Synthesis, SERS, Raman and FT-IR Investigation in Conjunction with DFT Theoretical Simulations on N-(2-cyanoethyl)-imidazole. I

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A thoroughly experimental and theoretical spectroscopic study (Surface-enhanced Raman Spectroscopy (SERS), Raman and FT-IR) concerning the structure of N-(2-cyanoethil)-imidazole have been performed. Limited information is bringing by Raman Spectroscopy, but when absorbed on the surface of the silver nanoparticles, strong vibrational signals were recorded. The influence of aggregation ions (F^-, Cl^-, Br, I^-) and the influence of pH on the adsorption mechanism was investigated. Ab initio HF and density functional theory calculation were carried out to compute the wavenumbers of N-(2-cyanoethil)-imidazole. All theoretical and experimental vibrational frequencies for N-(2-cyanoethil)-imidazole were carefully assigned, and are in agreement to each other.

Keywords: Surface-enhanced Raman Spectroscopy, FT-IR, DFT, substituted imidazole

Imidazole derivatives are common scaffolds in highly significant natural biomolecules, including vitamins (biotin, cobalamin, etc.), amino acids (histidine, histamine, etc.), alkaloids (hymenine, pilocarpine, etc.) etc, which have been shown to exhibit interesting biological activities such as antimicrobial, and cytotoxic activities [1, 2]. Synthetic imidazoles have also been found to be biologically and medicinally potent anticancer [3, 4], anti-HIV [5, 6], antibacterial and antifungal [7, 8].

The use of these compounds as medicine requires that they have to be identified quickly in very small amounts. Vibrational spectroscopy i.e. FT-IR, Raman and SERS are routinely used in this respect. During the last few years, surface-enhanced Raman Spectroscopy became a useful and powerful method for structural determination of bioorganic compounds [7]. Raman signal is amplified by the roughness of metal surfaces. There are two mechanisms that explain the enhancement of Raman signal: charge-transfer (CT) enhancement that is attributed to the first layer effect and electromagnetic (EM) enhancement which goes beyond the first absorbed layer [9]. Thus, this method allows the detection of very low sample concentration [10, 11]. Also, the SER spectra are enhanced by the presence of chloride anion [12].

Carrying on our work in the field of imidazole derivatives [13-15], and having in view the potential practical applications, we decided to perform a systematic study concerning structure of substituted imidazole. The influence of other anions (F^-, Br^-, I^-) and *p*H influence over SER spectra of N-(2-cyanoethil)-imidazole was investigated. Furthermore, the computed vibrational analysis was correlated with the spectral data in order to find how the molecule was adsorbed on the surface of the silver colloid. Our final goal is to construct a data base that could be used for quick and cheap identification of imidazole derivatives.

Experimental part

Synthesis

25 mmoles (1,744g) imidazole were dissolved at 80°C in 10mL toluene. 25 mmoles (1.325g ≈1.625 mL) acrylonitrile and 0.1 mL triethylamine were added and the mixture was refluxed for 30 h. The solvent was distilled and N-(2-cyanoethyl)-imidazole was obtained (yellow-orange oil) with a yield of ~ 99%. The reaction pathway is illustrated in figure 1.

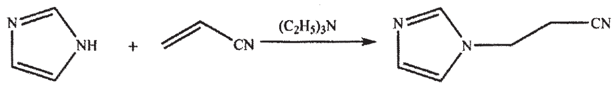

Fig. 1. Reaction pathway for the synthesis of N-(2-cyanoethyl)-imidazole

Computational details

The vibrational wavenumbers were performed using Firefly program [16, 17]. The computations were performed at HF/6-31+G**, B3PW91/6-31+G** and B3LYP/6-31+G** levels at theory to get the optimized geometry and vibrational wavenumbers of the normal modes of N-(2-cyanoethyl)-imidazole [18].

