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Surface-enhanced Raman Scattering of Aflatoxin B₁ on Silver by DFT Method

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The structure, electrostatic properties, and Raman spectra of aflatoxin B₁ (AFB₁) and AFB₁-Ag complex are studied by density functional theory with B3LYP/6-311G(d,p)/Lanl2dz basis set. The results show that the surface-enhanced Raman scattering (SERS) and pre-resonance Raman spectra of AFB₁-Ag complex strongly depend on the adsorption site and the excitation wavelength of the incident light. The SERS factors are found to enhance $10^{2}-10^{3}$ order compared to normal Raman spectrum of AFB₁ molecule due to the larger static polarizabilities of the AFB₁-Ag complex, which directly results in the stronger chemical enhancement in SERS spectra. The pre-resonance Raman spectra of AFB₁-Ag complex are explored at 266, 482, 785, and 1064 nm incident light wavelength, in which the enhancement factors are about $10^{2}-10^{4}$, mainly caused by the charge-transfer excitation resonance. The vibrational modes are analyzed to explain the relationship between the vibrational direction and the enhanced Raman intensities.

Key words: Aflatoxin B₁, Surface-enhanced Raman scattering spectrum, Pre-resonance Raman spectra, Density functional theory

I. INTRODUCTION

Aflatoxins (AFs) are a group of hepatoxic, carcinogenic, mutagenic, and teratogenic mycotoxins, which are mainly produced by Aspergillus flavus, A. parasiticus, and A. nomius [1]. As the most common mycotoxins detected in human food and animal feed, AFs have drawn an increasing attention because of their frequent occurrence in cereal, cotton and groundnuts [2]. Among more than 20 AFs derivatives, aflatoxin B₁ (AFB₁) has the most powerful toxicity and carcinogenicity to animals and human, which can cause malignant tumors in various animals and primary hepatocellular carcinoma in human [3]. The toxicity and carcinogenicity of AFB₁ are associated with its DNA binding properties, as well as its teratogenic properties to cause malformations in many organs in embryos [4].

In order to remove or destroy the toxin, many chemical, biological, and physical methods are used to detect AFs in contaminated crops [5]. Recently some novel biosensors based on surface plasmon resonance [6], for example surface enhanced Raman scattering (SERS) [7–9], have been developed to implement the rapid detection of chemical and biological samples. SERS, firstly observed by Fleischmann et al. in 1974, has been employed successfully for qualitative micro analyses because of the high sensitivity and selectivity [10–12]. However, it is not easy to apply SERS to quantitative microanalyses because of the intensity and a band shift of the enhancement of a Raman spectra depending on the vibrational mode [13]. Different vibrational modes correspond to different intensity and band shift. The SERS is affected by the molecular structural changes and the conditions of a metal colloid or a substrate. Based on metallic nanostructure substrates [14], the enhancement factor induced by nanostructure can reach as much as 14 to 15 orders of magnitude, which allows the SERS technique to be sensitive enough to detect small amount of molecules, even single molecule [15, 16]. AFB₁ is a Raman-active compound which can be detected or identified by SERS microscopy after capturing. Some experiments on the SERS technique have been performed to detect and track aflatoxins toxin by our cooperation group [17].

In order to explore the SERS mechanism of AFB₁ adsorbed on Ag nanoparticles, density functional theory (DFT) method is used to analyze the AFB₁-Ag complex structures and properties. The SERS spectra and pre-resonance Raman spectra of AFB₁ molecule have been calculated to explore the SERS enhance efficiency of single AFB₁ molecule absorbed on Ag nanoparticles.

II. COMPUTATIONAL METHODS

The simple microscopic active adsorption site modes are adopted to simulate the AFB₁ molecule adsorbed on the Ag nanoparticle. Two adsorption sites of AFB₁,
are considered in this work. The structures of AFB$_1$ and AFB$_1$-Ag complex are optimized using 6-311G(d,p) basis set for C, H, O atoms and Lanl2dz [18] ECP basis set for Ag atom with 1s-4p core kept frozen at the B3LYP level [19–21]. The B3LYP method is a hybrid HF/DFT method using a combination of Becke’s three-parameter exchange functional (B3) with the Lee-Yang-Parr (LYP) generalized gradient correlation functional. The Berny gradient method [22] is employed in complete geometry optimization for AFB$_1$ and AFB$_1$-Ag complexes. The SERS spectra and pre-resonance Raman spectra of AFB$_1$ molecule are calculated at the same functional and basis set. The absorption spectra and the excited state electronic structures are calculated to explore the resonance incident light wavelength by using the time-dependent density functional theory (TD-DFT) [23] at the same level. To better match experimental vibrational frequencies, the vibrational scaling factor [24] 0.98 is adopted. All of the computations are performed by the Gaussian 09 program [25], in which the fine grid (75302) is the default parameter exchange functional (B3) with the Lee-Yang-Parr. The adsorption energy is defined as:

