

## FT-IR, FT-Raman and SERS Spectra of L-Proline

Y. Sheena Mary<sup>a</sup>, L. Ushakumari<sup>b</sup>, B. Harikumar<sup>c</sup>, H. Tresa Varghese<sup>d</sup> and C. Yohannan Panicker<sup>b,\*</sup>

<sup>a</sup>Thushara, Neethinagar-64, Pattathanam, Kollam 691021, Kerala, India

<sup>b</sup>Department of Physics, TKM College of Arts and Science, Kollam 691005, Kerala, India

<sup>c</sup>Department of Chemistry, TKM College of Arts and Science, Kollam 691005, Kerala, India

<sup>d</sup>Department of Physics, Fatima Mata National College, Kollam 691001, Kerala, India

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IR, Raman and surface-enhanced Raman scattering (SERS) spectra of L-proline were recorded and analyzed. The molecular plane assumes a tilted orientation with respect to the metal surface. The vibrational wavenumbers and corresponding vibrational assignments are examined theoretically using the Gaussian 03 set of quantum chemistry codes.

**Keywords:** L-Proline, FTIR, FT-Raman, SERS, *Ab initio* HF Calculations

### INTRODUCTION

L-Proline, as an imino acid, contains an amino group and a carboxylic acid [1]. Several groups have reported the introduction of chirality into chromophores using L-proline as a donor residue [2]. Proline is the only naturally occurring amino acid with a secondary  $\alpha$ -amino group, which explains its more basic character with respect to many other  $\alpha$ -amino acids. Marino *et al.* reported the interaction of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  with proline amino acids [5]. Suh and Moskovits [6] reported the surface-enhanced Raman scattering (SERS) spectra of amino acids (glycine, alanine, 6-aminocaproic acid and aminobenzoic acid) and nucleic acid bases (adenine, cytosine and uracil) adsorbed onto a silver colloid surface. In the present study, the IR, Raman and SERS spectra of L-proline are reported, as are the theoretical calculations of the vibrational wavenumbers.

### EXPERIMENTAL

The IR spectra were recorded on Bruker IFS66 V FT-IR

spectrometer (KBr and polyethylene pellets). The FT-Raman and SERS spectra were obtained on a Bruker IFS66V NIR-FT instrument equipped with a FRA 106 Raman module. A Nd/YAG laser at 1064 nm with an output of 300 mW was used for excitation. The detector was a Ge-diode cooled to liquid nitrogen temperature. One thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution was  $6 \text{ cm}^{-1}$ . The silver colloid for SERS was prepared by the reduction of silver nitrate by sodium citrate, using the Lee-Meisel method [8]. Five milliliters of an aqueous solution of L-proline ( $2 \times 10^{-4} \text{ M}$ ) was added to an equal volume of the silver colloid.

### RESULTS AND DISCUSSION

#### Calculation of Wavenumbers

The vibrational wavenumbers of L-proline were calculated using the HF/3-21G\* basis set *via* Gaussian 03 software on a personal computer [7]. The vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies. The wavenumber values computed at the HF level contain known systematic

\*Corresponding author. E-mail: cyphyp@rediffmail.com

errors due to the negligence of electron correlation [9]. Therefore, we have used a scaling factor value of 0.9085 for the HF/3-21G\* basis set. Parameters corresponding to the optimized geometry of L-proline (Fig. 1) are given in Table 1.

The calculated vibrational spectrum has no imaginary wavenumbers, which helped to confirm that the structure of L-proline deduced following the optimization corresponds to the energy minimum. The optimum geometry was determined by minimizing the energy with respect to all geometric parameters without imposing molecular symmetry constraints. The assignments of the calculated wavenumbers were aided by the animation option of the MOLEKEL program, which gives a visual presentation of the vibrational modes [10,11].

