for SERS is up to $10^6$ to $10^7$ for several vibrational modes. Simultaneously, a theoretical methodology called CDDs is adopted in describing the CT between molecule and metal cluster which is thought to be the direct evidence for chemical enhancement of SERS spectra. The results reveal the relationship between chemical enhancement and the CT transition.

Acknowledgments

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