Ab initio calculations were performed at the restricted Hartree-Fock (RHF) level of theory. Density functional theory (DFT) calculation were carried out with the three-parameter hybrid functional Becke 3 (B3) [19] for the exchange part and the Lee-Yang-Parr (LYP) correlated function [20] and with Becke's 1988 exchange functional [21] and the Perdew-Wang 91 gradient corrected correlated function (BPW91) [22]. The 6-31+G** basis set was used to characterize all the stationary points as minima and to compute the wavenumbers N-(2-cyanoethil)-imidazole.

Vibrational mode assignments were made by visual inspection of modes animated by using the Gabedit—A graphical user interface for computational chemistry softwares [23].

Colloid preparation and instrumentation

The silver colloid was prepared by heating to boiling 200mL volume of 10^{-3}M $AgNO_3$ aqueous solution. 4mL of 1% trisodium citrate solution was added, and the mixture was kept boiling gently for 1h [24].

The resulting colloid shows a turbid grey color.

The final concentration of the analyte into the colloid suspension was approximately $1\cdot10^{-3}$ M. NaOH and H_2SO_4 were used in order to adjust the *p*H values.

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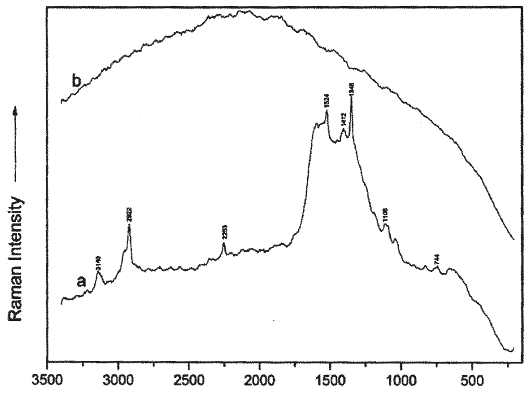

Fig. 2. (a) SER spectrum and (b) ordinary Raman spectrum of N-(2-cyanoethyl)-imidazole

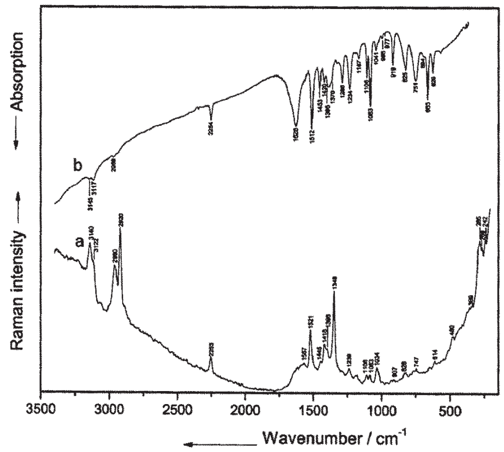

Fig. 3. Comparison of (a) SER spectrum containing 0.5 M Cl$^-$ in a ratio 10:1 and (b) FT-IR spectrum of N-(2-cyanoethil)-imidazole

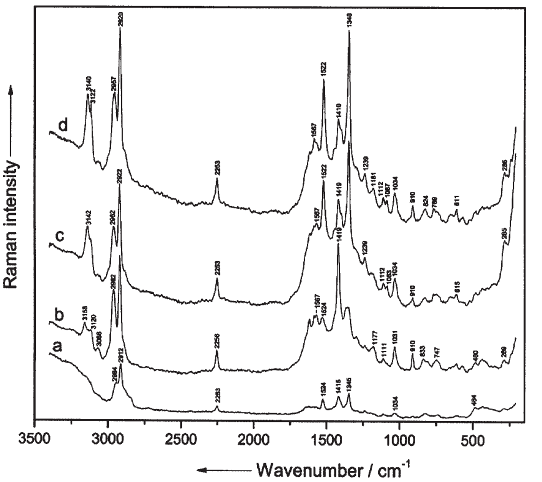

Fig. 4. SER spectra of N-(2-cyanoethyl)-imidazole containing various anions: (a) 0.5 M I$^-$ (b) 0.5 M Br$^-$ (c) 0.5 M Cl$^-$ (d) 0.5 M F$^-$

