Received: 4 April 2015

Revised: 18 May 2015

(wileyonlinelibrary.com) DOI 10.1002/jrs.4741

Accepted: 18 May 2015

Surface enhanced Raman spectroscopic (SERS) behavior of substituted propenoic acids used in heterogeneous catalytic asymmetric hydrogenation

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The strength and geometry of adsorption of substituted propenoic acids on silver surface were studied by means of surface enhanced Raman spectroscopy (SERS) using silver sol. Based on their SERS behavior, two classes of phenylpropenoic acids studied were distinguished. The first class of propenoic acids (atropic acid, (E)-2,3-diphenylpropenoic acid, (E)-2-(2-methoxyphenyl)-3phenylpropenoic acid, (E)-2,3-di-(4-methoxyphenyl)phenylpropenoic acid and (E)-2-(2-methoxyphenyl)-3-(4-fluorophenyl)propenoic acid) has shown strong charge transfer (CT) effect. We suggest bidentate carboxyl bonded species based on the SERS enhanced bands of vCOO⁻ around 1394 cm⁻¹ and vC—C of the —C— $\overline{COO^-}$ moiety at 951 cm⁻¹. In these series the plane of the α -phenyl group (γ CH out-of-plane vibrations at 850–700 cm⁻¹) is almost parallel to the silver surface, while the β -phenyl group is in tilted position depending on the type and the position of substituent(s) showing strong SERS enhanced bands of vCC + β CH (in-plane mode) at 1075 cm⁻¹, vCC (ring breathing mode, in-plane) at 1000 cm⁻¹ and vCCC (out-of-plane mode) around 401 cm⁻¹ . The other class of propenoic acids (cinnamic acid, (E)-2-phenyl-3-(4-methoxyphenyl)propenoic acid) has shown weak electromagnetic (EM) enhancement (C=C bands is enhanced in cinnamic acid). In this case no significant carboxyl enhancement was observed, so we suggest that adsorbed species lie parallel to the surface. The two types of adsorption can be related to the dissociation ability of the carboxylic group. In the first case the carboxylic H dissociates, while in the second case it does not, as indicated also by the characteristic vC=O band at 1686 cm⁻¹ in the FT-Raman spectra of methanolic solutions. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: SERS; 4-hydroxy benzoic acid; phenylpropenoic acids; adsorption geometry; enantioselective hydrogenation

Introduction

Analogously to the spectra obtained by other vibration techniques, the surface enhanced Raman spectrum can be regarded as a fingerprint of the studied compound.^[1,2] More, information can also be obtained about the orientation of adsorbed molecules,^[3–7] the changes in their chemical bonds^[8,9] or the formation of new chemical bonds between the adsorbed molecule and the metal surface.^[10–12] SERS can be applied on roughened metal surfaces and on metal colloids. Ag, Au and Cu colloids show not only enhanced Raman scattering but also catalytic activity; therefore, they are applicable for *in situ* investigation of catalytic reactions allowing the detection of both, surface adsorbed reagents and products. Despite the huge number of SERS studies in literature, there are relatively few reports in relation to heterogeneous catalytic reactions.^[13–20]

The enantiomeric pairs of biologically active compounds may have different pharmacological effects,^[21] consequently, the production of enantiopure materials is essential in pharmaceutical, agrochemical and cosmetic industry. Catalytic asymmetric processes are convenient methods to synthesize optically pure chiral compounds. The development of a heterogeneous catalytic process would be extremely beneficial, because the heterogeneous catalysts can be separated easily from the reaction mixture and can be reactivated for further use.^[22] Optically pure carboxylic acids and their substituted derivatives are important chiral building blocks.^[23] A possible way to synthesize them is the asymmetric hydrogenation of the appropriate prochiral unsaturated carboxylic acids, a reaction which can be successfully carried out over supported Pd catalyst modified with cinchona alkaloid chiral templates.^[24,25] Diphenylpropenoic acids (α -phenylcinnamic acid derivatives) are frequently used as starting materials. Substituents on both aromatic rings of α -phenylcinnamic acid have been found to influence significantly on the enantiomeric excess (ee (%) = $100 \times ([S] - [R]) / [S] + [R]$; where [S] and [R] are the concentration

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of the saturated acid enantiomers) and reaction rate.^[26–29] Although the geometry and strength of the adsorption of these compounds are supposed to play an important role in the asymmetric reaction, there are only a few studies on this topic.^[30] SERS studies of the chiral templates and the prochiral molecules can provide important new information about the heterogeneous catalytic asymmetric hydrogenations. SERS behavior of cinchonidine chiral template on polycrystalline platinum prepared by electrodeposition of ultrathin platinum films onto roughened gold surface has already been reported,^[4,5,9] but there are no SERS data on the hydrogenated molecules. To the best of our knowledge, this is the first SERS study on phenylpropenoic acids.