$$\Delta E = E(\text{complex}) - E(\text{AFB}_1) - E(\text{Ag})$$

When the AFB$_1$ molecule is adsorbed on Ag nanoparticle through the a adsorption site, the adsorbed energy is $-16.22$ kJ/mol, while for AFB$_1$-Ag$^b$, the adsorbed energy is much smaller than the AFB$_1$-Ag$^b$ complex ($-6.37$ kJ/mol, Table I). Therefore, the adsorption site is a more appropriate site for the AFB$_1$ molecule adsorbed on the Ag nanoparticles. Only the AFB$_1$-Ag$^a$ complex is discussed in the following section.

Because of the coupling interaction, the charges are redistributed between the AFB$_1$ molecule and Ag atom. 0.105 $e$ for the AFB$_1$-Ag$^a$ complex and 0.052 $e$ for the AFB$_1$-Ag$^b$ complex are transported from the AFB$_1$ molecule to Ag, which result in the static polarizability along x-axis being more increased, listed in Table II. Compared to the single AFB$_1$ molecule, the static polarizabilities of two complexes are increased obviously. The average static polarizabilities are increased from 246.11 to 323.68. The largest change is found for the AFB$_1$-Ag complex in the $xx$ components of the static polarizability, corresponding to C=O stretching vibrational mode. The Raman intensity is proportional to the square of the molecular induced dipole moment, while the molecular induced dipole moment is $\mathbf{P} = \alpha \cdot \mathbf{E}$, where $\alpha$ is the molecular polarizability and $\mathbf{E}$ is the external electric field. Thus when the molecular polariz-
TABLE II Calculated static polarizability in a.u. \( \langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \).

<table>
<thead>
<tr>
<th></th>
<th>( \alpha_{xx} )</th>
<th>( \alpha_{xy} )</th>
<th>( \alpha_{yy} )</th>
<th>( \alpha_{xz} )</th>
<th>( \alpha_{yz} )</th>
<th>( \alpha_{zz} )</th>
<th>( \langle \alpha \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFB1</td>
<td>388.89</td>
<td>36.31</td>
<td>238.09</td>
<td>-3.74</td>
<td>-0.03</td>
<td>111.36</td>
<td>246.11</td>
</tr>
<tr>
<td>AFB1-Ag</td>
<td>496.10</td>
<td>-40.07</td>
<td>307.32</td>
<td>1.47</td>
<td>1.34</td>
<td>167.62</td>
<td>323.68</td>
</tr>
</tbody>
</table>

\( xx, xy, yy, xz, yz, \) and \( zz \) are the direction of static polarizability, respectively.

TABLE III Comparison of vibration modes between AFB1 and AFB1-Ag complex. \( f \) is frequency and \( I \) is intensity.

<table>
<thead>
<tr>
<th>AFB1</th>
<th></th>
<th>AFB1-Ag</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( f/\text{cm}^{-1} )</td>
<td>( I )</td>
<td>( f/\text{cm}^{-1} )</td>
<td>( I )</td>
</tr>
<tr>
<td>653</td>
<td>0.34</td>
<td>655</td>
<td>3.45</td>
</tr>
<tr>
<td>928</td>
<td>19.98</td>
<td>925</td>
<td>27.47</td>
</tr>
<tr>
<td>986</td>
<td>13.56</td>
<td>986</td>
<td>19.04</td>
</tr>
<tr>
<td>1026</td>
<td>26.97</td>
<td>1031</td>
<td>75.53</td>
</tr>
<tr>
<td>1111</td>
<td>12.10</td>
<td>1112</td>
<td>19.42</td>
</tr>
<tr>
<td>1217</td>
<td>36.52</td>
<td>1235</td>
<td>120</td>
</tr>
<tr>
<td>1445</td>
<td>11.37</td>
<td>1444</td>
<td>8.55</td>
</tr>
<tr>
<td>1491</td>
<td>16.51</td>
<td>1492</td>
<td>16.15</td>
</tr>
<tr>
<td>1534</td>
<td>24.24</td>
<td>1531</td>
<td>17.80</td>
</tr>
<tr>
<td>1596</td>
<td>35.5</td>
<td>1588</td>
<td>609</td>
</tr>
<tr>
<td>1623</td>
<td>15.81</td>
<td>1613</td>
<td>103</td>
</tr>
<tr>
<td>1639</td>
<td>19.26</td>
<td>1636</td>
<td>46.62</td>
</tr>
<tr>
<td>1749</td>
<td>24.41</td>
<td>1740</td>
<td>101</td>
</tr>
</tbody>
</table>