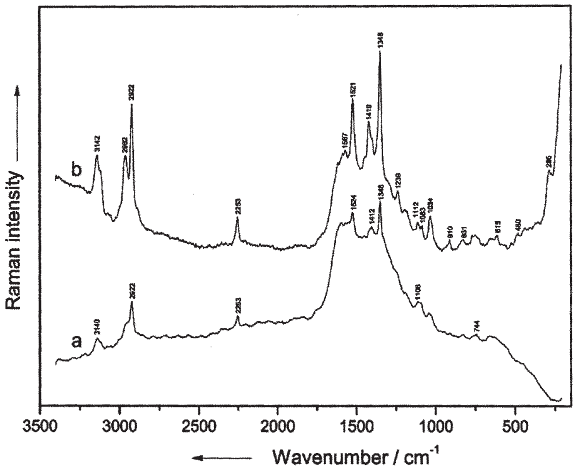

Fig. 5. SER spectra of N-(2-cyanoethyl)-imidazole: (a) in absence of anion and (b) in presence of 0.5M Cl$^-$

The Raman and SER spectra were recorded with a spectrometer Horiba Jobin Yvon RPA-HE 532. A Nd-Yag laser with 532nm frequency was used as source. The nominal power was 100mW, the spectral range between 3600 and 250cm^{-1} with the resolution of 3cm^{-1}. The system is provided with a "superhead" fiber optic Raman probe for contactless measurements.

FT-IR spectrum was recorded by KBr disc method in the range 3500 – 270cm^{-1}, number of scans 40, resolution 2cm^{-1} on a Brucker Vertex 70 spectrometer.

Results and discussions

In the case of N-(2-cyanoethyl)-imidazole, ordinary Raman spectroscopy showed little observational results due to the strong fluorescence background. Thus, the ordinary Raman spectrum N-(2-cyanoethil)-imidazole shows a very weak signal. Therefore, an appropriate method of investigation must be elected. Raman and SER spectrum of N-(2-cyanoethyl)-imidazole is shown in figure 2. Fluorescence is still present in SER spectrum, but several sharp and clear vibrational peaks occur.

FT-IR spectrum and SER spectrum of N-(2-cyanoethil)-imidazole containing 0.5 M Cl$^-$ in a ratio 10:1 are presented in figure 3.

The effect of anion in solution

In order to investigate the degree of coverage of anions on silver surfaces, several different anions were used: F$^-$, Cl$^-$, Br$^-$, I$^-$ [25]. The concentration of added anion was (0.5 M) in a ratio 10:1. As it could be seen from figure 4, the intensity of SER spectrum containing the iodine ion [case (a)] is decreased when compared with the other SER spectra containing bromine, chlorine or fluorine ions. We may also notice that, the intensity of SER spectrum containing the bromide ion [case (b)] is also reduced, but slightly. The iodide ion and bromide ion are strongly absorbed on the silver surface [25] and the molecule of N-(2-cyanoethyl)-imidazole is hindered to be adsorbed on the silver surface. Fluoride and chloride ions give the best SER signal observed in this experiment.

The role of chloride or other co-adsorbed species on the positively charger Ag surface has been experimentally verified [26, 27]. This enhancement originates from the induction of positive charges on silver surfaces by the co-adsorbed chloride, which leads to an increase in the interaction between the molecule and the silver surface [25]. This yields to a considerable enhancement of the SERS signal [12] as seen in figure 5.

Vibrational analysis

The schematic structure of N-(2-cyanoethyl)-imidazole with the labeling of the atoms is illustrated in figure 6.

