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Chemical Enhancement on Surface-Enhanced Resonance Raman Scattering of Au$_3$-1,4-Benzenedithiol-Au$_3$ Junction

Xiu-ming Zhao$^a$, Xiao-rui Tian$^b$, Sha-sha Liu$^c$, Yuan-zuo Li$^{a,b}$, Mao-du Chen$^a$ *

a. School of Physics & Optoelectronic Technology, College of Advanced Science and Technology, Dalian University of Technology, Dalian 116024, China
b. Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
c. Department of Chemistry, Northeastern University, Shenyang 110004, China

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Surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS) spectra of the 1,4-benzenedithiol molecule in the junction of two Au$_3$ clusters have been calculated using density functional theory (DFT) and time-dependent DFT method. In order to investigate the contribution of charge transfer (CT) enhancement, the wavelengths of incident light are chosen to be at resonance with four representative excited states, which correspond to CT in four different forms. Compared with SERS spectrum, SERRS spectra are enhanced enormously with distinct enhancement factors, which can be attributed to CT resonance in different forms.

Key words: Surface-enhanced Raman scattering, 1,4-Benzenedithiol molecule, Surface-enhanced resonance Raman scattering, Charge transfer

I. INTRODUCTION

Decades ago, surface-enhanced Raman scattering (SERS) was discovered [1, 2]. The Raman scattering is tremendously enhanced when a molecule adsorbed on the rough surface of noble metal. Because of its high sensitivity and potential in providing useful information regarding metal-adsorbate interactions, SERS is evolved as a useful tool in single-molecular detection [3−6]. In general there are two kinds of enhancement mechanisms accepted to explain the enormous enhancement in SERS spectra. One is electromagnetic enhancement mechanism (EM) which arises from the extremely high local fields due to the strong surface plasmon resonance of curved metal surfaces coupled to the incident light [7, 8]. The EM can get the enhancement factor in the order of $10^4$−$10^6$, even to $10^{12}$−$10^{14}$ at single-molecular SERS (SM-SERS) [9]. The other is chemical enhancement that can be attributed to charge transfer (CT) between the metallic surface and the adsorbed molecule [10−16]. In brief, the transfer of electrons from the metal to a molecular orbital on the adsorbate will change the potential in the molecule and increase the effective polarizability of the molecule, which results in some Raman peaks being enhanced enormously. The enhancement factor of chemical enhancement mechanism (CM) is only the order of about $10^2$ in previous reports, but recent study reported by Zhao et al. demonstrated that the chemical enhancement can reach the order of $10^5$ [17]. Therefore this effect cannot be ignored in total enhancement for its reflecting the electronic structure of the metal surface and the chemical nature of the molecule.

Since SERS was discovered, there have been a large number of experimental and theoretical researches about chemical enhancement mechanism for SERS [18−25]. In 2006, Fromm et al. explored the chemical enhancement for SERS with Au bowtie nanoantennas [26]. They found a small number of p-mercaptoaniline molecules on a single bowtie show chemical enhancement more than $10^7$, which is due to CT between Au surface and molecule. In recent years, more attention had been paid to the SERS mechanism since the observation of Raman lines apparently arising from single molecules adsorbed onto colloidal Ag and Au nanoparticles. Wu and co-workers reported a quantum chemical study of pyridine interacting with copper, silver, gold, and platinum metals [27]. The result showed that the relative Raman intensities of SERS spectra depend strongly on the electronic property of metal materials, the binding interaction between pyridine and the SERS active centers, and incident wavelengths. This study helps us go deep into understanding the chemical enhancement mechanism. Another report makes the study of the chemical enhancement mechanism brilliant and exciting, which was reported by Zhao et al. recently [17]. They presented an investigation of the adsorption and Raman spectra of a pyrazine molecule located at

*Author to whom correspondence should be addressed. E-mail: mdchen@dlut.edu.cn
the junction between two Ag20 clusters using time-dependent density functional theory (TDDFT) method. In previous reports, the enhancement factor of chemical enhancement is only of the order about 10². Surprisingly, in their work, the chemical enhancement is found to account for as much as 10⁵ [17], suggesting that this mechanism might be more important than that previously believed. Since then, the model such as a metal-molecule-metal junction was adopted in a large number of researches for normal and enhanced Raman scattering [28–34].