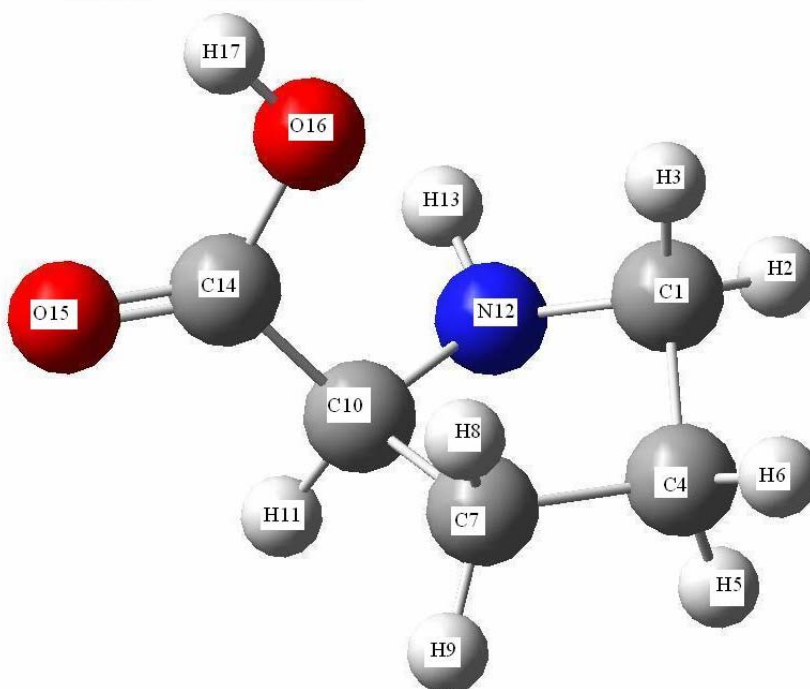
### Methylene Vibrations

The FT-IR, FT-Raman and SERS spectra for L-proline are shown in Fig. 2 and the wavenumbers and band assignments for L-proline are summarized in Table 2.

The vibrations of the CH<sub>2</sub> group, the asymmetric stretch  $\nu_{as}CH_2$ , symmetric stretch  $\nu_sCH_2$ , the scissoring vibrations of the  $\delta CH_2$ , and wagging vibration of the  $\omega CH_2$ , appear in the regions  $3000 \pm 50$ ,  $2965 \pm 30$ ,  $1455 \pm 55$  and  $1350 \pm 85$  cm<sup>-1</sup>,

respectively [12,13]. Methylene asymmetric and symmetric stretching bands of the pyrrolidine are usually observed near 2953 and 2868 cm<sup>-1</sup>, respectively [14]. The HF calculation gives three bands for the asymmetric and symmetric stretching corresponding to different methylene groups, C<sub>1</sub>H<sub>2,3</sub>, C<sub>4</sub>H<sub>5,6</sub> and C<sub>7</sub>H<sub>8,9</sub>. Electronic effects including back donation, mainly caused by the presence of the nitrogen atom adjacent to the methylene groups, can shift the position and alter the intensity of CH stretching and bending modes.

The lowering of wavenumbers and the increasing intensity of CH stretching modes of the CH<sub>2</sub> of the ring point to the influence of back donation in the ring owing to the presence of the nitrogen atom. For a molecule containing a methylene group, the electronic charge is back-donated from the lone pair of nitrogen to the  $\sigma^*$  orbital of the CH bonds, causing a weakening of the CH bonds. This is followed by the increase in C-H force constants and can result in the enhancement of IR band intensity of C-H stretching modes [15,16]. The asymmetric CH<sub>2</sub> stretching bands are observed at 3012, 2978 cm<sup>-1</sup> in the IR spectrum and at 3000, 2983 cm<sup>-1</sup> in the Raman spectrum. The calculated values are 3005, 2990 and 2980 cm<sup>-1</sup>. The symmetrical CH<sub>2</sub> stretching bands are observed at