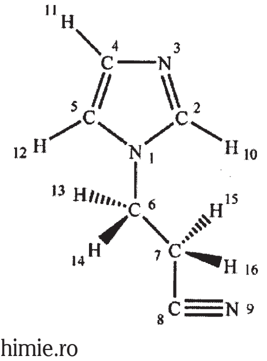

Fig. 6. Schematic structure of N-(2-cyanoethyl)-imidazole with the labeling of the atoms

Table 1
ASSIGNMENT OF THE THEORETICAL WAVENUMBERS VALUES (cm^{-1}) TO THE EXPERIMENTAL BANDS OF THE N-(2-CYANOETHYL)-IMIDAZOLE

Infrared	SERS pH=3	SERS pH=7	SERS pH=12	RHF/ 6-31+G** corrected	B3LYP/ 6-31+G** corrected	B3PW91/ 6-31+G** corrected	Vibrational assignment*
—	—	242w	242w	—	—	—	$\nu(AgN)$
—	269w	269w	270w	—	—	—	$\nu(AgCl)$
—	281w	285m	282m	—	—	—	$\nu(AgCl)$
—	369w	—	369w	387	373	376	$\tau(H_{13}C_6H_{14}) + s(C_7C_8N_9) + \delta(C6N1)$
—	484w	480w	480w	484	472	475	$s(C_7C_8N_9)$
626s	614w	614w	611w	608	605	609	γ(CC ring)
665s	—	—	—	647	644	646	γ(CC ring)
694sh	—	—	—	716	691	693	$\gamma(C_5H_{12})$
—	—	—	—	745	714	719	$\nu(C_6N_1) + \delta(C_2H_{10}) + \delta(C_5H_{12})$ + breathing (ring)
751s	—	747w	—	749	746	743	$\rho(H_{13}C_6H_{14}) + \rho(H_{13}C_6H_{14})$
—	770w	—	—	869	781	783	$\gamma(C_2H_{10}) + \gamma(C_4H_{11}) + \gamma(C_5H_{12})$
825s	—	828w	828w	887	835	837	$\gamma(C_2H_{10}) + \gamma(C_4H_{11}) + \gamma(C_5H_{12})$
—	—	—	—	898	875	874	breathing (ring)
919s	910w	907w	910w	903	919	928	$\nu(C_7C_8)$
977sh	—	—	—	993	979	994	$\nu(C_6C_7)$
998w	—	—	—	996	998	1000	breathing (ring) + $\rho(H_{13}C_6H_{14}) + \rho(H_{13}C_6H_{14})$
1041m	1031w	1034m	1035m	1024	1009	1012	breathing (ring) + $\rho(H_{13}C_6H_{14}) + \rho(H_{13}C_6H_{14})$
1083s	—	1083w	1087w	1071	1057	1059	$\delta(C_2H_{10}) + \delta(C_4H_{11}) + \delta(C_5H_{12})$
1108s	—	1108w	1112w	1092	1099	1110	breathing (ring) + $\delta(C_4H_{11})$
1167m	—	—	—	1154	1142	1143	breathing (ring) + $\tau(H_{13}C_6H_{14}) + \tau(H_{13}C_6H_{14})$
—	—	—	—	1231	1218	1221	$\delta(C_2H_{10})$
1234s	—	1239m	1236w	1263	1246	1248	$\tau(H_{13}C_6H_{14}) + \tau(H_{13}C_6H_{14}) + \delta(C_4H_{11}) + \delta(C_5H_{12})$
—	—	—	—	1280	1258	1254	$\omega(H_{13}C_6H_{14}) + \omega(H_{13}C_6H_{14})$
1288s	1284w	—	—	1282	1264	1269	$\delta(C_4H_{11}) + \delta(C_5H_{12}) + \delta(C_2H_{10}) + \tau(H_{13}C_6H_{14}) + \tau(H_{13}C_6H_{14})$
—	—	1348s	1349s	1365	1342	1345	breathing (ring) + $\omega(H_{14}C_6H_{13})$
1370sh	1361m	—	—	1374	1351	1363	$\nu(N_1C_6) + \omega(H_{13}C_6H_{14}) + \omega(H_{13}C_6H_{14})$
1395sh	—	1398m	1399m	1390	1363	1378	$\nu_{as}(C_2N_1C_5) + \tau(H_{13}C_6H_{14})$
1420m	1422m	1418m	1413m	1431	1420	1412	$s(H_{13}C_6H_{14}) + s(H_{15}C_7H_{16})$
1453s	1446sh	1445w	1445w	1456	1438	1434	$s(H_{13}C_6H_{14}) + s(H_{13}C_6H_{14}) + \delta(C_4H_{11}) + \delta(C_2H_{10})$
1512s	1505w	1521s	1522s	1500	1473	1483	$s(H_{13}C_6H_{14}) + \delta(C_4H_{11}) + \delta(C_2H_{10})$
—	1567w	1567w	1567s	1537	1488	1499	$\delta(C_4H_{11}) + \delta(C_5H_{12})$
1628 s	—	—	—	—	—	—	water absorption band
2254s	2256m	2253m	2253s	2330	2269	2279	$\nu(C_8N_9)$
—	2923s	2920s	2921s	2892	2946	2958	$\nu_s(H_{13}C_6H_{14}) + \nu_s(H_{15}C_7H_{16})$
2969w	2963m	2960s	2958s	2901	2955	2966	$\nu_s(H_{13}C_6H_{14}) + \nu_s(H_{15}C_7H_{16})$
—	—	—	—	2931	2991	3007	$\nu_s(H_{13}C_6H_{14}) + \nu_s(H_{15}C_7H_{16})$
3117w	—	3122sh	3120m	3067	3143	3152	$\nu(C_4H_{11}) + \nu(C_5H_{12})$
3145w	—	3140s	3143s	3088	3162	3172	$\nu(C_4H_{11}) + \nu(C_5H_{12})$