Our aim was to get information about the orientation of the adsorbed molecules relative to the silver surface of (E)-2,3 diphenylpropenoic acids (labeled below as Acid1–5) and to find correlation between the adsorbed structure and catalytic performance. Atropic acid (Acid6), cinnamic acid (Acid7), i.e. propenoic acids with only one phenyl group, and reference material 4-hydroxy benzoic acid (HBA) were also studied. Carboxylic acids investigated with SERS in this study and their abbreviations are shown in Fig. 1.

Experimental

Materials

Atropic acid was prepared as described previously^[31]. NaNO₃ (Reanal), HBA (Merck) and cinnamic acid (Sigma-Aldrich) were used as received. The substituted 2,3-diphenylpropenoic acids were prepared by Perkin condensation according to the Feiser method^[32–34] using the corresponding aromatic aldehydes and arylacetic acids purchased from Fluka and Aldrich.^[27,28]

Ag nanoparticles were prepared by using Lee and Meisel's method^[35] often used in SERS investigations to synthesize silver substrates.^[36–38] Briefly, 0.09 g AgNO₃ was dissolved in 500 ml^[3] double distilled water, the solution was boiled and 10 ml 1% trisodium–citrate aqueous solution was added dropwise into the boiling solution accompanied by vigorous stirring. Boiling was continued for 10 more minutes. Finally, a greenish slightly grey solution was received. The silver sol was used after a week of ageing time. The silver colloid solution was characterized by UV–Visible spectroscopy and by transmission electron microscopy (TEM). UV–Visible absorption spectra of silver colloids were recorded in the 800–300 nm region with a Unicam UV 500 spectrophotometer using cells with 1 mm path length at room temperature. TEM studies of the silver colloid were carried out in a FEI Morgagni 268D type TEM (100 kV accelerating voltage, W-filament).

Spectroscopic measurements of carboxylic acids

Raman and SERS spectra were recorded with the Bio-Rad (Digilab) dedicated FT-Raman spectrometer equipped with a Spectra-Physics Nd-YAG-laser (1064 nm) and high sensitivity liquid-N₂ cooled Ge detector. The laser power used was about 400 mW at the samples. The resolution of the Raman instrument was ca. 4 cm^{-1} , and a backscattered geometry was used. For each spectrum 256 individual spectra were averaged.

Raman spectra of the carboxylic acids were recorded in both, solid state and 1–4 w% methanol solution. For SERS measurements 10^{-3} M methanol solution of the carboxylic acids was used, and final concentration of carboxylic acids in colloidal solution was 2.4×10^{-4} M. In case of HBA the aqueous solution was also studied. For the SERS sample preparation 200 µl solution of carboxylic acid



(E)-2-(2-methoxyphenyl)-3-phenylpropenoic acid Acid1



(E)-2-(2-methoxyphenyl)-3-(4-fluorophenyl)propenoic acid Acid2

(E)-2,3-di(4-methoxyphenyl)propenoic acid

Acid4



(E)-2-phenyl-3-(4-methoxyphenyl)propenoic acid Acid3



(E)-2,3-diphenylpropenoic acid Acid5

O CH₂OH

atropic acid

Acid6



cinnamic acid Acid7



4-hydroxy benzoic acid HBA

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was added to $600 \,\mu$ I silver colloid, then $40 \,\mu$ I of water solution of NaNO₃ (5×10⁻¹ M) was added into the mixture, similarly to the method of Sanchez *et al.*^[10] SERS spectra were recorded after 5 min standing time.

