

Research Article

Exploring the Isomer Dependent SERS Spectra of (diphenylphosphoryl)(pyridin-2-, -3, and -4-yl)methanol Adsorbed on Gold Nanocolloids

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The surface-enhanced Raman scattering (SERS) spectra of three aminophosphonate derivatives of pyridine: (diphenylphosphoryl)(pyridin-2-yl)methanol (α -Pyr), (diphenylphosphoryl)(pyridin-3-yl)methanol (β -Pyr), and (diphenylphosphoryl)(pyridin-4-yl)methanol (γ -Pyr) were measured after immobilization onto colloidal gold surface. Changes in the wavenumber, broadness, and enhancement between the corresponding Raman and SERS bands allowed to deduce orientation of the α -, β -, and γ -isomers (α -, β -, and γ -refer to the position of the substituent relative to the ring nitrogen atom) of aminophosphonate derivatives of pyridine on the gold surface. Briefly, it was demonstrated that the α -Pyr and β -Pyr show the same mode of adsorption, whereas the adsorption process of the γ -Pyr isomer differs in this regard that pyridine assists in the interaction with the gold surface.

1. Introduction

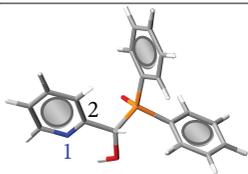
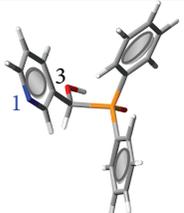
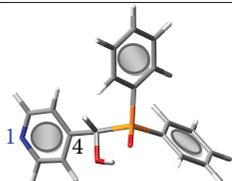
Aminophosphonic acids and their derivatives are very promising group of compounds due to their occurrence in organisms and numerous important biological activities [1]. Their biological capabilities are connected with the inter-action with metal ions [2]. In the last few years, there has been an increasing interest in the field of synthesis and investigation of pyridine aminophosphonic acids because of their potential and significant antitumor properties [2, 3]. The previous study on aminophosphonate derivatives of pyridine has proved the high reactivity of aminophosphonate ligands bearing *N*-heterocyclic donor atom [2, 4]. Consequently, it has been demonstrated that the nitrogen-containing heterocyclic compounds have a wide range of applications ranging from anticancer [5], antituberculosis [6], antiproliferation [7], to enzyme inhibitors or chelating agents for heavy metal ions [8]. Among the nitrogen-containing molecules, pyridine

derivatives play an essential role in many areas; that is, they are used as vitamins like nicotinic acid and nicotinic acid amide, vitamin B, herbicides, and insecticides [9].

In this study, we investigated three aminophosphonate derivatives of pyridine, including (diphenylphosphoryl)(pyridine-2-yl)methanol (α -Pyr), (diphenylphosphoryl)(pyridin-3-yl)methanol (β -Pyr), and (diphenylphosphoryl)(pyridin-4-yl)methanol (γ -Pyr) (Table 1 shows molecular structures of these compounds) using surface-enhanced Raman scattering (SERS) technique. We focused on the spectral changes related to the different position of the substituent (1-(diphenylphosphoryl)metanol) with respect to the pyridine nitrogen atom, in α -, β -, and γ -position, respectively.

Raman spectroscopy is a very useful method in the field of chemical analysis because it provides information about the vibrational structure and adsorption mode occurring at the solid/liquid interface [10]. However, the Raman process has extremely small cross section which limits its application

TABLE 1: Molecular structures of the investigated compounds.

Molecular structure	Abbreviation	Name
	α -Pyr	(diphenylphosphoryl)(pyridin-2-yl)methanol
	β -Pyr	(diphenylphosphoryl)(pyridin-3-yl)methanol
	γ -Pyr	(diphenylphosphoryl)(pyridin-4-yl)methanol

Color legend: : the carbon, : the oxygen, : the nitrogen, : the phosphorus, and : the hydrogen atoms.

