

# Vibrational characterization of $\alpha$ -aminophosphinic acid derivatives of pyridine: DFT, Raman and SERS spectroscopy studies<sup>☆</sup>



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## ABSTRACT

This paper shows Fourier-transform Raman (FT-RS) and surface-enhanced Raman spectroscopy (SERS) studies of three  $\alpha$ -aminophosphinic acid derivatives of pyridine: [(butylamino)(pyridin-2-yl)methyl]phenylphosphinic acid ( $\alpha$ -PyNH), [(butylamino)(pyridin-3-yl)methyl]phenylphosphinic acid ( $\beta$ -PyNH), and [(benzylamino)(pyridin-4-yl)methyl]phenylphosphinic acid ( $\gamma$ -PyNH) immobilized onto colloidal sol nanoparticles and electrochemically roughened surface of silver. The molecular geometries and vibrational wavenumbers were calculated based on density functional theory (DFT) at the B3LYP 6-311G (df,p) level of theory. Based on the comparison of the FT-RS experimental and theoretical vibrational bands with the SERS results the orientation of the  $\alpha$ -aminophosphinic acid derivatives of pyridine onto two silver substrates was proposed. The changes in the adsorption process under the influence of the position of substituent in regard to the ring N atom (in  $\alpha$ -,  $\beta$ -, and  $\gamma$ -positions, respectively) and modification of the substituent (replacement of the butyl chain by the phenyl ring of high affinity to silver ( $\gamma$ -PyNH)) were also discussed.

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## 1. Introduction

In recent years, there has been growing interest in the applications of phosphorous derivatives of pyridine because of their stability and durability in both neutral and basic conditions [1–5]. Interestingly, the combination of a heterocyclic moiety with a phosphorous-containing fragment makes these compounds very attractive in terms of biological and chemical applications [6,7]. This is because the C–P bond cleavage phenomenon of pyridine aminophosphonate and aminophosphinate, occurring in acidic aqueous media, play an essential role in the decomposition process of heterocyclic aminophosphonates, such as derivatives of imidazole, thiazole, and choline [6–8], and the formed products may serve as useful reagents in organic synthetic applications.

Pyridine-like compounds have a wide range of applications ranging from medicinal drugs to agriculture products, including:

insecticides, fungicides, herbicides, plant growth regulators [9–12], and enzyme inhibitors [13]. Pyridines are very promising class of compounds due to the properties of the pyridine ring (stable, 6- $\pi$ -electron,  $\pi$ -deficient, and nitrogen-containing aromatic structure, in which the ring nitrogen is more electronegative than the ring carbons) [10]. Chemical reactivity of this group of compounds is associated with the ability to the polarization of the  $\pi$ -electrons, presence of a large permanent dipole moment, and the tendency for electron donation due to the presence of the electron-deficient carbon atom. Pyridines also exhibit good miscibility with the most organic solvents [10]. Thus, this group of compounds is considered as promising serine protease inhibitors [13], especially as a potent inhibitors of aminopeptidase N [14] – a transmembrane protease located in various kind of human organs, cells, and tissues [15–18]. Inhibition of this ectopeptidase may shed some light on design of the anti-cancer and anti-inflammatory drugs [15]. This class of molecules also acts as very effective ligands of heavy metal ions, particularly Cu(II) [19].

Here, we used the surface-enhanced Raman spectroscopy technique to study the adsorption mechanism of three pyridine aminophosphinates, including:  $\alpha$ -aminophosphinic acid