Computational method

We have performed a goal-oriented computer simulation to estimate equilibrium geometries, proton affinities and partial charges of our probe molecules using the Spartan'06 package^[39] for *ab* initio (density functional (DFT)) and molecular mechanics (MM) calculations. In detail, the probe molecules were relaxed using MM (MMFF94 force field) to pre-equilibrate, and thereafter the more reliable theoretical level B3LYP/6-31 + G(d,p) calculation was performed to locate more accurate equilibrium geometries and to estimate proton affinities and partial charges. Moreover, an additional frequency calculation on each molecular system has confirmed that the optimized geometries correspond to minima on the potential energy surface, not reported here for the sake of brevity. Proton affinities have served a comparison among our molecules in relation to the subject of this work, particularly the reaction R-COO⁻ + H⁺ \rightarrow R-COOH, wherein the negative (exotherm) value means that the anion attracts the proton. Ground state of the two relaxed entities (anion and acid) was calculated, as well as because this calculation has served an approximate ranking only, there were no additional calculations like entropy, thermodynamics or zero point energy estimations, only energy calculation.

Results and discussion

The feasibility of SERS measurements

Adding the solution of probe molecules to the silver colloid did not induce the aggregation of the Ag nanoparticles and SERS spectra could not be recorded. Well-detectable SERS spectra were obtained only by adding NaNO₃ solution which partially aggregated the silver sol (scattering at 220 cm⁻¹). This observation is in accord with that of Sanchez *et al.*^[10] on caffeic acid and other hydroxyl-carboxylic acids. UV–Visible spectra of silver colloid with and without NaNO₃ solution are depicted in Fig. 2A (line b and a, respectively). The decrease of the peak about 430 nm parallel with the increase of new shoulder at 720 nm indicated the partial aggregation of the colloid. TEM images (Fig. 2B–C) have confirmed the presence of partial aggregation.

Raman spectroscopic behavior of the 4-hydroxy-benzoic acid reference material

Figure 3 shows the Raman spectrum of solid HBA, HBA in methanol solution, as well as SERS spectra of aqueous and methanol solution of HBA nominated as HBA solid, HBA met, AgHBA aq, AgHBA met, respectively. Aqueous solution of hydroxyl-benzoic acids is often used in SERS studies,^[40] but here, the methanol as a solvent was also chosen for sample preparation, because the solubility of the phenylpropenoic acids in water is much lower than in alcohols.

In accord with the literature data,^[41,42] no significant wavenumber shift in the SERS spectrum of the AgHBA aq could be observed comparing to the Raman spectrum of HBA solid. This fact indicates the presence of π -bonding between the benzene ring and the Ag surface. The appearance of a well-developed v_sCOO⁻ band at 1378 cm⁻¹ in the SERS spectrum of AgHBA aq shows that the majority of molecules is attached to the Ag surface through the $-COO^-$ as bidentate ligand. The antisymmetric $-COO^-$ stretch





Figure 2. Influence of the addition of NaNO₃ solution to the silver colloid. A: UV–Visible spectra of silver colloid. a—in the absence of NaNO₃; b—in the presence of NaNO₃. B: TEM image of silver colloid in the absence of NaNO₃. C: TEM image of silver colloid in the presence of NaNO₃.

500 nn

is expected around 1600 cm^{-1} which overlaps with the aromatic ring vCC vibrations and is usually weak in the Raman spectrum. A weak feature near 1250 cm^{-1} can be ascribed to the minor fraction of monodentate —C(=O)—O—Ag coordination. The characteristic aromatic ring vibrations of AgHBA aq at 1607 (strong), 857 (strong), ~630 (weak) and ~400 (weak) cm⁻¹ and their relative intensities are very similar to those obtained for HBA solid Raman spectrum (1611, 841, 639 and 390 cm⁻¹, respectively). Consequently, there are no silver-aromatic ring interactions in this case.

However, big differences can be observed in the SERS spectrum of water (AgHBA aq) and methanol (AgHBA met) solutions. The strong SERS band at 1232 cm⁻¹ can be interpreted as monodentate carboxylate group: $-C(=O)-O-Ag.^{[43]}$ A weak feature near 1370 cm⁻¹ indicates that a minor fraction of HBA may coordinate to the silver surface as bidentate ligand. The slightly shifted and enhanced bands recorded at 1585, 806, 632 and 419 cm⁻¹ are assigned to ring vibrations as ring stretching, vCC (8a), out-of-plane CH deformation, γ CH (11), in-plane ring deformation, δ CCC (6b) and out-of-plane ring deformation, γ CCC (16a), respectively. (These



Figure 3. Raman spectroscopic behavior of 4-hydroxy benzoic acid (HBA) under different conditions. HBA solid: FT-Raman of HBA in solid state; HBA met: FT-Raman of HBA in methanol solution; AgHBA met: SERS spectrum of HBA dissolved in methanol on Ag colloid; AgHBA aq: SERS spectrum of HBA dissolved in water on Ag colloid.