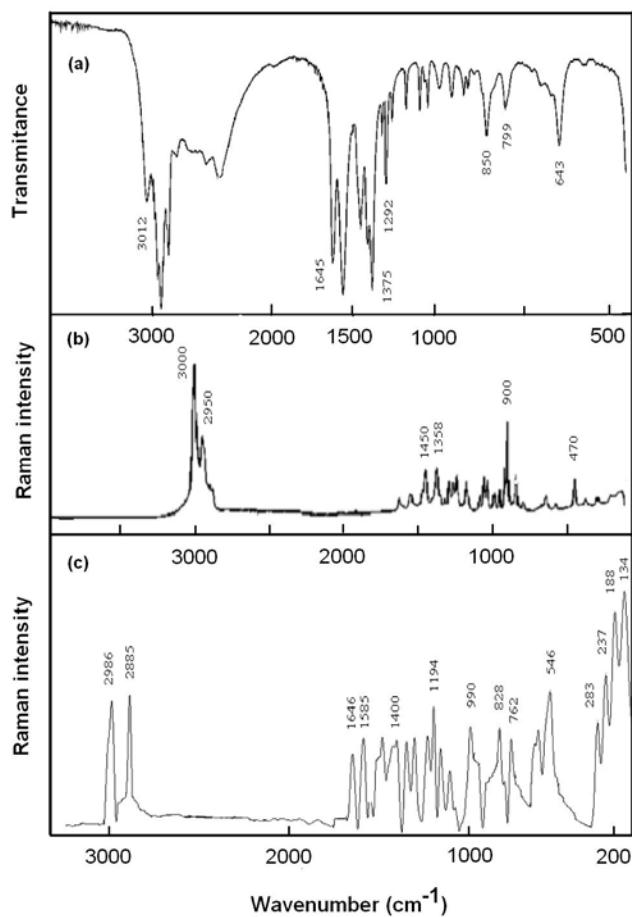


**Fig. 1.** Optimized geometry of L-proline.

**Table 1.** Optimized Geometric Parameters of L-Proline<sup>a</sup>

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
C <sub>1</sub> -H <sub>2</sub>	1.0808	A(2,1,3)	109.8	D(2,1,4,5)	80.1
C <sub>1</sub> -H <sub>3</sub>	1.0849	A(2,1,4)	112.9	D(2,1,4,6)	-42.2
C <sub>1</sub> -C <sub>4</sub>	1.5353	A(2,1,12)	110.4	D(2,1,4,7)	-159.1
C <sub>1</sub> -N <sub>12</sub>	1.4741	A(3,1,4)	110.4	D(3,1,4,5)	-43.0
C <sub>4</sub> -H <sub>5</sub>	1.0814	A(3,1,12)	112.5	D(3,1,4,6)	-165.3
C <sub>4</sub> -H <sub>6</sub>	1.0816	A(4,1,12)	101.0	D(3,1,4,7)	77.8
C <sub>4</sub> -C <sub>7</sub>	1.5464	A(1,4,5)	113.0	D(12,1,4,5)	-162.2
C <sub>7</sub> -H <sub>8</sub>	1.0819	A(1,4,6)	109.2	D(12,1,4,6)	75.5
C <sub>7</sub> -H <sub>9</sub>	1.0798	A(1,4,7)	102.6	D(12,1,4,7)	-41.4
C <sub>7</sub> -C <sub>10</sub>	1.5689	A(5,4,6)	109.6	D(2,1,12,10)	157.0
C <sub>10</sub> -H <sub>11</sub>	1.0785	A(5,4,7)	112.0	D(2,1,12,13)	-69.5
C <sub>10</sub> -N <sub>12</sub>	1.4673	A(6,4,7)	110.2	D(3,1,12,10)	-80.0
C <sub>10</sub> -C <sub>14</sub>	1.5055	A(4,7,8)	109.2	D(3,1,12,13)	53.5
N <sub>12</sub> -H <sub>13</sub>	1.0017	A(4,7,9)	113.1	D(4,1,12,10)	37.7
C <sub>14</sub> -O <sub>15</sub>	1.2025	A(4,7,10)	104.3	D(4,1,12,13)	171.2
C <sub>14</sub> -O <sub>16</sub>	1.3622	A(8,7,9)	109.0	D(1,4,7,8)	-85.9
O <sub>16</sub> -H <sub>17</sub>	0.9686	A(8,7,10)	109.7	D(1,4,7,9)	152.6
		A(9,7,10)	111.4	D(1,4,7,10)	31.4
		A(7,10,11)	111.8	D(5,4,7,8)	35.6
		A(7,10,12)	104.2	D(5,4,7,9)	-85.9
		A(7,10,14)	108.7	D(5,4,7,10)	152.9
		A(11,10,12)	111.7	D(6,4,7,8)	157.9
		A(11,10,14)	107.5	D(6,4,7,9)	36.4
		A(12,10,14)	113.0	D(6,4,7,10)	-84.9
		A(1,12,10)	110.1	D(4,7,10,11)	111.5
		A(1,12,13)	116.0	D(4,7,10,12)	-9.3
		A(10,12,13)	115.5	D(4,7,10,14)	-130.1
		A(10,14,15)	127.0	D(8,7,10,11)	-131.7
		A(10,14,16)	111.1	D(8,7,10,12)	107.6
		A(15,14,16)	121.9	D(8,7,10,14)	-13.2
		A(14,16,17)	111.6	D(9,7,10,11)	-10.9
				D(9,7,10,12)	-131.6
				D(9,7,10,14)	107.6
				D(7,10,12,1)	-17.9
				D(7,10,12,13)	-151.6
				D(11,10,12,1)	-138.6
				D(11,10,12,13)	87.6
				D(14,10,12,1)	100.0
				D(14,10,12,13)	-33.7
				D(7,10,14,15)	-104.2
				D(7,10,14,16)	74.2
				D(11,10,14,15)	16.9
				D(11,10,14,16)	-164.7
				D(12,10,14,15)	140.6
				D(12,10,14,16)	-41.0
				D(10,14,16,17)	-178.2
				D(15,14,16,17)	0.3

