Darling–Dennison resonance of thiourea adsorbed on the silver electrode revealed by surface enhanced Raman spectroscopy

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We report surface enhanced Raman spectroscopy (SERS) of Darling–Dennison resonance of thiourea on Ag electrode excited at 514.5 nm laser excitation. Darling–Dennison resonance indicates that two degenerate Raman modes interact with each other and their degenerate first-order overtone modes obtain energy and appear in Raman spectra. Our study showed that the ratio of intensity of the Darling–Dennison resonance is up to 0.24 of its fundamental Raman intensity, when the applied electrode voltage is at \(-0.4\) V versus the saturated calomel electrode. This phenomenon was also observed on the Ag island film surface at ambient condition. These observations demonstrated strong evidence for Darling–Dennison resonance band in SERS. The implications of these observations are also discussed. Copyright © 2013 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: surface-enhanced Raman scattering; combinational resonance bands; Darling–Dennison resonance

Introduction

In the past years, there has been great progress both experimentally and theoretically in the surface enhanced Raman scattering (SERS)\textsuperscript{[1–3]} and tip-enhanced Raman spectroscopy (TERS).\textsuperscript{[4–12]}

Due to the high sensitivity of SERS and TERS in detecting the adsorbates on the metal interfaces even at the level of single molecules, there has been wide application of this novel technique in surface science, electrochemistry, material science and biochemistry.\textsuperscript{[1–19]} In general, it is considered that there are two enhanced mechanisms in SERS: the charge transfer\textsuperscript{[13–17]} and electromagnetic effects.\textsuperscript{[1–3]}

The former mechanism regards that the electron shuttle between the adsorbed molecule and the metal surface is the cause while the latter regards that the high electromagnetic field around the tips (kinks) on the roughened surface is responsible for SERS. The combination resonance band has been scarcely observed in SERS\textsuperscript{[18]}, and in quite a long time, people have attributed its weakness or absence as a characteristic of SERS. Meanwhile, the combinatorial modes and the unexpected overtone peaks can not be easily assigned theoretically in these linear enhanced Raman spectra, which severely hinder the application of this technology of finger print spectral analysis. These ‘additional’ Raman peaks result from different mechanisms, and it is difficult to distinguish and attribute them. For example, Fermi resonance\textsuperscript{[19,20]} Darling–Dennison resonance\textsuperscript{[18,21]} and Coriolis coupling\textsuperscript{[21]} can result in appearances of the overtone and/or combinational modes in SERS and TERS, due to the strong anharmonicity of molecular vibrations. However, few report concerning the condition for the combination resonance band and overtone show up.\textsuperscript{[18]}

To clearly interpret these unexpected ‘additional’ Raman peaks, thiourea (TU) molecule is employed, which may arouse interest in anharmonic research. TU molecule is such a species which shows significant SERS. The interactions between the adsorbed TU molecule and the silver surface have been studied.\textsuperscript{[22–28]}

It is concluded that that TU molecule is bonded to the metal surface via its S atom. About its adsorption orientation on metal, Fleischmann\textsuperscript{[20]} reported an orientation that it is essentially perpendicular to parallel with increasing negative potential. Tian and coworkers\textsuperscript{[25]} proposed an orientation slightly inclined to the surface at an intermediate angle based on the observation of the out-of-plane bending band. Liu \textit{et al.} reported that TU was adsorbed on the electrode via the S atom with a tilted orientation from bond polarizability derivatives elucidated from the Raman intensities.\textsuperscript{[27]} For this simple molecule, \(N = 8\), so there are total of 18 normal modes which can be observed in spectra. For the other ‘additional’ Raman peaks, they should be nonlinear Raman peaks in the enhanced Raman peaks, and it can be possibly distinguished.

In this paper, we try to interpret these observed ‘additional’ nonlinear Raman peaks of TU in SERS. The detailed experimental processes and theoretical calculations were described detailed in the next section. The observation shows that the Darling–Dennison resonance band is exceedingly strong \(I_{\text{combination}} / I_{\text{fundamental}} \approx 0.24\) at \(-0.4\) V versus the saturated calomel electrode (SCE) and applied voltage dependent on both its Raman shift and intensity. To the best of our knowledge, this observation is unusual if one notices that few SERS-combination resonance band have been reported previously. Hildebrand \textit{et al.}\textsuperscript{[22]} have...
measured signal from fundamental Raman scattering of R6G on colloidal silver, which are approximately 10 times stronger than the overtone signals. We consider that the coupling effect of Darling–Dennison resonance is significant in our understanding the SERS mechanism.