Although there have been so many experimental and theoretical studies, there are still lacking in the researches about the contribution of CT in different forms (such as, the CT from molecule to cluster, cluster to molecule, molecule to molecule and cluster to cluster CT). To gain a deep insight into CM, we adopted the 1,4-benzenedithiol (1,4-BDT) molecule located at the junction between two Au₃ clusters as a model for this work. When the 1,4-BDT molecule interacted with gold clusters, the −SH group easily spits to form Au−S bond [28], because the molecule is terminated with two thiol groups that bind strongly to gold clusters. Besides, its symmetric structure gives strong SERS signal.

In this work, we measured the normal Raman scattering (NRS) spectrum of 1,4-BDT powder and SERS spectrum of 1,4-BDT in Au sol solution. In addition, we calculated the NRS spectrum of 1,4-BDT and surface-enhanced resonance Raman scattering (SERRS) spectrum of 1,4-BDT-Au₃ junction by density functional theory (DFT) and TDDFT methods and discussed the contributions of CT mechanism. Besides, the COSMO approach has been used to investigate the solvent effect that influences the spectral properties of the 1,4-BDT molecule and the Au₃-1,4-BDT-Au₃ junction.

II. EXPERIMENTS

The 1,4-BDT was purchased from Alfa Aesar. The aqueous Au colloid (diameter is 60 nm) was purchased from BB International. 30 µL (1 mmol/L) ethanol solution of 1,4-BDT was added dropwise into 30 µL Au sol solution. The solution of 1,4-BDT in aqueous Au colloid (10 µL) was introduced into glass slide for SERS measurement. SERS spectra were recorded by the Renshaw inVia Raman system equipped with an integral microscope (LEICA, DMLM). In our Raman experiment, the 632.8 nm laser was irradiated on the SERS sample with 100 times objective. Raman scattering was detected using a peltier cooled CCD detector (576×384 pixels). Data acquisition time used in the experiment was 10 s.

III. COMPUTATIONAL METHODS

All quantum chemical calculations presented in this work are performed with Amsterdam density functional (ADF) [36]. The ground state geometries are optimized using DFT [37] with Becke-Perdew (BP86) exchange-correlation functional [38, 39]. A triple-ξ polarized Slater-type (TZP) basis set from the ADF basis library is chosen to optimize ground state geometry, with the 1s-4f core remained frozen for Au. The calculations for adiabatic electronic state optical absorption of 1,4-BDT and Au₃-1,4-BDT-Au₃ junction are carried out by the TDDFT method [40] with the same functional and basis set as ground state, and only singlet-singlet excitations are calculated. The vibrational frequencies and normal modes are calculated within the harmonic approximation. The BP86 functional is chosen because it gives harmonic frequencies close to the results of experiments [41]. No scaling of vibrational frequencies is applied in this work. There are two methods to calculate resonance Raman spectra (RRS). One is to optimize the geometry for the excited state and examine the change in molecular geometry on going from the ground state to the excited state [42–44]. The other is calculating RRS without optimizing the geometry of excited state, which has been employed by Zhao and coworkers [17, 45].

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 [46],

$$\frac{d\sigma}{d\Omega} = \frac{\pi^2}{\varepsilon_0^2} (\omega_{in} - \omega_p)^4 \frac{h}{8\pi^2 c \omega_p} \cdot \frac{S_p}{45 [1 - \exp(-h\omega_p/k_B T)]}$$

where, $h$ is Plank constant, $c$ is speed of light in vacuum, $\sigma$ is cross section, $\Omega$ is solid angle, $\varepsilon_0$ is dielectric constant in free space, $k_B$ is Boltzmann constant, $T$ is thermodynamic temperature, $\omega_{in}$ 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),

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

which is a pure molecular property and independent of experimental setup. $\omega_p$ and $\gamma_p$ are the isotropic and anisotropic polarizabilities, $Q_p$ is the $p$th normal mode. In this work, $S_p$ is directly calculated by ADF program.