<sup>a</sup>Atomic labeling is delineated in Fig. 1.



**Fig. 2.** FT-IR (a), FT-Raman (b) and SERS (c) spectra for L-proline.

**Table 2.** Wavenumbers and Band Assignments for L-Proline<sup>a</sup>

Calculated (HF)	Wavenumbers (cm <sup>-1</sup> )			Band assignments
	IR	Raman	SERS	
3518				νOH
3410				νNH
3005	3012 s	3000 vs		ν <sub>as</sub> CH <sub>2</sub>
2990		2983 s	2986 s	ν <sub>as</sub> CH <sub>2</sub>
2980	2978 s			ν <sub>as</sub> CH <sub>2</sub>
2969				νCH
2951	2956 s	2950 s		ν <sub>s</sub> CH <sub>2</sub>
2944	2938 vs	2938 sh		ν <sub>s</sub> CH <sub>2</sub>

**Table 2.** Continued

2908		2900 w	2885 s	ν <sub>s</sub> CH <sub>2</sub>
1782	1645 vs	1643 w	1646 m	νC=O
1535	1544 vvs	1540 w	1585 m	δNH
1502				δCH <sub>2</sub>
1491		1483 sh	1480 m	δCH <sub>2</sub>
1453	1446 s	1450 m		δCH <sub>2</sub>
1365	1375 vs	1373 vw	1400 m	δOH
1363		1358 m		ωCH <sub>2</sub>
1351		1350 vw		ωCH <sub>2</sub>
1342			1346 m	ωCH <sub>2</sub>
1317	1320 m	1317 vw		τCH <sub>2</sub>
1298	1292 s	1293 w	1301 m	δCH
1244	1242 m	1248 w	1229 m	νC-O
1205				τCH <sub>2</sub>
1191	1189 m	1186 w	1194 s	τCH <sub>2</sub>
1136			1154 m	τNH
1112			1117 m	νCN
1083	1090 m	1083 vw		uring
1016	1025 m	1023 w	990 s	uring
949	950 wbr	941 m		γOH
908	907 vw	900 s		uring
898				uring
876	866 vw	880 vw		uring
855	850 m	850 w	828 m	ρCH <sub>2</sub>
796	799 m	789 vw		ρCH <sub>2</sub>
746			762 m	ρCH <sub>2</sub>
724	721 vw			δC=O
620	630 m	633 w	612 m	δring
588		583 vw		δring
572			546 s	γC=O
493		470 m		ρC(=O)O
404		383 w		tOH
289		300 w	283 s	γring
252			237 s	γring
204		217 vw		tCOOH
			188 vs	νAg-O
			134 vs	νAg-N
77				tring
44				tring