[11]. This limitation can be overcome and strongly enhanced Raman spectra (by up to 10^{14} - 10^{15}) can be obtained when the molecule is adsorbed onto roughened or colloidal metal surface [12, 13]. The tremendous increase of the SERS signal can be achieved with relatively few metals: Ag, Au, Cu, and less frequently with Pt [14]. Generally, there are two major factors responsible for this enhancement. The first mechanism is due to the metal plasmon resonance excitation, which increases the local fields in close proximity to the roughened metal surface or metal nanoparticles. The second, less significant factors concern the chemical effects, in particular the metal-molecule charge-transfer transition and other changes due to the adsorption process [12]. Analysis of the SERS signal (enhancement, wavenumber, and broadness) due to the molecular fragment vibrations of the investigated compound is essential for description of the possible way in which the adsorbate can interact with the surrounding medium [15–20]. Thus, SERS is a great tool for low-level detection and analysis, even for the single molecule detection. In a broader sense, this technique can be used for studying transport phenomenon across biological membranes or the kinetics of charge-transfer processes at an electrochemically roughened substrate [14].

2. Materials and Methods

2.1. *(Diphenylphosphoryl)(pyridin-2-, -3, and -4-yl)methanol Synthesis.* (Diphenylphosphoryl)(pyridin-2-yl)methanol, (diphenylphosphoryl)(pyridin-3-yl)methanol, and (diphenylphosphoryl)(pyridin-4-yl)methanol were synthesized according to a previously described procedure [21, 22]. The purity and chemical structures of the samples were proved by

^1H , ^{31}P , and ^{13}C NMR spectra and electrospray mass spectrometry analysis.

2.2. *FT-Raman Measurements.* The FT-Raman spectra were recorded using a Nicolet spectrometer (model NXR 9650) coupled with a liquid-nitrogen-cooled germanium detector. All spectra were acquired with a resolution of 4 cm^{-1} and 1000 scans were usually collected. The spectrometer was equipped with a continuum-wave Nd:YAG laser emitting light at 1064 nm with total output power of up to 200 mW.

2.3. *SERS Measurements.* Colloidal gold nanoparticles (20 nm, concentration: 0.02 mg/mL in aqueous buffer, contains sodium citrate as stabilizer) were purchased from Sigma-Aldrich Co. (Poznan, Poland). Aqueous sample solutions were prepared by dissolving each compound in deionized water. The concentration of the sample before mixing with the colloid was adjusted to 10^{-4} M . Briefly, 20 μL of the aqueous sample solution was added to 40 μL of the gold colloid and stirred vigorously.

The SERS spectra of the investigated compounds were collected three times with InVia Renishaw spectrometer equipped with an air-cooled charge-coupled device (CCD) detector. The spectral resolution was set at 4 cm^{-1} . The continuous-wave diode laser (HP NIR) with the 785 nm excitation line was used as an excitation source. The laser power at the sample was set at 10 mW.

All of the SERS spectra were recorded within one hour of adding the sample to the Au colloid. The obtained spectra were almost identical, except for small differences (up to 5%) in some band intensities. No spectral changes that could be