The solvent effect [47] is investigated by means of the conductor-like screening model of solvation (COSMO) [48, 49] approach, which is implemented within ADF. The solvent adopted in this work is water with two main parameters, which are static dielectric constant $\varepsilon_\infty = 78.5$ and effective radius $R_{\text{solv}} = 1.9$ Å, respectively [50].
FIG. 1 Optimized geometries of (a) isolated 1,4-BDT molecule and (b) Au$_3$-1,4-BDT-Au$_3$ junction.

FIG. 2 Experimental Raman spectrum of (a) 1,4-BDT powder, (b) 1,4-BDT in aqueous Au colloid solution at an incident wavelength of 632.8 nm.

IV. RESULTS AND DISCUSSION

A. Geometry

Herein we adopt 1,4-BDT molecule located at the junction between two Au$_3$ clusters for our simulation. Kim and coworkers reported an investigation of the orientations when 1,4-BDT molecule was adsorbed on silver and gold surfaces [51]. They found that 1,4-BDT ring is parallel to the metal surface when it adsorbed to the silver surface while it has a perpendicular orientation on the gold surface. Therefore in our work we located the 1,4-BDT molecule perpendicular to the surface of the gold clusters. Figure 1 shows the optimized structures of isolated 1,4-BDT molecule and Au$_3$-1,4-BDT-Au$_3$ junction. For 1,4-BDT molecule, there are two optimized geometries with S−H bonds oriented in the same or in the opposite direction, which are rather close in energy. In this work, the 1,4-BDT molecule presented a geometry structure with two S−H bonds oriented in the same directions. When the 1,4-BDT molecule interacted with gold clusters, the −SH group easily spitted to form Au−S bond, which came into being the Au$_3$-1,4-BDT-Au$_3$ junction.

B. NRS spectra and SERS spectra

The experimental NRS spectrum of isolated 1,4-BDT powder and the SERS spectrum of 1,4-BDT adsorbed on Au nanoparticles in water excited at 632.8 nm are shown in Fig.2. The Raman peak at 2555 cm$^{-1}$ in Fig.2(a) is the S−H vibrational mode of isolated 1,4-BDT powder. Figure 3 shows the calculated NRS spectrum of isolated 1,4-BDT molecule and the SERS spectrum of Au$_3$-1,4-BDT-Au$_3$ junction in water at 632.8 nm using COSMO approach. As shown in Fig.2 and Fig.3, the profiles of calculated spectra agree well with those of experimental spectra. Compared with the NRS spectrum of isolated 1,4-BDT, the Raman intensities of SERS spectrum of Au$_3$-1,4-BDT-Au$_3$ junction in water are enhanced by two orders of magnitude. Because of the coupling interaction between 1,4-BDT and the Au$_3$ clusters, the charge is redistributed as forming the junction. This charge redistribution results in increased static electronic polarizabilities (Table I), which directly influences the static chemical enhancement to NRS (Fig.3). As shown in the absorption spectra (Fig.4), the wavelengths of all the excited states are far away from 632.8 nm (wavelength of incident light), which means there is no resonant effect on NRS of 1,4-
FIG. 4 The optical absorption spectra of (a) isolated 1,4-BDT molecule and (b) Au$_3$-1,4-BDT-Au$_3$ junction.

FIG. 5 Molecular orbitals of Au$_3$-1,4-BDT-Au$_3$ junction for the 4A, 10A, 35A, and 46A electronic transitions, where the blue and red represent different phases of wave functions for HUMOs, and the green and orange represent different phases of wave function for LUMOs. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

TABLE I The calculated static polarizabilities of 1,4-BDT molecule and Au$_3$-1,4-BDT-Au$_3$ junction.

