Surface-enhanced Raman Scattering of Ethyl Carbamate Adsorbed on Ag₂₀ Cluster: **Enhancement** Mechanism

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Abstract: The normal and surface-enhanced Raman scattering of EC are studied by using the M06-2X functional. Different contributions to Raman enhancements of EC adsorbed on Ag₂₀ cluster are analyzed in detail to explore the **enhancement** mechanism. The **adsorption of EC** on Ag₂₀ cluster involves the static chemical enhancement with enhancements factor (EF) of 10 by forming a new EC-Ag₂₀ complex. The charge-transfer enhancement with EF of 10⁴ is found when a 352nm wavelength, corresponding to the absorption maximum of EC-Ag₂₀ complex, is taken as an incident light. The electromagnetic enhancement EF of 3.6×10⁶ due to the localized surface plasmon resonance (LSPR) of Ag nanosphere at the same excitation wavelength are acquired by the discrete dipole approximation (DDA) method. The combined effect of the chemical and electromagnetic enhancement results in the total relative enhancements factor up to 3.6×10¹⁰. The **enhancement** mechanisms are successfully explained by the combination of ab initio calculation and discrete dipole appropriation method.

Keyword: Ethyl carbamate, Ag₂₀ cluster, Surface-enhanced Raman Scattering , Raman enhancements, chemical enhancements, electromagnetic enhancements

I. Introduction

Ethyl carbamate ($\text{H}_2\text{NCOOC}_2\text{H}_5$, EC, CAS No.51-79-6), also known as urethane, is a potentially toxic carcinogen contained in fermented food and alcoholic beverages, which is a by-product of the fermentation and the storage of food and beverages[1]. The carcinogenic and mutagenic effect of EC to animals was detected in the 1940s[2]. It has been classified as a group 2A carcinogen, “probably carcinogenic to humans”, by the World Health Organization’s International Agency for Research on Cancer (IARC) in 2007[3]. Researches reveal that more than $30 \times 10^{-6} \text{g/L}$ of Ethyl carbamate in wine can greatly enhance the risk of cancer[4]. The Liquor Control Board of Ontario in Canada detected that high levels of EC and introduced maximum residue level for EC in alcoholic beverages ranging from 30 to $400 \mu\text{g}^{-1}$ for the first time[5]. The USA sets maximal levels for EC of 15 mg/L in Table wines and 100 mg/L in fortified wines, respectively[6]. Therefore, the low levels of EC and the complex matrix require sensitive and selective methods to detect EC contained in the fermented food and alcoholic beverages.

The study of Ethyl carbamate started in the Mid-20th century[4], including series of measurements by the microwave, millimeter wave and infrared regions together with high-level ab initio calculations[7]. Raman scattering of molecules adsorbed on a rough metal surface can be enhanced by several orders of magnitude. This phenomenon is referred to as surface-enhanced Raman scattering (SERS) and was discovered some 30 years ago [8]. SERS takes advantages of its low detection limits, sensitivity to the molecular environment, highly enhanced vibrational signals, and good selectivity for adsorbents. Danting Yang et al.[1] have already done experimental and theoretical research on the SERS of Ethyl carbamate interacting with Ag particles. However, the previous research failed to express the SERS **enhancement** mechanisms of EC clearly. Since

the experimental conditions are highly complex, electronic structure studies of molecules adsorbed on metal surfaces have the potential to elucidate the physical phenomena involved in SERS. In this article, we adopt a 20-atom silver cluster to represent the metal surface and explore the SERS enhancement mechanisms of EC **in detail** . The mechanisms are discussed in this paper through ab initio calculation combined with the discrete dipole approximation (DDA) method based on electrodynamics principles.

II. Computational details

The SERS enhancement mechanisms usually include physical enhancement and chemical enhancement. Chemical enhancement can be explored by Gaussian 09 program package[9] via simulated the Raman spectra. The physical enhancement mechanism can be described via the local enhanced electromagnetic field distributions, calculated by the DDSCAT code [10].

Calculations including optimization and Raman vibrational frequencies presented in this work were performed with Gaussian 09 package using the M06-2X functional[11]. The effective core potential (ECP) **and basis set** LANL2DZ (Los Alamos National Laboratory 2 double zeta) is employed for Ag atom, while the all-electron basis set 6-311+g(d, p) which included polarization function and diffuse function are employed for all other non-transition-metal atoms (C, N ,O) [12]. Moreover, the absorption spectra and excited state electronic structures are simulated using the time-dependent density functional theory (TD-DFT) method[13]. To get close to the experimental results, the vibrational frequencies are scaled by a factor 0.983[14].

