Insight into vibration mode-resolved plasmon enhanced Raman optical activity

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1. Introduction

Raman optical activity (ROA) is a vibrational spectroscopic technique that is reliant on the difference in intensity of Raman scattered right and left circularly polarized light due to molecular chirality. Barron and Buckingham developed the definitive theory of ROA in 1971 [1], and made the first observations in 1973 [2].

However, ROA signals are even weaker than the Raman signals, and it is very hard to be detected, especially at low and high frequencies, due to the limitation of instrument for chiral Raman (for example, there is no suitable optical grating and cannot resolve the signal of chiral Raman). Also, the measurements on the molecular chirality need large molecular concentration and longtime accumulation (several hours).

Surface enhanced Raman scattering (SERS) has been widely used for the ultrasensitive chemical analysis [12,13], even at single molecular level [14], where the Raman signals can be enhanced up to $10^{11}$ by the electromagnetic mechanism [14], as well as the chemical enhancement [15]. Following SERS method, the ROA signals can also be strongly enhanced by surface plasmon resonance [16–21]. It is expected that plasmon enhanced ROA (PE-ROA) can resolve above intrinsic weaknesses of ROA. However, it is a great challenge that how to correctly understanding the plasmon enhanced ROA, due to the very weak chiral Raman signals and the influence of chemical enhancement as well as the substrate, which might change molecular chirality. The new stereo structure introduced by substrate may break molecular intrinsic stereo center. New symmetric minor, induced new chiral center by metal surface, and then the orientation of molecular charge is reversed, the chirality is changed. Chiral molecular vibrational motion induced electric dipole coupling with the magnetic dipole, which is the excited electronic charges, relaxed during Raman process.

In this communication, we try to insight into vibration mode-resolved PE-ROA of L-alanine and D-alanine experimentally and theoretically at high, low and middle frequencies, respectively. L-alanine and D-alanine are of the opposite chirality. So, they are the best molecules to study the influence of plasmon enhancement for the chirality of PE-ROA. If the plasmon can enhanced ROA spectra and the their chirality can be kept during the plasmon enhancement. We can conclude the plasmon enhancement is a valid and effective method for the enhancement of ROA by plasmon. The influences of charge transfer between molecule and metal, the new chemical bond between molecule and substrate, and the adsorption status of molecule on metal were comprehensively investigated. It is found that PE-ROA is not a universal method.

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for the enhancement of ROA. It should be very carefully for the using of plasmon enhancement for POA.

The solid L-alanine and D-alanine of over 99% purity were purchased from Aldrich Chemical Co., Ltd. and used without further purification. Aqueous solution of L-alanine was prepared with a concentration of 100 mg/ml. The ROA spectra were measured with the backscattering SCP Biotools µ-ChiralRAMAN-2X instrument with 532 nm excitation laser [22]. Laser power was set to 400 mW, with total acquisition time of 4 h. The SERS active silver colloid was prepared by citrate reduction of AgNO₃ [23]. AgNO₃ (90 mg) was dissolved in 650 mL of quartz distilled water. Five hundred milliliters of this solution was brought to boiling and then a solution of 1% sodium citrate (10 mL) was added. Thirty minutes later the remaining 150 mL AgNO₃ solution was added 3 times every 15 min. The solution was kept on boiling about 1.5 h. The final Ag nanoparticle concentration was estimated to be ≈35 pM with an average radius size of about 40 nm [24]. The SERS measurements were performed with left and right polarized lights, respectively, in the confocal Raman spectroscopic system (Renishaw, Invia) through an objective of 100× with a numerical aperture (NA) of 0.85. The wavelength of laser is 632.8 nm, and the laser power is about 7 mW. Lastly, the obtained difference of SERS spectra excited with left and right polarized lights is the experimental PE-ROA spectra. For comparison, the molecular ROA spectra of L-alanine at high frequencies was simulated, using density functional theory [25], B3LYP functional [26] and 6–31 + +g(2d,p) basis set. To theoretically interpret the PE-ROA, the vibrational modes of molecule adsorbed on the Agₙ cluster were theoretically calculated, using DFT, B3LYP functional and 6–31 g(d) basis set for C, N, O and H, and LanL2DZ basis set [27] for Ag. The optimized geometry can be seen from Supporting information. All the quantum chemical calculations were done with Gaussian 09 software [28].