notations for benzene ring vibrations are taken from Ref.^[44,45]). Because the umbrella mode of CH deformation (11) is downshifted to 806 cm⁻¹ and the ring skeletal deformations (δ CCC and γ CCC) are well enhanced, it can be concluded that the benzene ring is also coordinated to the Ag surface and positioned close to parallel orientation. This can be described by a geometry wherein the carboxyl is rotated out from the molecular plane. Furthermore, the strong coordinative binding between the carboxyl group oxygen and the silver surface involves charge transfer (CT) which is part of the surface enhancement mechanism.^[42]

Raman spectroscopic behavior of unsaturated carboxylic acids

Based on their SERS behavior, two classes of the studied phenylpropenoic acids were distinguished. The members of the

first series of propenoic acids are Acid1–2 and Acid4–6 (series I). Raman and SERS spectra of these probe molecules are presented in Fig. 4, while the SERS band assignments are summarized in Table 1.

Two bands (around 1394 cm^{-1} and at 951 cm^{-1}) exhibit strong enhancement in the SERS spectra. The former band can be assigned to symmetric —COO⁻ stretching of bidentate carbonyl group while the lower wavenumber band at 951 cm^{-1} is the enhanced C—C stretching mode of C—COO⁻ group. This band is missing from the SERS spectrum of AgHBA (Fig. 3) when the carboxylic group is directly bonded to the aromatic ring.

The stronger relative intensity of the 951 cm⁻¹ band with respect to the v_sCOO⁻ indicates stronger adsorption of probe molecule to the Ag surface. Based on the SERS spectra, the following order of relative intensity can be established: Acid6 > Acid2 > Acid1 > Acid5 > Acid4. The lower acidity of Acid4 as compared to



Figure 4. Raman spectroscopic behavior of Acid1–2 and Acid4–6 (Series I). A: Raman spectra in solid form; B: Raman spectra in methanol solution; C: SERS spectra of acids dissolved in methanol on a Ag colloid.

Table 1. Band assignment for the SERS spectra of HBA, series I and series 2								
HBA met	Acid1	Acid2	Acid4	Acid5	Acid6	Acid3	Acid7	Band assignment
							1693 w	vCOOH (vC=0)
	1631 s	1632 s	1623 w	1624 s		1624 w	1634 w	vC=C (8a)
1585 m	1596 vs	1597 s	1602 s	1598 vs	1588 s	1603 m	1599 w	vCC (ring) (8b)
							1473 m, br	vCC (ring) (19a)
	1398 s, br	1391 vs, br	1394 m, br	1393 m, br	1398 vs			v_s COO—Ag (bidentate)
							1262 w	δCH (3)
1232 s								vCOO—Ag (monodentate)
	1213 w	1216 w		1211 m	1216 w			vCCX (7a)
	1182 w	1170 w	1175 s	1183 w	1176 w	1176 m		βCH (15)
	1075 s	1037 vs	1077 m	1076 m	1081 vs			vCCX (18a)
	1000 s			1000 s, sh	1004 s, sh		1003 w, sh	Ph ring (ring breathing mode, 1)
	951 m-s	951 s-m	951 w-m	951 m	951 s			νC—COO (νC—C)
	928 m	923 m						γCH (17a)
	830 w	839 w			835 w			γCH (11)
806 m	810 w	795 w	810 m		779 w	800 w, br		γCH (11)
	746 m	738 w		763 w	734 w			δCCX (12)
632 vs		644 s, br						δCCC (6a)
418 vvs	401 vs		403 vs	403 w-m	401 vs			γCCC (16a)
Notation of benzene ring vibrations are taken from Ref. ^[44] and Ref. ^[45]								

the Acid5 is in line with this order. Acid6 has the highest adsorption strength: it contains only one aromatic ring without any methoxy substituents on the phenyl ring. The adsorption strength of Acid2 and Acid1 might be determined by the steric effect of the methoxy substituent in *orto* position on the α -phenyl moiety. Accordingly, the latter substituent must have a decisive effect on the adsorption strength through the carboxylic acid group, which could be the origin of its significant influence on the enantioselectivities obtained in the asymmetric hydrogenations of these acids.