The differential Raman scattering cross section (DRSC) is calculated by using the equations(1) and (2) as follows [15,16]:

$$I_{\text{Raman}}^k = (2\pi)^4 (\tilde{\nu}_{\text{in}} - \tilde{\nu}_k)^4 \frac{h}{8\pi^2 c \tilde{\nu}_k} \frac{S_k}{45} \frac{1}{[1 - \exp(-hc\tilde{\nu}_k/k_B T)]} \quad (1)$$

$$S_k = 45\alpha'_k{}^2 + 7\gamma'_k{}^2 \quad (2)$$

Where h , c , k_B and T are the Planck constant, light speed, Boltzmann constant and Kelvin temperature, respectively. $\tilde{\nu}_{in}$ and $\tilde{\nu}_k$ are frequencies (in cm^{-1}) of the incident light and the k th vibrational mode. For the pre-resonance Raman spectrum of EC, 352nm is chosen as an incident light, which is corresponding to the absorption maximum of EC-Ag₂₀ complex.[8,17]. S_k is the Raman scattering factor (RSF, in $\text{\AA}^2/\text{amu}$), which is directly obtained from the Gaussian 09 package. α_k and γ_k are derivatives of isotropic and anisotropic polarizabilities with respect to a given normal coordinate, which were calculated by numerically differentiating method. Discrete dipole approximation (DDA) is a numerical method first introduced by Purcell and Pennypacker[18] and has been described in detail elsewhere[19-22]. We use the public open source program, DDSCAT code, to obtain the extinction spectra and local enhanced electromagnetic field distributions. The bulk dielectric constants of Ag are obtained from reference [23]. The extinction efficiency, $Q_{ext} = C_{ext}/\pi a_{eff}^2$, is used to describe the optical absorbance property, where a_{eff} is the effective radius of the nanoparticles and extinction cross section C_{ext} is calculated from DDA. Note that the E-field enhancement, $|E|^2/|E_0|^2$, where E_0 is magnitude of the incident field and $|E|$ is the magnitude of local electric field surrounding the nanostructure and calculated by DDA, may have an uncertainty factor of 2 to 3 uncertainty compared to the Mie theory for a sphere[24].

III. Results and discussion

1. Structures of EC-Ag₂₀ complex

The adsorption of EC onto a silver surface can occur either through N6 or O3 with lone pair electrons or through O1 by lying flat on the surface or just standing upright or inclinable on the

surface. Compared all the possible adsorption sites, EC molecule is found to be adsorbed on the silver surface by an amide group, which is consistent with the results of reference [1]. Two modes of EC molecule adsorbed on Ag atom are shown in Figure 1. The shortest distance (2.618 (Å)) between Ag atom and EC molecule corresponds to site a. Besides, the adsorption energy (-0.00805 a.u) of site a is lower than that of site b (-0.00799 a.u). Thus, the site a corresponds to the most probable configuration for the adsorption of EC on the silver surface.

The adsorption properties of a 20-atom silver tetrahedral cluster behave quite similar to the plasmon excitation observed in nanoparticles, and the Raman enhancement due to this cluster is comparable to that from large nanoparticles (>10 nm)[17,25,26]. Thus, Raman spectra of the molecule EC adsorbed on Ag₂₀ cluster is simulated to EC adsorbed on Ag nanoparticles.

Tetrahedral Ag₂₀ is a relaxed fragment of the face-centered cubic (fcc) lattice of bulk silver, which allows three different binding sites, denoted as the S-complex(surface), V-complex (Vertex) and E-complex(edge) (Figure 2). The calculated bond distances between amide group and closest silver atom are 2.657Å, 2.452Å and 2.527Å respectively. Besides, the relative total energies are 15.169(KJ/mol), 0 (KJ/mol) and 6.493 (KJ/mol) respectively. Considering the stability of the EC-Ag₂₀ complex, V-complex (Vertex) , this model was chosen for Raman calculations.

2. Normal and Surface Enhancement Raman Scattering Spectra of EC

The simulated normal spectrum, the Surface-enhanced Raman scattering and pre-resonance Raman scattering (SERRS) spectra of EC are presented in Figure 3 with the frequencies range between 200 cm⁻¹ and 3650cm⁻¹. Furthermore, a collection of important bands together with their intensities and assignments are presented in Table 1.