**Experimental and theoretical**

Our experiment was typical. The Raman spectra were recorded with a Renishaw R-2000 micro-spectrophotometer equipped with a CCD detector. A 50x long working-length objective was used to perform an 180° backward scattering configuration. The excitation source was the 514 nm line of a Spectral-Physics Ar⁺ laser. The power of laser on the sample was about 4 mW. The slit-width was 25 μm, and the integral time was 20 s.

A tri-electrode cell was used to perform the oxidation–reduction cycles (ORCs). The working electrode was an Ag plate with 99.9% purity. An SCE was employed as the reference and a platinum wire was employed as the counter electrode. All chemicals were of analytical grade, and all solutions were prepared using triply distilled water. The electrode potential was controlled with a HDV-7 potentiostat made in China.

The Ag electrode surface was first mechanically polished using alumina powder of particle size about 0.5 μm and then washed with distilled water before it was mounted in the cell filled with 0.1 M KCl solution. Several ORCs were performed with a double potential step: −0.2 V to +0.3 V, kept for 30 s at +0.3 V and then back to −0.2 V. This ex situ pretreatment was performed to form a relatively stable silver surface which could sustain rather constant Raman intensity for measurement. After this, the Ag electrode was immersed in a solution of 0.1 M TU with KCl for constant Raman intensity for measurement. After this, the Ag electrode was immersed in a solution of 0.1 M TU with KCl for SER measurement.

The SER intensities were corrected by an intensity-correction file attached to the data acquisition system of the Raman spectroscopic system (Renishaw, Invia), and the incident wave-source was the 514 nm line of a Spectral-Physics Ar⁺ laser. A 50× long working-length objective was used to a CCD detector. A 50× long working-length objective was used to a CCD detector. A 50× long working-length objective was used to a CCD detector. The power of laser on the sample was about 4 mW. The slit-width was 25 μm, and the integral time was 20 s.

The substrate was prepared by evaporating 100 nm silver film to a newly cleaned mica film under high vacuum. The film was immersed in a 1 × 10⁻⁵ M TU in ethanol solution for 24 h, respectively, and then washed with ethanol for 10 min to guarantee that there was only one monolayer of molecules adsorbed on the silver film. Then, the sample was immediately put into the high vacuum chamber. To get a good signal-to-noise ratio, the SERS signals were collected with an acquisition time of 40 s and accumulated 20 times for each spectrum. We also measured normal Raman scattering spectra of TU powder and ambient SERS of TU adsorbed on Ag film at the concentration of 10⁻⁴ M, using Leica microscopy equipment in a confocal Raman spectroscopic system (Renishaw, Invia), and the incident wavelength is 632.8 nm.

Theoretical simulations were done with density functional theory,[29] B3LYP functional,[30] 6-31G(d) basis for S, C and N, LANL2DZ basis[31] for Ag. The cluster of Ag₂₀ tetrahedron[14] is used for metal substrate. All of quantum chemical calculations were done with Gaussian 09 software.[32] The optimized geometry of TU–Ag₂₀ complex can be seen from supporting information (Table 1).

**Results and discussion**

Figure 1 shows the SERS spectra of TU on Ag electrode (b–h) along with that the normal Raman spectra (a) of solid TU. Assignment of the different vibrational bands is performed by referring the literature.[33] The Raman spectrum of solid TU exhibits five strong bands in the frequency region 200–1600 cm⁻¹. Bands at 3, 5 and 8, 9, 10 are assigned as NCN bending (479 cm⁻¹), SCNN bending out of face (600 cm⁻¹), CS stretching (735 cm⁻¹) and strong coupling of NCN stretching with the NH2 group rocking (1094 cm⁻¹); NCN symmetric stretching modes (1385 cm⁻¹), respectively, which are the fundamental Raman modes. These fundamental vibrational modes can be seen from Fig. 2. Others three bands 2, 4, 10 are also evident at 403 cm⁻¹ (NH₂ torsion), NH₂ swaggling (497 cm⁻¹) and NCN antisymmetric stretching modes (1497 cm⁻¹). In Fig. 1, it is found that there are two additional Raman peaks around 935 and 976 cm⁻¹, which are strongly dependent on electrode voltages.