Ability is increasing, the Raman intensity is also greatly enhanced. The static polarizabilities are one of decisive factors of the ground state chemical enhancement which is not associated with any excitation of the molecule-metal system. The calculated static polarizability in Table II predicts that the static chemical enhancement will be found in the surface-enhanced Raman spectra due to the static polarizability changes.

B. The Raman spectra of AFB1-Ag complex

The surface enhanced Raman effect is observed in the Raman spectra of AFB1-Ag complex compared to the normal Raman spectrum (NRS) of single AFB1 molecule, shown in Fig.2. The Raman peaks frequencies, the Raman intensities and the corresponding vibration assignments are listed in Table III. The profile of SERS for AFB1-Ag complex is consistent with the normal Raman spectrum, however, obvious enhanced Raman intensities are found at some vibrational modes. The vibration modes assignments in this work are consistent with the experimental results, which are obtained at the 785 nm excitation wavelength [17]. The Raman enhanced factor \( I_{EF} \) is given by \( I_{EF} = I_{SERS}/I_{NRS} \) at the corresponding vibrational modes.

According to the surface plasmon resonance theory [28], the vibrations along the direction perpendicular to the absorption surface are expected to occur more enhancement than the vibrations in the parallel direction. For the single AFB1 molecule and the AFB1-Ag complex, the peaks with the maxima enhanced intensity are found at 1596 and 1588 cm\(^{-1}\), whose Raman intensities are up to 609, belonging to the C2=C4 and C=O vibrations.
stretching vibrations of cyclopentene ring with O moving toward silver surface. The C=O (cyclopentene ring and pyrane ring) stretching vibrations of AFB$_1$-Ag complex are found at 1613 and 1740 cm$^{-1}$, whose Raman intensities are 103 and 101, respectively. While the two vibrational modes are found at 1693 and 1756 cm$^{-1}$ in experiment [17]. The C1=C18 stretching vibration in the complex is found at 1636 cm$^{-1}$, with the blue shift of 16 cm$^{-1}$ compared to the experiment. The C–C–C stretching vibration is found at 1235 cm$^{-1}$, with vibrational direction along with x-axis, resulting the Raman enhancement factors up to 120. The other vibrational modes agreed approximately with the ones in the AFB$_1$ molecule.

For AFB$_1$-Ag complex, the static polarizabilities incensement along z-axis can result in the NRS spectrum intensity enhancement due to the static chemical enhancement. Compared to the NRS of the single AFB$_1$ molecules, the enhanced SERS effects mainly result from the chemical environment modification when the AFB$_1$ molecule is adsorbed on Ag-nanoparticle. The charge redistribution and the structural perturbation lead to greater increases of the static polarizabilities in the complex. Therefore, the enhancement mechanism of SERS for AFB$_1$ molecule can be ascribed to the ground state chemical enhancement.

C. Pre-resonance Raman spectra of AFB$_1$-Ag complex

When the incident light wavelength is close to the molecule electronic excitation energy, the incident electronic field can excite the electron transition to induce resonance, which leads to the Raman scattering signal intensity enhanced by a factor up to $10^4$–$10^5$. This process is referred as the resonance Raman scattering, in which the enhancement is proportional to the oscillator strength of the electron transition. For the AFB$_1$-Ag complex, the metal-molecule charge transfer (CT) is found due to the interaction between the molecule and the metal when the molecule is adsorbed on the metal nanoparticle surface.