<sup>a</sup>ν, stretching; δ, in-plane bending; γ, out-of-plane bending; ω, wagging; τ, twisting; ρ, rocking; t, torsional; v, very strong; s, strong; w, weak; m, medium; br, broad; sh, shoulder; as, asymmetric; s, symmetric.

2956, 2938  $\text{cm}^{-1}$  in the IR and at 2950, 2938, 2900  $\text{cm}^{-1}$  in the Raman spectra. For L-prolinium tartrate, the  $\nu\text{CH}$  is reported at 294  $\text{cm}^{-1}$  [17].

The bending vibrations of the C-H bonds in the methylene group are identified in their respective positions. The scissoring mode of the  $\text{CH}_2$  group gives rise to a characteristic band near 1465  $\text{cm}^{-1}$  in IR and Raman spectra [18]. This mode is unambiguously correlated with the strong band at 1483  $\text{cm}^{-1}$  in the Raman spectrum. The twisting and rocking vibrations of the  $\text{CH}_2$  group appear in the regions  $1290 \pm 45$  and  $890 \pm 55$   $\text{cm}^{-1}$ , respectively [12]. The twisting and rocking modes are also identified. For proline oligomers and poly-L-proline [19] the  $\text{CH}_2$  deformation bands are reported at 1446, 1261, 1237 ( $\delta\text{CH}_2$ ), 1198, 1187, 1172 ( $\tau/\omega\text{CH}_2$ ), 781, 662  $\text{cm}^{-1}$  ( $\rho\text{CH}_2$ ). For the title compound, the bands observed at 1446  $\text{cm}^{-1}$  in the IR spectrum, 1483, 1450  $\text{cm}^{-1}$  in the Raman spectrum and 1502, 1491, 1453  $\text{cm}^{-1}$  calculated values are ascribed to the  $\delta\text{CH}_2$  scissoring modes. The  $\omega\text{CH}_2$  wagging modes are observed at 1358, 1350  $\text{cm}^{-1}$  in the Raman spectrum and at 1363, 1351, 1342  $\text{cm}^{-1}$  theoretically. For L-proline, the bands at 1317, 1186  $\text{cm}^{-1}$  in the Raman spectrum, 1320, 1189  $\text{cm}^{-1}$  in the IR spectrum and 1317, 1205, 1191  $\text{cm}^{-1}$  calculated values are assigned to the  $\tau\text{CH}_2$  twisting modes, whereas the bands at 850 and 789  $\text{cm}^{-1}$  in the Raman spectrum, 850 and 799  $\text{cm}^{-1}$  in the IR spectrum and 855, 796 and 746  $\text{cm}^{-1}$  (HF) are assigned to the  $\rho\text{CH}_2$  modes.

### COOH Vibrations

The  $-\text{C}(=\text{O})\text{OH}$  group is best characterized by the OH stretch, the C=O stretch and the OH out-of-plane deformation as well as the C-O stretch and the OH in-plane deformation. The C=O stretching vibration gives rise to characteristic bands in the IR and Raman spectra and the intensity of these bands can increase due to conjugation or the formation of hydrogen bonds [20]. C=O stretching vibration gives rise to a strong band in the region  $1725 \pm 65$   $\text{cm}^{-1}$  [12]. For L-proline, the HF calculation assigns the mode at 1782  $\text{cm}^{-1}$  to a C=O stretch. The band at 1645  $\text{cm}^{-1}$  in the IR spectrum and 1643  $\text{cm}^{-1}$  in the Raman spectrum is assigned to a  $\nu\text{C}=\text{O}$  band. Rippon *et al.* [19] reported a value of 1647  $\text{cm}^{-1}$  for the carbonyl stretching mode. The OH in-plane deformation, coupled to the C-O stretching vibration is expected in the region  $1390 \pm 55$   $\text{cm}^{-1}$ . The C(=O)O stretching vibration, coupled to the OH in-plane

