Journal of Colloid and Interface Science 415 (2014) 165–168

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Insight into vibration mode-resolved plasmon enhanced Raman optical activity

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ARTICLE INFO

Article history:
Received 16 August 2013
Accepted 13 October 2013
Available online 29 October 2013

Keywords:
Plasmon enhancement
Raman optical activities
Vibration mode-resolved

ABSTRACT

Vibration mode-resolved plasmon enhanced Raman optical activities (PE-ROA) are investigated experimentally and theoretically. It is found that the profile of PE-ROA is significantly different from that of ROA. 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 ROA.

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]. Due to its sensitivity to chirality, Raman optical activity is a useful probe of biomolecular structure and behavior in aqueous solution. It has been used to study protein, nucleic acid, carbohydrate and virus structures [3–11]. However, ROA signals are even weaker 10^{-3} 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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0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.10.022

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 $AgNO_3$ [23]. $AgNO_3$ (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 $AgNO_3$ 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 Ag_{20} 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.

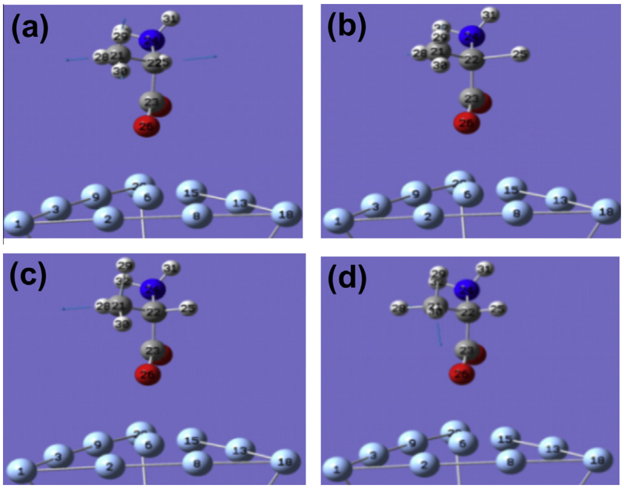

Fig. 2. The vibrational modes of ROA peaks (a-d) of L-alanine in Fig. 1(a).

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}.

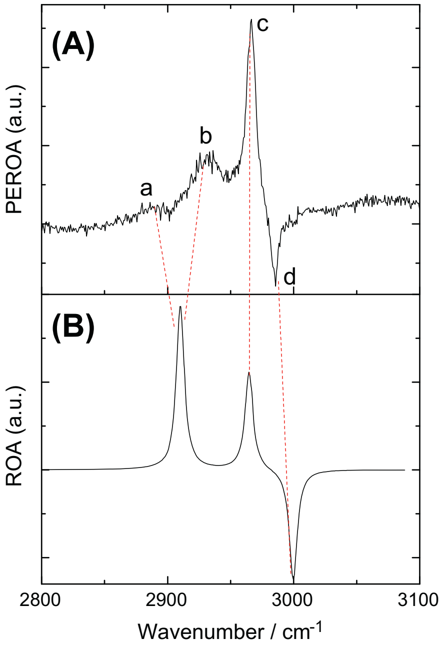

Fig. 1. (A) and (B) are the experimental PE-ROA of L-alanine and simulated ROA spectra of L-alanine, respectively.

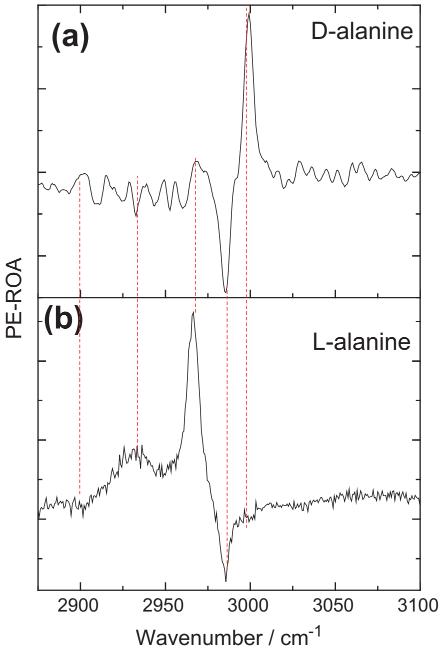

Fig. 3. (a) and (b) are the experimental PE-ROA and simulated ROA spectra, respectively.