<table>
<thead>
<tr>
<th></th>
<th>$xx$</th>
<th>$yy$</th>
<th>$zz$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-BDT</td>
<td>175.460</td>
<td>100.339</td>
<td>60.412</td>
</tr>
<tr>
<td>Au$_3$-1,4-BDT-Au$_3$</td>
<td>437.478</td>
<td>435.120</td>
<td>328.998</td>
</tr>
</tbody>
</table>

BDT and SERS of Au$_3$-1,4-BDT-Au$_3$ junction. Therefore, the enhancement of SERS at 632.8 nm can be attributed to the static chemical enhancement.

C. Absorption spectra

The absorption spectra of isolated 1,4-BDT molecule and the Au$_3$-1,4-BDT-Au$_3$ junction in water solution have been calculated by means of TDDFT method and COSMO model (Fig.4). It is found that the optical absorption of isolated 1,4-BDT is in the ultraviolet region (Fig.4(a)). When the molecule absorbed to the metal cluster, the absorption spectrum presents remarkable red shifted. As a result of the interaction between gold clusters and the 1,4-BDT molecule, some new excited states occur, including 4A, 10A, 35A, and 46A excited states with large intensities (Fig.4(b)). According to the components of orbital transitions in electronic excitations and the density of state on these orbitals (shown in Table II and Fig.5), these states are CT states of molecule to cluster, cluster to cluster, molecule to molecule, and cluster to molecule excitation, respectively. The energies of these four excited states have been chosen as the energies of incident lights in the SERRS calculation, since they not only have large intensities but also represent four kinds of excited states.

D. SERRS spectra

To study the CT resonance enhancement, the wavelengths of incident light have been chosen as 277.9,
FIG. 6 Calculated SERRS spectra of Au₃-1,4-BDT-Au₃ junction with incident lights. (a) λ=277.9 nm, 46A excited state, cluster→molecule, (b) λ=305.9 nm, 35A excited state, molecule→molecule, (c) λ=428.5 nm, 10A excited state, cluster→cluster, (d) λ=534 nm, 4A excited state, molecule→cluster.

TABLE II Four electronic transitions in the form of CT.

<table>
<thead>
<tr>
<th>Electronic transitions</th>
<th>λ/Å</th>
<th>f</th>
<th>Components of orbital transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A (molecule→cluster)</td>
<td>534.0</td>
<td>0.225056</td>
<td>84.1% (77a→80a), 12.5% (76a→81a)</td>
</tr>
<tr>
<td>10A (cluster→cluster)</td>
<td>428.5</td>
<td>0.233147</td>
<td>48.0% (76a→81a), 17.4% (74a→79a), 13.9% (75a→80a)</td>
</tr>
<tr>
<td>35A (molecule→molecule)</td>
<td>305.9</td>
<td>0.089361</td>
<td>53.5% (75a→82a), 30.8% (77a→87a)</td>
</tr>
<tr>
<td>46A (cluster→molecule)</td>
<td>277.9</td>
<td>0.100004</td>
<td>78.1% (73a→82a)</td>
</tr>
</tbody>
</table>

305.9, 428.5, and 534.0 nm, respectively, which are corresponding to four representative CT exited states of Au₃-1,4-BDT-Au₃ junction mentioned 4A, 10A, 35A, and 46A. The calculated SERRS spectra of Au₃-1,4-BDT-Au₃ junction are shown in Fig. 6. As the results show, the profiles of SERRS spectra calculated with corresponding incident light are significantly different from each other. For all the four SERRS spectra, Raman intensities are enhanced significantly with different enhancement factor, compared to the SERS spectrum. Some Raman peaks of the SERRS spectra are enhanced enormously. For instance, the vibrational modes at 932, 1040, 1153, and 1368 cm⁻¹ are strongly enhanced, which are C–H out-plane deformation, ring breathing, C–H in-plane deformation and C–C stretching motions, respectively. All the enhancements of these vibrational modes can exceed the magnitude order of 10⁴, compared to the intensities of SERS spectrum. The selective huge enhancement should be attributed to the contribution of chemical enhancement, which couldn’t be interpreted by the electromagnetic enhancement mechanism.