2.1 Normal Raman Spectrum

The simulated normal spectrum are quite similar to the experiment (Figure 3 and Table 1). Every important band in the experiment spectrum is identified in the simulated spectrum at the approximate wavenumber within the inaccuracy of 20cm^{-1} . The peaks at 3006cm^{-1} , 3032cm^{-1} and 3066cm^{-1} assigned to stretching vibration of C-H_3 and C-H_2 are consistent with the experiment. However, some discrepancies between the calculated and experimental spectrum have been found. The most noticeable difference is for the peaks at 377cm^{-1} and 780cm^{-1} assigned to strong in-plane deformation vibration of C-O-C=O and C-H wagging, which are not detected in the experimental spectra although the intensities of this two bands are weak. What's more, the frequencies of several modes shift significantly. For example, there are red shifts of 35 and 155 cm^{-1} for the EC compared with the experimental modes at 1622 and 396 cm^{-1} . In addition, there are blue shifts of 67, 72, 75, 132, and 178cm^{-1} for the EC compared with the experimental modes at 3032, 3006, 3066, 1820 and 3592 cm^{-1} . Besides, the simulated band at 3592cm^{-1} assigned to N-H_2 stretching vibration gains more intensities than the experiment while the intensities of mode at 511cm^{-1} belonged to off-plane coiling vibration of N-H_2 decreases compared with it. The differences between the observed and the calculated spectra are either due to the approximate model has been performed for the computation or to the fact that the calculation has been performed for the isolated molecule in the gas state while the experiment dealt with molecule embedded in small crystals.

2.2 Surface Enhancement Raman Spectrum

The calculated SERS spectrum of the EC is dominated by one intense peak at 3543 cm^{-1} , which corresponds to N-H_2 stretching vibration mode. The weaker peaks at 1751cm^{-1} and 3009cm^{-1} are observed belonging to C-N-H ring bending and C=O stretching vibration and C-H_3

ring stretching vibration. Comparing the SERS spectrum obtained here with the normal spectrum of EC, we find in general quite good agreement with respect to the frequencies except one band at 1751cm^{-1} with 69cm^{-1} red shift comparing to NRS spectrum. Moreover, the intensities of most bands are obviously enhanced even though the degrees being different. The most noticeable enhancement in the intensities is for bending and stretching vibration modes found at 1751cm^{-1} about 17 times. The Raman-enhanced factor (I_{EF}) is given by $I_{EF} = I_{SERS} / I_{NRS}$ at the corresponding vibration modes. The static polarizabilities which increased along x-axis and y-axis result in this phenomenon. The weaker enhancements in the intensities are observed at 231cm^{-1} , 546cm^{-1} , 3543cm^{-1} assigned to wagging, twisting and stretching of N-H₂, and another is 1360cm^{-1} assigned to the rocking of C-H₂ and bending of C-N-H. However, the intensities of some bands decrease. For example, the most noticeable decrease of intensities is for the peaks at 1167cm^{-1} , of which the I_{EF} is 0.2. EC molecule adsorbed on Ag₂₀ cluster form a new complex, which changes its electronic structure and force constants. Thus, interactions with the surface will, of course, have some effect, but past studies of the other molecules suggest that these effects can be of secondary importance[27]. The calculated SERS spectrum are quite similar to the experimental SERS spectrum[8] (Figure 3). The major difference is the surface enhancement factor of calculated mode at 1009 cm^{-1} (stretching of C-C and wagging of C-H) is smaller than the SERS experiment's. Because the solvent effect is not considered, the calculated band at 1751 cm^{-1} is not seen in the experimental spectrum.

3. Enhancement mechanisms

There are two commonly considered mechanisms for SERS, one is polarizability change result from the chemical effects such as static chemical and charge-transfer excited states, and the

other is the field intensity enhancement as a result of plasmon resonance excitation[28].

3.1 Static Chemical Enhancement

The Raman intensities are enhanced when EC adsorbed on Ag₂₀ cluster forms a new EC-Ag₂₀ complex. As a matter of fact, Raman intensity is proportional to the square of the induced molecule dipole moment, while the induced molecule dipole moment $P = \alpha \cdot E$. α is the molecule polarizability and E is the external electric field. The static polarizabilities are one of the decisive factors for the ground state chemical enhancement. Thus, the Raman intensity is greatly enhanced when static polarizabilities are greatly increased from 50.306 a.u to 1057.962 a.u while the Ag₂₀ cluster interacts with EC as Table 2 shown. All calculations are done in the static limit to ensure that there is no contribution from the resonance of the exciting wavelength with CT excitations. Therefore, any enhancement of the Raman cross section is solely due to the direct cluster-molecule chemical coupling and should reflect the static chemical enhancement mechanism.