deformation, exhibits a moderate to strong band in the region  $1250 \pm 80$   $\text{cm}^{-1}$ . The out-of-plane OH deformation [21] exhibits a moderate band in the region  $905 \pm 65$   $\text{cm}^{-1}$ . The C=O in-plane deformation is weakly to moderately active in the region  $725 \pm 95$   $\text{cm}^{-1}$ . Most carboxylic acids display  $\gamma\text{C}=\text{O}$  in the region  $595 \pm 85$   $\text{cm}^{-1}$ , in the vicinity of that of methyl and ethyl esters. The  $-\text{C}(=\text{O})\text{O}$  deformation or rock has a weak to moderate intensity and appears in the region  $445 \pm 120$   $\text{cm}^{-1}$ .

For glutamic acid dipeptides, the intensity of  $\gamma\text{OH}$  bands [22] is reported at  $\sim 940$   $\text{cm}^{-1}$ . For L-proline, the band at 1242  $\text{cm}^{-1}$  in the IR spectrum and 1248  $\text{cm}^{-1}$  in the Raman spectrum are assigned to the  $\nu\text{C}(=\text{O})\text{O}$  mode, with a calculated value of 1244  $\text{cm}^{-1}$ . The bands observed at 950  $\text{cm}^{-1}$  in the IR spectrum and 941  $\text{cm}^{-1}$  in the Raman spectrum are assigned to the  $\gamma\text{OH}$  mode. The C=O deformation bands are at 721 for IR, and 724 and 572  $\text{cm}^{-1}$  for HF.

### Ring Modes

The ring stretching modes of the pyrrolidine ring are in the region from 1100 to 800  $\text{cm}^{-1}$  and the ring bending modes appear below 800  $\text{cm}^{-1}$  [23]. The most prominent ring stretching mode is the symmetrical ring breathing mode, which usually appears as an intense band at 902  $\text{cm}^{-1}$  for pyrrolidine [14]. For L-proline, this mode is identified as a strong Raman band at 900  $\text{cm}^{-1}$  and as a medium band at 907  $\text{cm}^{-1}$  in the IR spectrum. The ring stretching modes of the pyrrolidine ring in the vapor phase generally give rise to a strong IR band at 1095  $\text{cm}^{-1}$  along with a reasonably weak Raman band at 980  $\text{cm}^{-1}$  at room temperature [23]. Rippon *et al.* [19] reported the proline ring stretching vibrations at 914, 983 and 1000  $\text{cm}^{-1}$ . In the present case, the assignments of the proline ring modes, which are in agreement with those reported by Podstawka *et al.* [24], were observed at 1090, 1025, 907, 866  $\text{cm}^{-1}$  in the IR spectrum, 1083, 1023, 900, 880  $\text{cm}^{-1}$  in the Raman spectrum and 1083, 1016, 908, 898, 876  $\text{cm}^{-1}$  (HF), all of which are assigned to the ring stretching modes.

The bond lengths  $\text{C}_4-\text{C}_7$ ,  $\text{C}_1-\text{C}_4$ ,  $\text{C}_7-\text{C}_{10}$  of the proline ring from the HF calculations are found to be 1.5464, 1.5353 and 1.5689 Å, respectively. Padmaja *et al.* [23] reported the corresponding experimental values as 1.5 Å (HF) and 1.46 to 1.52 Å. The C-N bond length in the proline ring is calculated

to be 1.4741 Å ( $C_1-N_{12}$ ) and 1.4673 Å ( $C_{10}-N_{12}$ ), whereas the reported experimental values are 1.49, 1.5 Å and 1.4, 1.5 Å by HF calculations [23]. In the present case, the CH bonds lengths are in the range 1.0849-1.0785 Å, which is in agreement with the reported values [23].