Herein, we pay attention to the SERRS spectra of Au₃-1,4-BDT-Au₃ junction at 277.9 and 534.0 nm, which are corresponding to the energy of 46A excited state and 4A excited state, respectively. 46A is a (cluster to molecule) CT excited state (see Table II and Fig. 5). As a result of resonance between the incident light and the CT state, Raman intensities of SERRS spectra at 277.9 nm (Fig. 6(a)) are enhanced significantly by the magnitude order of 10⁴ at least, compared to the SERS spectrum of Au₃-1,4-BDT-Au₃ junction. In particular, the intensities of the vibrational modes at 1153 and 1263 cm⁻¹ are higher than those of the other three SERRS spectra by one order of magnitude. When the wavelength of incident light is 534 nm, corresponding to the 4A excited state, which is a molecule to cluster CT excited state, the SERRS spectrum (Fig. 6(d)) is remarkably different from SERRS spectrum at 277.9 nm. For the vibrational mode at

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1040 cm\(^{-1}\), enhancement of Raman intensities of the former is one order of magnitude higher than that of the latter. However, it is on the contrary for the modes at 1153 and 1544 cm\(^{-1}\). In brief, for SERRS spectra at 277.9 and 534.0 nm, the enhancement of resonant Raman intensities arises from resonant enhancement via CT from cluster to molecule and on the reverse direction. Raman intensities of different vibrational modes are enhanced by distinct enhance factor, which shows the evidence for CT enhanced mechanism.

Figure 6(b) shows the resonance Raman spectra of Au\(_3\)-1,4-BDT-Au\(_3\) junction at 305.9 nm, which is corresponding to the energy of 35A excited state. 35A excited state is the mixed state (intramolecular excitation and molecule to cluster charge transfer excitation), in which the intramolecular excitation is dominant. It can be seen in Table II and Fig.6 the enhancement of resonance Raman intensities at 305.9 nm is one order of magnitude smaller than the other three SERRS spectra. Because the oscillator strength of 35A state is weaker than that of the others, the resonance between incident light and excited state is not as strong as that of the others.

The SERRS spectrum of Au\(_3\)-1,4-BDT-Au\(_3\) junction at 428.5 nm (Fig.6(c)) has the highest enhancement factor of Raman intensities in the four SERRS spectra. Compared to the SERS spectrum of Au\(_3\)-1,4-BDT-Au\(_3\) junction, the resonance Raman intensities are enhanced by the magnitude order of 10\(^5\). The energy of incident light at 428.5 nm is corresponding to the 10A excited state, which is a cluster to cluster CT excited state. This excited state has the largest oscillator strength (Table II), so the resonance between incident light and excited state is the strongest, result in the highest enhancement of Raman intensities. Compared to the NRS spectrum, the Raman prop-

VI. ACKNOWLEDGMENTS

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In summary, the chemical enhancement of the Raman spectra of 1,4-BDT molecule at the junction between two Au\(_3\) clusters have been investigated experimentally and theoretically. The results calculated in this work agree well with the experimental data. Because of the interaction between 1,4-BDT molecule and gold clusters, the static polarizabilities increase greatly, which are the main factors of ground state enhancement in NRS spectrum. The COSMO approach is employed to investigate the solvent effect for Raman properties. Compared to the NRS spectrum, the Raman intensities of SERRS spectra are enhanced enormously, in which the enhancement of SERRS spectrum with incident light at 428.5 nm is the highest. For the SERRS spectra at 277.9 and 534 nm, the enhancement is mainly due to the CT resonance enhancement arising from the new produced CT excited states which are resonant with the incident light. In the case of SERRS spectrum at 428.5 nm, the enhancement is contributed by electromagnetic enhancement and CT resonance enhance-