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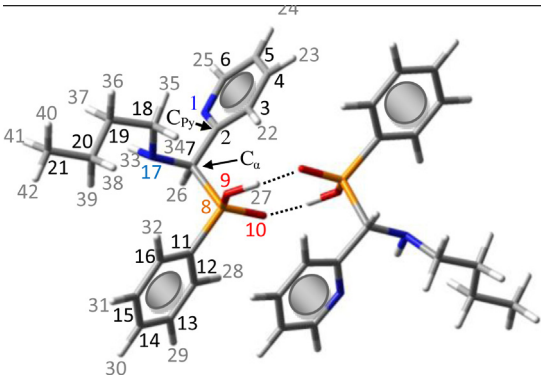
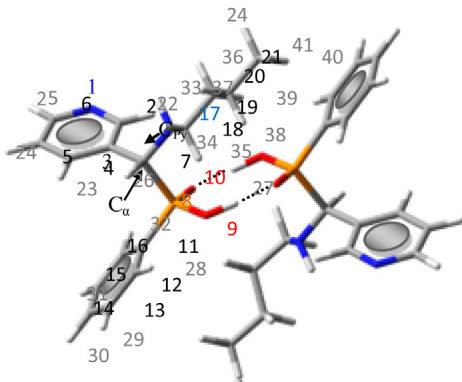
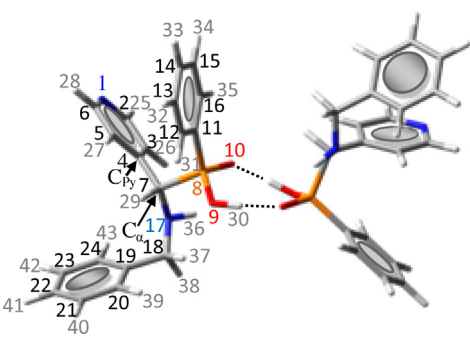
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derivatives of pyridine ([[(butylamino)(pyridin-2-yl)methyl]phenylphosphinic acid ( $\alpha$ -PyNH), [(butylamino)(pyridin-3-yl)methyl]phenylphosphinic acid ( $\beta$ -PyNH), and [(benzylamino)(pyridin-4-yl)methyl]phenylphosphinic acid ( $\gamma$ -PyNH)) (Table 1) immobilized onto colloidal and roughened in the oxidation-reduction cycles (ORC) silver substrates. This is important because SERS gives information about supramolecular architectures and adsorption phenomena occurring at solid/liquid interface, which may provide new insights into *in vivo* behavior of these molecules in the physiological conditions. In this paper we focused mainly on the changes in the molecular orientation onto the silver substrates due to the different position of the substituent relative to the ring nitrogen atom (in  $\alpha$ -,  $\beta$ -, and  $\gamma$ -positions, respectively), the modification of the substituent (replacement of the butyl chain by the phenyl ring of high affinity to silver ( $\gamma$ -PyNH)), and due to the development of the silver surface.

We also employed Fourier-transform Raman (FT-RS) spectroscopy to determine the vibrational properties of the investigated compounds. To make a reliable assignment of the experimental frequencies to the normal mode motions we performed theoretical analysis using density functional theory (DFT) calculations with the B3LYP method at the 6-311G(df,p) level of theory [20–22].

The SERS technique is a very useful way to analyze adsorption process at the molecular level [23–26]. In SERS, the unique Raman signal amplification (up to  $10^{14}$ ) is observed for molecules adsorbed or being in close proximity to a surface of a metallic substrate [21]. The most common SERS-active substrate is silver used as chemically or electrochemically roughened surface or in a colloidal form. Depending on the structure, some of the molecular moieties interact stronger with a metal surface than another. It was proved that compounds, which contain a molecular fragment with

**Table 1**  
Molecular structure of the dimeric structure of the investigated  $\alpha$ -aminophosphinic acid derivatives of pyridine together with the atom numbering scheme.

Molecular structure	Abbreviation	Name of monomer
	$\alpha$ -PyNH	[(pyridino-2-yl)-N-(butyl)amino]-phenyl-methylphosphinic acid
	$\beta$ -PyNH	[(pyridino-3-yl)-N-(butyl)amino]-phenyl-methylphosphinic acid
	$\gamma$ -PyNH	[(pyridino-4-yl)-N-(benzyl)amino]-phenyl-methylphosphinic acid

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