3.2 Charge-transfer Resonance Enhancement

In Raman scattering measurements where the wavelength of the radiation is close to an electronic excitation of the molecule, the intensity of the signal can be enhanced by a factor of up to 10^4 - 10^6 . This process is referred to as pre-resonance Raman scattering, and the enhancement is proportional to the oscillator strength of the transition[17]. When the energy of the incident light is close to the gap of the metal-molecular complex's electronic transition state, the charge-transfer (CT) resonance enhancement between metal and molecular occurs.

We are particularly interested in the SERRS spectrum at the wavelength of the absorption maximum and the resonance enhancement associated with it. So, the absorption spectrums of

EC-Ag₂₀ complex is calculated by the time dependent density functional theory (TDDFT) method (Figure 4). The maximum oscillator strength of 3.00 is found with the excitation energy of 3.45eV (wavelength of 359.35 nm) by the M06-2X functional. However, the better SERRS spectrum occurred at the excitation energy of 3.52eV (wavelength of 352nm) as Figure 3 shown. The excitation energy being 0.07eV higher than 3.45eV is acceptable since M06 functional with mean unsigned error of excitations energy about 0.37 eV or less[29]. The charge is found to be transferred from Ag₂₀ to EC as Figure 5 shown.

Compared the spectrum with NRS spectrum, the main changes are in the intensities but the spectrum looks quite similar. Due to resonances with the silver cluster, many previously “silent” modes get an enhancement of around 10^5 and CT resonance enhancements of around 10^4 . The intensities of the most intense Raman modes at 231cm^{-1} , 1751cm^{-1} and 3543cm^{-1} enhanced a factor of 10^6 , 10^6 and 10^5 , respectively, compared with the NRS spectrum at 241cm^{-1} , 1820cm^{-1} and 3592cm^{-1} mode which attributes to N-H₂ twisting vibration, C-N-H ring bending and C=O stretching vibration and N-H₂ stretching vibration. The largest enhancements of Raman intensities modes at 231cm^{-1} , 546cm^{-1} and 784cm^{-1} assigned to wagging, twisting vibration of N-H₂ and wagging vibration of C=O increases by about a factor of 10^6 compared with the NRS spectrum at 241cm^{-1} , 511cm^{-1} and 780cm^{-1} mode. The intensities of bands at 675cm^{-1} ($\delta(\text{OCO})$) and 3543cm^{-1} ($\nu(\text{NH}_2)$) increase closely up to a factor of 10^6 compare with NRS spectrum due to the C=O functional group is close to the surface of Ag₂₀ cluster and the vibration of N-H₂ is parallel along Z-axis. Such large surface enhancements are in agreement with predictions of CT resonance enhancements.

3.3 Electromagnetic Enhancement

Electromagnetic enhancement involves amplification of the local electric field at the molecule's position due to plasmon excitation of the metallic structure. Enhancements in the range of 10^4 to 10^8 are commonly reported[30].

The electromagnetic enhancement of silver nanoparticles has been of interest, especially to estimate of the total SERS enhancement factor. Because the E-field enhancement is wavelength dependent, and the largest local E-field enhancement occurs at a resonance wavelength corresponding to the peak of extinction spectrum [24], it is necessary to calculate the extinction spectra for silver nanostructure by DDSCAT code. The peak of the extinction spectra locates at a special wavelength of 352nm when simulating the Ag nanosphere with a 15nm radius as Figure 6 shown. Moreover, the E-field enhancement contours along XY plan at resonance wavelength 352nm for the Ag sphere nanostructure are presented in Figure 7. The maximum E-field enhancement occurs at the surface of Ag nanosphere with a factor as high as 3.6×10^6 . Such strong enhancements are consistent with the surface Plasmon resonance theory[31].

IV. Conclusion

The normal and surface-enhanced Raman scattering of Ethyl carbamate (EC) are calculated with the M06-2X functional. The simulated spectra are in good agreement with the experimental spectra. Moreover, a systematic study of different contributions to SERS enhancements of the EC is presented. An EC-Ag₂₀ complex without an incident light involves in static chemical enhancements, whose enhancement factor is 10. Simulating SERRS spectrum with a 352nm wavelength incident light, respecting to the absorption maximum, the charge-transfer enhancements is found and the enhancement factor is 10^4 . Meanwhile, the same incident wavelength resonant is predicted for Ag sphere (R=15nm), where the electromagnetic

enhancements factor is 3.6×10^6 . Above all, the total relative enhancement factor can be 3.6×10^{10} while regarding it as a product of both chemical and electromagnetic effect which express as $RE_{total} = RE_{chem} \cdot RE_{em}$ (Where RE means relative enhancements)[32]. Such enhancements are in agreement with predictions of SERS enhancements. The enhancement mechanisms are successfully investigated by the ab initio calculation and discrete dipole appropriation method.