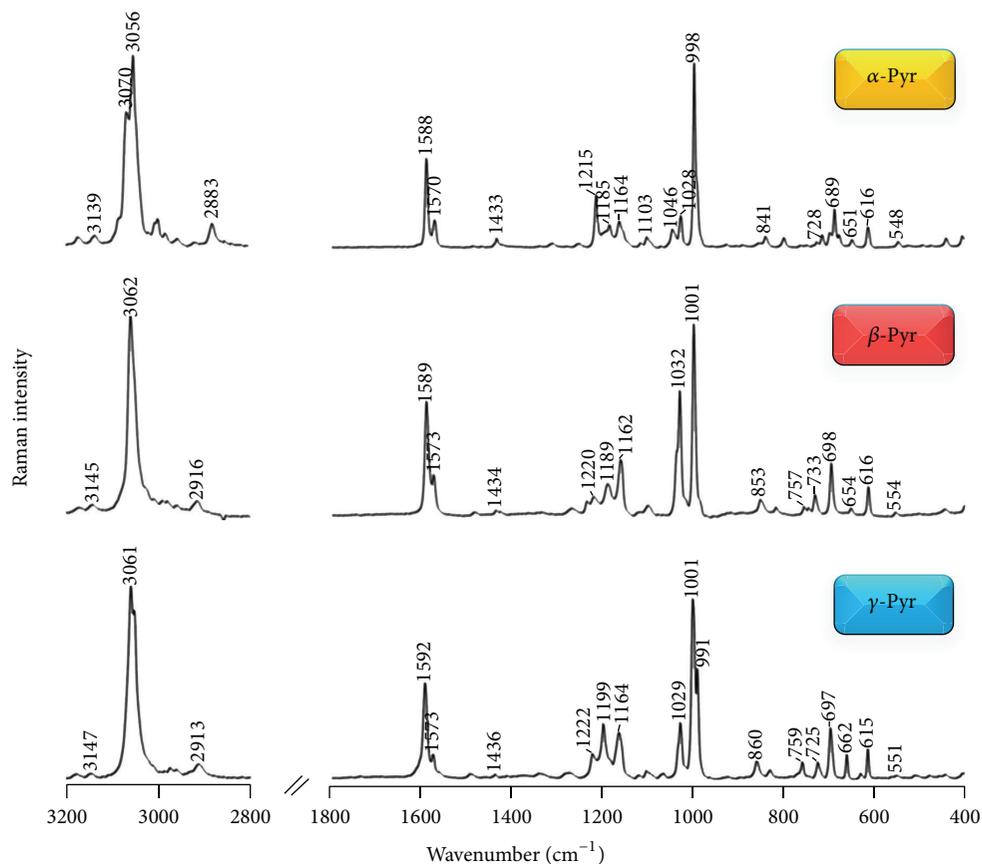


FIGURE 1: The FT-RS spectra of α -Pyr, β -Pyr, and γ -Pyr in the spectral ranges of 3200–2800 and 1800–400 cm^{-1} .

associated with sample decomposition were observed during these measurements.

3. Results and Discussion

Figure 1 shows the FT-Raman spectra of the three amino-phosphonate derivatives of pyridine: α -Pyr, β -Pyr, and γ -Pyr, in the solid state in the spectral ranges between 3200–2800 and 1800–400 cm^{-1} . Figure 2 presents the SERS spectra of these compounds in an aqueous gold sol. Table 2 summarized wavenumbers, full band widths at half maximum (FWHM), and proposed band assignments of the SERS bands together with those observed in the corresponding Raman spectra. The proposed band allocation to the normal mode motions is based on the density functional theory calculations performed for these molecules [23] and the Raman spectra of compounds that contain similar molecular fragments [10, 24–32].

Comparison of the SERS (Figure 2) spectrum of each of the investigated pyridine α -hydroxymethyl biphenyl phosphine oxides with the proper Raman spectrum (Figure 1) reveals similarity in the corresponding bands width and wavenumbers (see Table 2). However, few differences are noticeable in the enhancement of certain bands. These differences concern mainly the 1570 [ν_{8b}], 1215 [ν_{9a} (Pyr)], 1046 [ν_{12} (Pyr)], and 992 cm^{-1} [ν_1 (Pyr)] Raman and

the 550 [$\gamma(\text{CO}) + \rho_{\text{as}}(\text{Phe})$] and 530 cm^{-1} [$\gamma(\text{CO}) + \rho(\text{CP}=\text{O}) + \rho_{\text{as}}(\text{Phe}) + \delta_{\text{oop}}(\text{CC}(\text{P})\text{C})$] SERS bands (see Table 2 for detailed band wavenumbers). The former Raman spectral features are weak or absent in the SERS spectra. In addition, increase in the relative intensity of the 998 [$\nu_{12}(\text{Phe})$] and 1102 cm^{-1} [$\nu(\text{CO}) + \nu(\text{PC}_{\text{phe}})$] SERS signals and decrease in the 1588 cm^{-1} [ν_{8a}] SERS band relative enhancement are evident for all the investigated molecules in comparison with those in the Raman spectra.

Group theory provides the most elegant framework to use of the aforementioned bands' relative intensity changes to predict the geometries of aromatic molecules adsorbed onto SERS-active substrates [33]. Under assumptions that the vibrations involving atoms close to the metal surface are enhanced due to their interactions with the metal surface, the "surface selection rules" for a perpendicular ring orientation designate the in-plane vibrations to be enhanced to a greater extent than the out-of-plane vibrations. The opposite should be the case for the horizontal adsorption geometry. In addition, according to the propensity rules of the electromagnetic mechanism of SERS, the strongest SERS bands of the perpendicular phenyl ring with respect to the metal surface are due to the ν_{12} mode [34]. Gao and Weaver reported that ν_{12} of alkylbenzenes shifts down by 10–15 cm^{-1} upon adsorption at the surface. In contrast, the observed downshift by 4–5 cm^{-1} for this mode of halogenobenzenes