Based on the experience with reference molecule HBA, we suggest an EM enhancement of the α -phenyl group (except Acid2 containing fluorine), because only a slight shift of wavenumbers compared to corresponding solid Raman spectra could be observed. The plane of the α -phenyl group must be almost parallel to the silver surface indicated by the enhanced yCH out-of-plane vibrations at 850–700 cm⁻¹. The β -phenyl groups, however, are involved in a strong CT, as indicated by the strongly enhanced bands around 1075 cm^{-1} (vCC + β CH (14), in-plane), 1000 cm⁻¹ (vCC (1, ring breathing mode), in-plane) and 400 cm^{-1} (vCCC (17b), out-of-plane), coming from the conjugation between the carboxylate, the double bond and the β -phenyl group. The relative intensity of out-of-plane and in-plane bands is indicative for the tilting position of β -phenyl group. Based on band intensity ratio of 400 cm⁻¹ versus 1075 cm⁻¹, the following trend of β -phenyl group tilting from the perpendicular to Ag surface can established: Acid4 > Acid6 > Acid1 > Acid5. Interestingly, in case of Fsubstituted phenylpropenoic acid (Acid2), because of the existence of trans-fluorinated ring, these two bands are downshifted to 1037 cm⁻¹ and possible below 350 cm⁻¹, respectively. The enhanced vibration bands around 850–700 and 650 cm⁻¹, however, can be assigned to α -phenyl ring vibrations participating in CT, similarly to the reference molecule, AgHBA met.

Acid3 and Acid7 belong to the second series (series II) of our probe molecules; their Raman and SERS spectra are presented in Fig. 5.

Comparing the SERS spectrum of Acid3 dissolved in methanol (Fig. 5C) to the Raman spectrum of solid Acid3 (Fig. 5A), one can

see that no new band appears and the electromagnetic (EM) enhancement is weak. Also, a very small EM enhancement can be observed in case of Acid7. The —COOH group is not involved in the adsorption on the Ag surface; no bands belonging to COO⁻ moiety are present in the SERS spectra, only the vC=C (1634 cm⁻¹), δ CH (1252 cm⁻¹) vibrations are enhanced.^[46] These observations suggest that the C=C bond is positioned parallel to the Ag surface. Consequently, the adsorbed probe molecule as a whole lies parallel to the metal surface.

In order to support the SERS behavior of the two types of propenoic acids, molecular modeling calculations were performed. Figure 6 shows the calculated Mulliken charges and equilibrium geometries of the studied propenoic acids.

The calculated energies and equilibrium geometries of Acid1 and Acid5 are similar to the literature data^[47] (Acid1 is named as 3a and Acid5 is named as 1a in Fig. 1 of Ref.^[47]). Although the protonation $(R-COOH + H^+ \rightarrow R-C(OH)_2^+)$ of α -substituted cinnamic acids in superacidic media was studied in that work,^[47] the neutral molecules can be compared to our case. As shown in Fig. 6, no direct correlation between the types of SERS behavior and the calculated equilibrium geometries can be observed indicating that the adsorption is responsible for the change in the geometry of these molecules. Polarization of α - and β -phenyl rings also does not have influence on the types of SERS behavior and seems independent from the partial charge on the carbonyl oxygen atoms. On the other hand, the appearance of the different types of adsorption could be related to the different dissociation ability of the carboxylic group in methanol solution (compare Fig. 4B to Fig. 5B). In the first class of probe molecules (series I) the carboxylic H dissociates (indicated by the lack of vC=O band in the Raman spectra) in methanol solution of the investigated propenoic acids. Conversely, in the second class of probe molecules (series II) the carboxylic H exists in un-dissociated form as indicated by the characteristic vC=O band at 1686 cm⁻¹ in the Raman spectra of methanol solution. This observation is supported partly by the computational estimation of the acidity of phenylpropenoic acids. Calculated proton affinities (Table 2) show the most negative value in case of Acid7 (series II)



Figure 5. Raman spectroscopic behavior of Acid3 and Acid7 (Series II). A: Raman spectra in solid form; B: Raman spectra in methanol solution; C: SERS spectra of acids dissolved in methanol on a Ag colloid.