According to the absorption spectra of the AFB$_1$-Ag complex, 266 and 482 nm incident wavelengths, in the proximity of the two absorption maxima of AFB$_1$-Ag complex, are chosen to explore the pre-resonance spectrum of AFB$_1$-Ag complex. Meanwhile 785 and 1064 nm incident wavelengths, which are away from resonance absorption of the AFB$_1$-Ag complex but correspond to the S$_2$ and S$_3$ electron excitation states, are selected to compare the pre-resonance Raman spectra. The total enhancement factors are up to $10^2$–$10^3$ in pre-resonance Raman spectra of the AFB$_1$-Ag complex at four chosen incident wavelengths. The pre-resonance Raman spectra and molecular orbital corresponding to charge transfer between AFB$_1$ molecule and Ag atom are shown in Fig.4. Due to the charge transfer resonances between the molecule and the atom Ag, the most enhancement factor of C=O stretching vibration is up to $10^3$ at 1740 cm$^{-1}$ at the 266 nm incident light, the stretching vibration of C–C and C=O at 1588 cm$^{-1}$, the enhancement factor is only 63. But for 482 nm incident wavelength, the most enhancement factor 10$^4$ is found at 1531 cm$^{-1}$, corresponding to C–C stretching and stretching vibration of C–C–C with the wiggle of C–H. The C–C and C=O stretching vibration at 1588 cm$^{-1}$ along x-axis, the enhancement factor is up to 10$^2$. The stretching vibration of the bonds near the Ag atom (C–C, C–O–C) and C=O stretching are also obviously enhanced up to 10.

Compared to incident wavelength 266 and 482 nm, the maximum enhancement factor is up to $10^3$ at 785 nm incident wavelength, which is C–C stretching vibration with the wiggle of C–H at 1531 cm$^{-1}$ along x-axis, because of electric transfer between HOMO and LUMO of AFB$_1$-Ag complex. The C=C and C=O stretching vibration is enhanced up to $10^2$ at 1588 cm$^{-1}$, the C=O stretching vibration modes are found at 1740 cm$^{-1}$, their enhancement factor are only up to 10. For 1064 nm excitation energy, the most enhancement factor is $10^2$, corresponding to C–C stretching vibration and ring(s) skeleton vibration at 1531 cm$^{-1}$. The enhancement Raman intensities at 892, 1031, 1461, 1588, and 1593 cm$^{-1}$ are also up to $10^3$, corresponding to the pyrane ring breath vibration and C–C, C–C–C, C–O–C stretching vibration mode with ring deformation, ring(s) skeleton vibration, and the C=O stretch peaks, respectively. Therefore, when the incident light is away from resonance absorption of excitation energy, the more vibrational modes enhanced simultaneously.

Compared to the SERS intensities of isolated AFB$_1$, the enhancement due to the charge transfer resonance contributes an additional 2–4 orders of magnitude to the chemical enhancement at four chosen incident wavelengths. It is proven that the CT mechanism significantly contributes to the enhancement of pre-resonance Raman intensity, which is also used to explain the dependence of the certain bands in SERS experiments on the electrode potential [29, 30].

IV. CONCLUSION

The SERS and pre-resonance spectra of the AFB$_1$ molecule are studied by DFT method. Raman scattering intensity not only depends strongly on the local chemical environment of adsorption site but also depends on the incident excitation wavelength. The geometry structure and the adsorption energy show that a site of AFB$_1$ molecule is a more favorable adsorption site than b site. When AFB$_1$ molecule is adsorbed on silver nanoparticle by a site, the enhancement factor of AFB$_1$-Ag complex is up to $10^3$ compared to normal Raman spectrum of the isolated AFB$_1$ molecule, which results from a great change of the perpendicular polar-
FIG. 3 The pre-resonance Raman spectra of AFB\textsubscript{1}-Ag complex at four different incident light wavelengths of 266, 482, 785, and 1064 nm. The molecular orbitals corresponding to charge transfer between AFB\textsubscript{1} molecule and Ag atom are also shown.

izabilities due to the chemical environment modification in AFB\textsubscript{1}-Ag complex.

For the pre-resonance Raman spectra at the incident wavelength 266, 482, 785, and 1064 nm, the enhancement factors at some specific vibration modes are up to 10\textsuperscript{3}, which are mainly attributed to the charge-transfer excitation resonance enhancement but not the plasmon resonance of the nanoparticle because Ag atom or cluster is too small to have a real plasmon resonance. The SERS enhancement mechanism of AFB\textsubscript{1}-Ag complex can be ascribed to the chemical enhancement in which the static chemical enhancement of ground state and the charge transfer resonance enhancement of excitation state work is together due to the chemical interaction between the AFB\textsubscript{1} molecule and the Ag nanoparticle. The stronger SERS enhancements effects should be predicted for the real nanoparticles because of the combination of the chemical enhancement and the electromagnetic enhancement.

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