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Table 1. Calculated normal, SERS and SERRS spectra for EC (Frequencies in cm^{-1} , Raman intensities in a.u and assignments of experiment)

Experiment		Calculated Wavenumbers			Raman Intensities			Assignments
Normal	SERS	Normal	Ag20-urthane	RI^{exp}	RI^{normal}	RI^{SERS}	$RI^{352\text{nm}}$	
396	393	241	231	m	0.2	2.63	0.17×10^6	$\omega(\text{NH}_2)$
—	—	377	391	—	0.17	0.58	0.91×10^5	$\beta(\text{COCO})$
512	510	511	546	m	0.04	0.38	0.84×10^5	$\tau(\text{NH}_2)$
672	711	668	675	m	0.33	0.16	0.12×10^6	$\delta(\text{OCO})$
—	—	780	784	—	0.02	0.13	0.25×10^5	$\omega(\text{CO})$
854	850	867	871	s	0.4	1.2	0.34×10^5	$\rho(\text{CH}_3)$
996	1006	998	1009	w	0.15	0.09	0.06×10^5	$\nu_s(\text{CC})+\omega(\text{CH})$
1076	1082	1089	1092	w	0.19	0.45	0.22×10^5	$\nu_s(\text{OC})+\delta(\text{NH})+\delta(\text{CH}_2)$
1127	1133	1120	1126	m	0.42	1.3	0.5×10^5	$\rho(\text{NH}_2)+\rho(\text{CH}_3)$
1150	1160	1165	1167	w	0.43	0.09	0.02×10^4	$\rho(\text{CH}_2)+\tau(\text{CH}_3)$
1273	1238	1285	1295	s	0.45	0.49	0.02×10^4	$\rho(\text{CH}_2)+\tau(\text{CH}_3)$
1346	1316	1340	1360	w	0.07	0.64	0.3×10^5	$\rho(\text{CH}_2)+\delta(\text{CNH})$
1440	1390	1420	1437	m	0.16	2.22	0.17×10^5	$\rho(\text{CH}_3+\text{CH}_2)+\nu_s(\text{CC})$
1457	1455	1464	1463	s	0.57	0.72	0.98×10^5	$\delta(\text{CH})$
1622	1587	1587	1595	w	0.13	0.6	0.53×10^5	$\beta(\text{NH}_2)$
1688	—	1820	1751	w	0.36	6.09	0.15×10^6	$\delta(\text{CNH})+\nu(\text{CO})$
2934	—	3006	3009	s	6.43	8.82	0.13×10^5	$\nu_s(\text{CH}_3)$
2965	—	3032	3034	s	3.61	2.64	0.15×10^4	$\nu_s(\text{CH}_2)$
2991	—	3066	3075	s	3.23	2.68	0.01×10^4	$\nu_{\text{as}}(\text{CH}_2)$
3414	—	3592	3543	m	3.6	26.86	0.17×10^6	$\nu_s(\text{NH}_2)$

Table 2. Calculated static electronic polarizability components and the isotropic polarizability in

a.u

Complex	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	α
C3H7NO2	59.458	3.846	39.675	0.396	-0.757	51.786	50.306
C3H7NO2-Ag ₂₀	1101.046	-19.69	1040.354	-4.603	-0.978	1032.486	1057.962

Figure captions

Figure 1. The optimized **structures** of two EC-Ag complexes (a site: Ag in cis configuration to O₁; b site: Ag in trans configuration to O₁)

Figure 2. The optimized geometries of EC-Ag₂₀ with different binding site

Figure 3. Experimental spectrum of EC and simulated NRS spectra of EC, EC-Ag₂₀ and resonance Raman spectra of EC-Ag₂₀ complex

Figure 4. The absorption spectrum of EC-Ag₂₀ complex

Figure 5. Charge density difference of the EC-Ag₂₀ complex involved in the major CT excitation with the contour plot value of 0.04 a.u and enhanced electronic density in purple and depletion density in blue

Figure 6. The calculated extinction spectrum for Ag nanoparticle in shape of sphere and with radii of 15nm

Figure 7. E-field enhancement contour of sphere nanoparticle with 15nm radius at incident light of 352 nm along XY plane

Figure 1.

Figure 2.

(a) Surface(S) complex

(b) Vertex (V) complex

(c) Edge(E) complex

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.