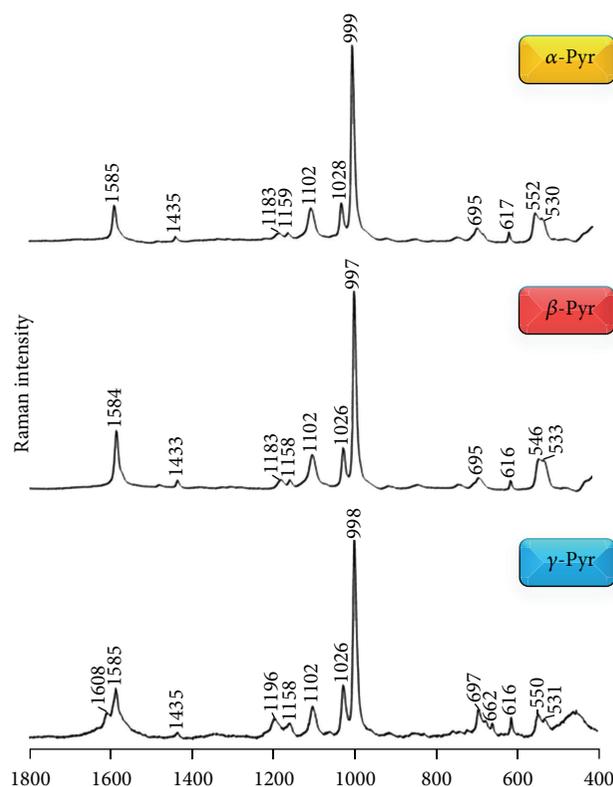


FIGURE 2: The SERS spectra of α -Pyr, β -Pyr, and γ -Pyr adsorbed onto colloidal gold surface.

was interpreted as evidence of no direct interaction between the π -electron systems and the metal surface. Also, significant band broadening for the aromatic ring modes was reported in the case of π adsorption caused by an interaction between the ring and the metal surface [35].

The foregoing “surface selection rules” and spectral changes as well as the c.a. 1590 [ν_{8a}], c.a. 1435 [ν_{19b}], c.a. 1198 [ν_{9a} and/or $\nu_{sym}(C_{\beta}C_{\gamma}H_2C_{\delta})$], c.a. 1026 [ν_{18a}], c.a. 998 [ν_{12}], c.a. 695 [ν_{6a}], and c.a. 616 cm^{-1} [$\nu_{6b}(Phe)$] SERS signals imply an essentially perpendicular orientation of the phenyl rings of α -Pyr, β -Pyr, and γ -Pyr on the colloidal gold nanoparticles, whereas the pyridine ring of these molecules is not involved in the adsorption process. However, considering the molecular structure of pyridine α -hydroxymethyl biphenyl phosphine oxides, it seems unlikely that both the phenyl rings adopt the same vertical geometry with respect to the gold surface (one the 998 cm^{-1} band, FWHM = 9 cm^{-1}). Thus, we postulate that only one of the equivalent phenyl rings is involved in the interaction with Au. On the other hand, the moderate strengthening of the 1102, 550, and 530 cm^{-1} spectral features between the Raman and SERS spectra results from bonding interaction between Au and the $-OCP(=O)-$ molecular fragment. Therefore, the O–C and P=O bonds should adopt a tilted orientation with respect to the gold surface. Such an arrangement favors interaction of the oxygen atom’s lone pair with the metal surface.

The modes at 1608 [$\nu_{8a}(Pyr)$] and 662 cm^{-1} [$\rho_{as}(Pyr) + \delta(C_{pyr}CO) + \delta(C_{pyr}CP)$] distinguish the SERS spectrum

of γ -Pyr from those of α -Pyr and β -Pyr. The appearance of these two bands in the γ -Pyr SERS spectrum and the slight strengthening of the 1196 and 1158 cm^{-1} spectral features (see Table 2 for bands assignment) suggest that in the case of 4-isomer of α -hydroxymethyl biphenyl phosphine oxide pyridine assists in the adsorption process of this molecule.