The 976 cm⁻¹ band can be assigned as Darling–Dennison resonance of 3 and 4, which perturbed each other, due to strong coupling. Shown in Fig. 1 are also their intensity variations (the intensity of band 5 at −0.8 V is scaled as 100). These intensities attain their maxima at −0.8 V and drop greatly as the voltage reaches −1.0 V. The observation shows that the Darling–Dennison resonance band (796 cm⁻¹) is exceedingly strong (I(combination/ fundamental) ≈ 0.24 at −0.4 V versus the SCE. It is noted that, in 933 cm⁻¹, the Raman line comes from the electrolyte anion ClO₄⁻, which is assigned to its totally symmetric stretching of ClO₄⁻[29].

The SERS spectrum in Fig. 1 also shows it is a very intense band, despite no changes of the frequency of this band compared to the free anion; the enhanced band intensity indicates the coadsorption of this species with TU.

To reveal the origin of Darling–Dennison resonance band in electrochemical SERS of TU in Fig. 1, we measured the SERS spectrum of TU adsorbed on Ag island film at ambient condition.
with excitation wavelength 632.8 nm. (see Fig. 3). It is found that the Darling–Dennison resonance at 970 cm$^{-1}$ can be obtained which is attributed to the Raman peaks of TU 3 and 4. As shown in Table 1 (all the predicted bands by simulation). According to theoretical calculations and the experimental results, these two first overtone modes were shifted 30 and 7 cm$^{-1}$, respectively. One of the most striking features is the observation of a new band located at ca. 250 cm$^{-1}$ in the low-frequency region (the band 1). It does not correlate with any intramolecular vibrational bands of TU but relates to the metal-adsorbate vibrations, which is indicative of the strong interaction of TU with Ag surface.

The Raman intensity of Darling–Dennison resonance is, in general, very small, only 10$^{-2}$ of the fundamental. In SERS, the intensity is reported, at most, as large as one tenth of the fundamental.$[28]$ In our case, the Darling–Dennison resonance band intensity is unusually strong up to 0.24 of the fundamental. This observation is intimately related to the very delicate mechanism of SERS which needs further exploration, though it was argued that the overtone and combination band is due to resonance$^{[34,35]}$ originated from the electron–hole pair coupling in the surface plasma by the laser excitation.

### Table 1. All the predicted bands by simulation

<table>
<thead>
<tr>
<th>Predicted SERS bands (in cm$^{-1}$)</th>
<th>Attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>315.5</td>
<td>NH$_2$ rocking</td>
</tr>
<tr>
<td>397.4</td>
<td>NH$_3$ rocking</td>
</tr>
<tr>
<td>414.6</td>
<td>SCN bending</td>
</tr>
<tr>
<td>470.2</td>
<td>NCN bending</td>
</tr>
<tr>
<td>490.4</td>
<td>NH$_2$ swagging</td>
</tr>
<tr>
<td>606.7</td>
<td>SCN out-of-plane bending</td>
</tr>
<tr>
<td>644.1</td>
<td>SCN out-of-plane bending</td>
</tr>
<tr>
<td>753.3</td>
<td>SC stretching</td>
</tr>
<tr>
<td>1093.0</td>
<td>NH$_2$ rocking</td>
</tr>
<tr>
<td>1101.1</td>
<td>NH$_2$ rock and NCN stretching</td>
</tr>
<tr>
<td>1429.7</td>
<td>NH$_2$ rock and SC stretching</td>
</tr>
<tr>
<td>1501.5</td>
<td>NCN asymmetric stretching</td>
</tr>
<tr>
<td>1681.5</td>
<td>NH$_2$ deformation</td>
</tr>
<tr>
<td>1705.7</td>
<td>NH$_3$ deformation</td>
</tr>
</tbody>
</table>

In summary, the nonlinear enhanced Raman spectra were obtained, and the combinational modes which attributed to Darling–Dennison resonance were observed in SERS on electrode and on silver island film, respectively, due to strong anharmonicity. The Raman intensity of the Darling–Dennison resonance is, in general very small, only 10$^{-2}$ of the fundamental. In SERS, few cases were reported on the Darling–Dennison resonance on the coupling of metal surface and molecule, as well as with its intensity, at most, as large as one fifth of the fundamental. This observation is intimately related to the very delicate mechanism of SERS which needs further exploration. Similar to the overtone mode, this combination mode may be originated from the electron–hole pair coupling in the surface plasma by the laser excitation. There are much more Raman peaks than the fundamental modes, providing more information for finger print analysis. So, these unexpected ‘additional’ nonlinear Raman spectrum can be rationally interpreted and extended the application of SERS in the application of enhanced Raman spectroscopy in the fields of surface and material science.
Acknowledgement

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References