Fig. 1(A) and (B) are the experimental PE-ROA of L-alanine and simulated ROA of L-alanine, respectively. It is found that PE-ROA peaks can be well observed experimentally, and interpreted with the simulated ROA spectrum. Note that the simulated ROA spectrum does not consider metal in the calculation, which results in the difference of ROA intensities. The vibrational modes a-d in Fig. 1(A) can be seen from Fig. 2. For peak a, it is symmetric vibrations of 3 H atoms on C(21) as well as symmetric H’s vibration on C(22). For peak b, it is symmetric vibrations of 3 H atoms on C(21) as well as asymmetric H’s vibration on C(22). For peak c, it is stretching mode of H(28) on C(21). For peak d, it is stretching mode of H(30) on C(21). So, the PE-ROA at high frequencies can overcome the instrument limitation of chiral Raman for ROA.

For comparison, we also measured the PE-ROA spectra of D-alanine at high vibrational frequencies (see Fig. 3(a)). Comparing Fig. 3(a) and (b), we found that their PE-ROA spectra cannot be completely reversed, and strongly influenced by the introduced metal substrate. So, for the plasmon enhancement for D-alanine is not a good choice.

Secondly, we measured the PE-ROA spectrum of L-alanine and compared with the ROA spectrum of L-alanine, see Fig. 4. It is found that the profiles of them are significantly different below 600 cm⁻¹.

Fig. 1. (A) and (B) are the experimental PE-ROA of L-alanine and simulated ROA spectra of L-alanine, respectively.

Fig. 2. The vibrational modes of ROA peaks (a-d) of L-alanine in Fig. 1(a).

Fig. 3. (a) and (b) are the experimental PE-ROA and simulated ROA spectra, respectively.
PE-ROA peaks e and f are strongly enhanced, due to the interaction between molecule and metal, and charge transfer results in the further chemical enhancement. Fig. 5 revealed that these PE-ROA peaks also include the vibration of new chemical bonds between O atoms and metal. Furthermore, the large amounts of charge transfer between O atoms and metal (see Fig. 6) can result in the chemical enhancement for PE-ROA. So, some of PE-ROA peaks can be chemical enhanced at low frequencies, especially for the new chemical bonds between molecule and metal, when the molecule chemically adsorbed on the metal substrate.

Thirdly, we interpret the reason that the PE-ROA peaks g and h of i-alanine were strongly selected enhanced. Fig. 7 revealed that for these two PE-ROA peaks, the new stereo structure introduced by substrate may break molecular intrinsic stereo center, and there is a new symmetric face that is perpendicular to the substrate. The C=O stretching vibrations were also involved in these two vibrational modes, as we know the chemical bond between substrate and O atoms can also influence the intensities of PE-ROA peaks (see Fig. 8).

For the PE-ROA peaks i, j, k, l and m of in Fig. 4(b), the chirality was reversed, compared with their ROA peaks of i-alanine in Fig. 4(a). These vibrational modes can be seen from Fig. 7. New symmetric minor by the substrate and new chiral center by metal surface, can results in the orientation of molecular charge is re-
versed, the chirality is changed. Chiral molecular vibrational motion induced electric dipole coupling with the magnetic dipole is also reversed, when excited electronic charges relaxed during Raman processes.

Lastly, to study the substrate influence of the substrate and plasmon, we measured the PE-ROA spectra of D-alanine, see Fig. 9. It is found that the molecular chirality cannot be realized at all. Though L-alanine and D-alanine have the reversed ROA, but they have almost the same chirality for PE-ROA, except for the ROA peak at 850 cm\(^{-1}\). So, the plasmon enhanced effect is not valid for our studied chiral molecules.

In summary, vibration mode-resolved PE-ROA of \(\alpha\)-alanine and \(\beta\)-alanine were investigated experimentally and theoretically. It is found that the plasmon can strongly enhanced ROA spectra, but the their chirality cannot be kept during the plasmon enhancement. We can conclude the plasmon enhancement is not a valid and effective method for the enhancement of ROA by plasmon. Our experimental results revealed that PE-ROA is not a universal method for the enhancement of ROA. It should be very carefully for the using of plasmon enhancement for POA.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2013.10.022.

References