Figure 6. Mulliken charges and equilibrium geometries of the studied propenoic acids calculated at B3LYP/6-31 + G(d,p)^[39] level of theory.

which is in accord to the spectroscopic results observed. However, the second most negative value is the case of Acid4 (series I), while the third negative value is the case of Acid 3 (series II). The difference in the dissociation ability is obviously caused by the substituents on the β -phenyl ring combined with the steric constrain of the α -phenyl moiety. According to the literature,^[27] Acid3 (pK_a=7.23, named as pMeOFFS in Ref.^[27]) is weaker acid

than Acid5 ($pK_a = 7.00$, named as a-FFS in Ref.^[27]). As can be seen from Table 2, the polarization of the olefin double bond (C8–C7, i. e. the difference between the Mulliken charges on C8 and C7 carbon atoms) is a peaking negative value in case of Acid7 (series II), which can be correlated to the observation that C=C was significantly enhanced in this probe molecule (SERS enhancement of C=C at 1634 cm⁻¹).

Table 2.	Calculated proton affinities and partial charges. (See the num-
bering for	C7 and C8 on Fig. 1, marked only on Acid1)

No	Proton	Mulliken charges					
	kcal/mol	H8	C7	C8	C8–C7 difference		
Acid1	-354.0	+0.34	-0.12	-0.06	0.06		
Acid2	-352.5	+0.34	-0.11	-0.06	0.05		
Acid3	-354.3	+0.32	-0.11	-0.07	0.04		
Acid4	-355.4	+0.32	-0.12	-0.06	0.05		
Acid5	-352.6	+0.32	-0.12	-0.05	0.07		
Acid6	-353.6	+0.32	-0.24	+0.03	0.27		
Acid7	-356.2	+0.32	-0.08	-0.19	-0.11		

Heterogeneous catalytic asymmetric hydrogenation of the unsaturated carboxylic acids in relation to our SERS experiments

It is necessary to mention that the surface and electronic properties of silver nanoparticles differ from that of the real catalyst (Pd/ Al₂O₃). Furthermore, the strongly adsorbing cinchona alkaloid chiral template and the hydrogenated molecule exist together on the surface in the asymmetric hydrogenation. In spite of these deviations between the SERS and the real reaction conditions, the order of strength of ---COOH adsorption by the SERS experiments and the proton affinity of the five 2,3-diphenylpropenoic acid derivatives correlates well, these results may be useful to interpret the enantioselective hydrogenations of these acids over Pd catalyst modified by cinchonidine.^[28,48] Although, as shown in Fig. 7, no clear correlation between the proton affinity or the --COOH adsorption strength and the enantiomeric excess (ee) was obtained, the lower acidity of Acid3 and Acid4 as compared to Acid 5 could explain the enantioselectivities obtained in the reactions of these acids. Weaker acids will result in the formation of carboxylates of stronger basic character, which are able to interact stronger with the protonated cinchona alkaloid modifier, resulting an increase in enantiomeric excess. On the other hand, results obtained in reactions of Acid1 and Acid2 could be attributed to the steric effect of the methoxy group in orto position. Although the proton affinity and the adsorption strength of these acids are the highest, higher ee's can be obtained



Figure 7. Enantiomeric excesses (ee) obtained in the hydrogenation of the studied (*E*)-2,3-diphenylpropenoic acids over Pd catalyst modified by cinchonidine (for reaction conditions see Ref⁽²⁸⁾),at 295 K (dark columns), at 273 K (light columns).

as compared to Acid 5, because of this steric effect, which guides the adsorption of the molecule in presence of the modifier.

Summary

Based on their SERS behavior, the phenylpropenoic acids selected for this work were divided into two classes. The members in the first group (Acid1-2 and 4-6) show a strong charge transfer (CT) effect and the plane of the α -phenyl group is almost parallel to the silver surface, while the β -phenyl group is in tilted position depending on the type and the position of substituent(s). Contrary, a weak electromagnetic (EM) enhancement is characteristic for the members of the second group (Acid3 and 7), where the C=C bands are enhanced and no significant carboxyl enhancement is observed. Consequently, the adsorbed species lie parallel to the surface. The two types of adsorption can be related to the dissociation ability of the carboxylic group. Although no direct correlations were obtained between the adsorption strength and modes derived from the SERS measurements and the enantiomeric excess measured in the hydrogenation of these acids over Pd catalyst modified by cinchonidine, the results have shown clear multiple effects, which have influence on the enantiodiscrimination in these asymmetric heterogeneous processes.

Acknowledgement

The authors would like to express their thanks to Beáta Hermán for the preparation of substituted diphenylpropenoic acids.

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