4. Conclusions

In this work, we discussed the mode of adsorption for three isomers (2-, 3-, and 4-) of pyridine α -hydroxymethyl biphenyl phosphine oxide immobilized onto a colloidal gold surface. We demonstrated that the investigated molecules interact with the gold substrate surface through the phenyl ring that is oriented vertically in respect to the surface. For γ -Pyr, we suggested also that the pyridine ring located in the vicinity of the gold surface is able to assist in the adsorption process. Although the interaction of α -Pyr, β -Pyr, and γ -Pyr with the gold surface was suggested by the phenyl ring, the hydroxyl ($-OH$) and phosphonate oxygen ($=O$) fragments assisted in this process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of the paper.

TABLE 2: Wavenumbers, full band widths at half maximum, and proposed band assignments for FT-RS and SERS spectra of α -Pyr, β -Pyr, and γ -Pyr adsorbed onto colloidal gold surface.

Mode	FT-RS		SERS Au colloid	
	ν [cm ⁻¹]	FWHM [cm ⁻¹]	ν [cm ⁻¹]	FWHM [cm ⁻¹]
α -Pyr				
$\nu(\text{CO}) + \rho(\text{CP=O}) + \rho_{\text{as}}(\text{Phe}) + \delta_{\text{oop}}(\text{CC(P)C})$	528	6	530	17
$\nu(\text{CO}) + \rho_{\text{as}}(\text{Phe})$	548	7	552	14
$\nu_{6a}(\text{Pyr})$ and/or $\nu_{6b}(\text{Phe})$	616	7	617	6
$\rho_{\text{as}}(\text{Pyr}) + \delta(\text{C}_{\text{pyr}}\text{CO}) + \delta(\text{C}_{\text{pyr}}\text{CP})$	651	7	—	—
$\nu_{11}(\rho_{\text{as}}(\text{Pyr}))$ and/or $\nu_{6a}(\text{Phe}; \delta_{\text{oop}}(\text{CC(H)C}))$	689	6	695	17
$\nu_{10b}(\rho_t(\text{Pyr}))$ and/or $\rho_{\text{as}}(\text{Phe}) + \nu(\text{PC}_{\text{phe}})$	728	3	—	—
$\nu_{10a}(\text{Phe}; \nu(\text{CH}))$	841	9	—	—
$\nu_1(\text{Pyr}; \delta_{\text{oop}}(\text{CC(H)C}) + \nu(\text{CN}) + \delta_{\text{trig}}(\text{Pyr}))$	992	7	—	—
$\nu_{12}(\text{Phe})$	998	5	999	9
$\nu_{18a}(\text{Phe})$	1028	7	1028	9
$\nu_{12}(\text{Pyr})$	1046	11	—	—
$\rho_r(\text{CC(H)C})_{\text{pyr}} + \nu(\text{CC})_{\text{pyr}} + \nu(\text{CO}) + \nu(\text{PC}_{\text{phe}})$	1103	9	1102	11
$\nu(\text{P=O})$ and/or $\delta(\text{CH})$	1164	6	1159	7
$\nu_{9a}(\text{Phe}; \delta(\text{CH}))$ and/or $\nu_{\text{sym}}(\text{C}_{\beta}\text{C}_{\gamma}\text{H}_2\text{C}_{\delta})$	1185	6	1183	18
$\nu_{9a}(\text{Pyr})$ and/or $\nu_{7a}(\text{Phe}; \text{phenyl-C stretch})$	1215	7	—	—
$\nu_{19b}(\text{Pyr/Phe})$	1433	8	1435	8
$\nu_{8b}(\text{Pyr/Phe})$	1570	10	—	—
$\nu_{8a}(\text{Pyr/Phe})$	1588	10	1585	9
β -Pyr				
$\nu(\text{CO}) + \rho(\text{CP=O}) + \rho_{\text{as}}(\text{Phe}) + \delta_{\text{oop}}(\text{CC(P)C})$	534	10	533	17
$\nu(\text{CO}) + \rho_{\text{as}}(\text{Phe})$	554	7	546	14