### SERS Spectrum

Regarded as a highly sensitive method, SERS allows for the detection of individual molecules [25]. The vibrational information contained in the Raman spectrum provides the molecular specificity required to characterize the adsorbate-surface interactions, specifically, the orientation of the adsorbed species on the metal surface. The relative intensities from the SERS spectra are expected to differ significantly from normal Raman spectra owing to specific surface selection rules [26]. These rules suggest that, for a molecule adsorbed flat on the silver surface, its out-of-plane vibrational modes will be enhanced compared to its in-plane vibrational modes and vice versa when its adsorbed position is perpendicular to the surface [26,27]. It is further seen that vibrations involving atoms that are close to the silver surface will be enhanced. When the wavenumber difference between Raman bands in the normal and SERS spectra is not more than 5  $cm^{-1}$ , the molecular plane is perpendicular to the silver surface [28].

In the SERS spectrum of L-proline, prominent bands are observed at 2986, 2885, 1585, 1480, 1346, 1301, 1229, 1194, 990, 828, 762, 283, 237, 188 and 134  $cm^{-1}$ . In the case of the SERS spectra of thymine molecules on silver [29], the deformation bands of the methyl group are present at 1355  $cm^{-1}$ , with the position of the methyl group close to the metallic surface. For 2-methylpyridine, Bunding *et al.* [30] noticed significant shift and broadening of the CH modes in the SERS spectrum. They explained this in terms of the interaction of the methyl group with the metal surface. In the present case, the asymmetric CH stretching of the methylene group appears at 2986  $cm^{-1}$  in the SERS spectrum. Also, the symmetric CH stretching of the methylene group, a weak band in the Raman spectrum at 2900  $cm^{-1}$ , is shifted to 2885  $cm^{-1}$  as a strong band in the SERS spectrum. This is related to the closeness of the  $CH_2$  group to the silver surface, which is justifiable because the modes in the groups directly interacting with the metal surface are prominent in the SERS spectrum

and undergo a wavenumber shift [31]. Furthermore, the presence of the deformation bands of the  $CH_2$  group in the SERS spectrum also supports the above argument.

The C=O and C-O stretching bands are also present in the SERS spectrum at 1646 and 1229  $cm^{-1}$ . In the SERS spectrum, the presence of strong band at 188  $cm^{-1}$  is due to the  $\nu Ag-O$  vibration, giving evidence of an interaction of the silver surface with the carbonyl group [32]. The interaction between the carboxylate group and the metal surface is supported by the presence of a strong band at 546  $cm^{-1}$  in the SERS spectrum due to the C=O deformation band, which is absent in the normal Raman spectrum.

According to surface selection rules [33,34], the presence of in-plane and out-of-plane modes of the proline ring at 612, 283, 237  $cm^{-1}$  in the SERS spectrum of L-proline suggest that there is a certain angle between the ring and the metal surface. Also, L-proline interacts with the silver surface through the NH group. This is supported by the SERS bands at 1585  $cm^{-1}$  ( $\delta NH$ ), 1154  $cm^{-1}$  ( $\tau NH$ ) and 1117  $cm^{-1}$  ( $\nu CN$ ). The presence of a strong band  $\nu Ag-N$  at 134  $cm^{-1}$  in the SERS spectrum also supports this argument [24].

### CONCLUSIONS

A useful technique for studying the adsorption of molecules on metal surfaces, SERS spectroscopy aided in determining the tilted orientation of L-proline on a silver surface due to the presence of the in-plane and out-of-plane modes of the proline ring. The presence of significant metal-molecule interaction is confirmed by the appearance of intense Ag-O and Ag-N modes in the SERS spectrum, indicative of the nearness of carboxylate and NH groups to the silver surface. The presence of methylene group modes in the SERS spectrum verifies the proximity of the methylene group to the metal surface, affecting the orientation and the interaction of the metal with the L-proline molecules. The calculated vibrational wavenumbers obtained by HF are in good agreement with the experimental values obtained for the investigated molecule.

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