$\nu_{6a}(\text{Pyr})$ and/or $\nu_{6b}(\text{Phe})$	616	6	616	6
$\rho_{\text{as}}(\text{Pyr}) + \delta(\text{C}_{\text{pyr}}\text{CO}) + \delta(\text{C}_{\text{pyr}}\text{CP})$	654	7	—	—
$\nu_{11}(\rho_{\text{as}}(\text{Pyr}))$ and/or $\nu_{6a}(\text{Phe}; \delta_{\text{oop}}(\text{CC(H)C}))$	698	8	695	11
$\nu_{10b}(\rho_t(\text{Pyr}))$ and/or $\rho_{\text{as}}(\text{Phe}) + \nu(\text{PC}_{\text{phe}})$	733	6	—	—
$\nu_{\text{as}}(\text{Pyr}) + \delta_{\text{oop}}(\text{CC(H)C})_{\text{phe}} + \delta_{\text{oop}}(\text{CC}_{\text{phe}}(\text{P)C})$	757	7	—	—
$\nu_{10a}(\text{Phe}; \nu(\text{CH}))$	853	12	—	—
$\nu_{12}(\text{Phe})$	1001	6	997	9
$\nu_{18a}(\text{Phe})$	1032	8	1026	9
$\nu_{12}(\text{Pyr})$	1041	7	—	—
$\rho_r(\text{CC(H)C})_{\text{pyr}} + \nu(\text{CC})_{\text{pyr}} + \nu(\text{CO}) + \nu(\text{PC}_{\text{phe}})$	1103	9	1102	10
$\nu(\text{P=O})$ and/or $\delta(\text{C-H})$	1162	14	1157	9
$\nu_{9a}(\text{Phe}; \delta(\text{CH}))$ and/or $\nu_{\text{sym}}(\text{C}_{\beta}\text{C}_{\gamma}\text{H}_2\text{C}_{\delta})$	1189	19	1183	17
$\nu_{9a}(\text{Pyr})$ and/or $\nu_{7a}(\text{Phe}; \text{phenyl-C stretch})$	1220	20	—	—
$\nu_{19b}(\text{Pyr/Phe})$	1434	8	1433	8
$\nu_{8b}(\text{Pyr/Phe})$	1573	8	—	—
$\nu_{8a}(\text{Pyr/Phe})$	1589	8	1584	14
γ -Pyr				
$\nu(\text{CO}) + \rho(\text{CP=O}) + \rho_{\text{as}}(\text{Phe}) + \delta_{\text{oop}}(\text{CC(P)C})$	528	4	531	14
$\nu(\text{CO}) + \rho_{\text{as}}(\text{Phe})$	551	9	550	14
$\nu_{6a}(\text{Pyr})$ and/or $\nu_{6b}(\text{Phe})$	615	5	616	5
$\rho_{\text{as}}(\text{Pyr}) + \delta(\text{C}_{\text{pyr}}\text{CO}) + \delta(\text{C}_{\text{pyr}}\text{CP})$	662	5	662	5
$\nu_{11}(\rho_{\text{as}}(\text{Pyr}))$ and/or $\nu_{6a}(\text{Phe}; \delta_{\text{oop}}(\text{CC(H)C}))$	697	9	697	8
$\nu_{10b}(\rho_t(\text{Pyr}))$ and/or $\rho_{\text{as}}(\text{Phe}) + \nu(\text{PC}_{\text{phe}})$	725	9	—	—
$\nu_{\text{as}}(\text{Pyr}) + \delta_{\text{oop}}(\text{CC(H)C})_{\text{phe}} + \delta_{\text{oop}}(\text{CC}_{\text{phe}}(\text{P)C})$	759	5	—	—
$\nu_{10a}(\text{Phe}; \nu(\text{CH}))$	860	11	—	—

TABLE 2: Continued.

Mode	FT-RS		SERS Au colloid	
	ν [cm ⁻¹]	FWHM [cm ⁻¹]	ν [cm ⁻¹]	FWHM [cm ⁻¹]
ν_1 (Pyr; δ_{oop} (CC(H)C) + ν (CN) + δ_{trig} (Pyr))	991	6	—	—
ν_{12} (Phe)	1001	6	998	9
ν_{18a} (Phe)	1029	9	1026	10
ρ_r (CC(H)C) _{pyr} + ν (CC) _{pyr} + ν (CO) + ν (PC _{phe})	1103	8	1102	11
ν (P=O) and/or δ (C-H)	1164	15	1158	16
ν_{9a} (Phe; δ (CH)) and/or ν_{sym} (C _{β} C _{γ} H ₂ C _{δ})	1199	12	1196	—
ν_{9a} (Pyr) and/or ν_{7a} (Phe; phenyl-C stretch)	1222	13	—	—
ν_{19b} (Pyr/Phe)	1436	5	1435	9
ν_{8b} (Pyr/Phe)	1573	8	1585	10
ν_{8a} (Pyr/Phe)	1592	11	1608	15

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