*Abbreviations: w=weak; m=medium; s=strong; sh=shoulder; ν – stretch; ν_s – symmetric stretch; s – scissoring; δ – in plane bending; ρ – rocking; τ – twisting; ω – wagging; γ – out of plane bending; ring - imidazole ring(N_1-C_2-N_3-C_4-C_5)

DFT methods include electron correlation in the study of the vibrational wavenumbers of moderately large molecules [28, 29]. The DFT hybrid B3LYP functional tends to overestimate the fundamental modes, therefore scaling factors have to be used for obtaining a considerable better agreement with the experimental data [30, 31]. Thus, according to the work of Rauhut and Puley [32] and Scott and Radom [30] scaling factor according to the method used has been uniformly applied to HF, B3LYP and B3PW91 calculated wavenumbers values from the table 1. All scaling factors have been kept fixed. For the HF method the scaling factor of 0.8953 was used while for the B3LYP and B3PW91 methods the scaling factor of 0.9614 was used. The disagreement between the theory and the experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry [30]. The scaled theoretical calculation in the table 1, reproduce well the experimental data and allow the assignment of the vibrational modes.

The observed (IR and SERS) and calculated frequencies by *ab initio* and DFT methods and their probable assignments are summarized in table 1.

FT-IR spectrum

The FT-IR spectrum is characterized by sharp and clear band bellow 2500cm^{-1}. The large band at 1628cm^{-1} is due to the water absorption which indicates that the N-(2-cyanoethyl)-imidazole is slightly hygroscopic.

The molecule of N-(2-cyanoethyl)-imidazole has only one functional group, the stretching vibration of nitrile group occurs at 2254cm^{-1}.

Carbon – carbon and carbon - nitrogen vibrations

The C-C stretching modes of N-(2-cyanoethil)-imidazole are assigned to the bands observed at 919 and 977cm^{-1} in FT-IR spectrum. The band at 919cm^{-1} is very strong.

The imidazole ring performs ring breathing vibrations that are observed at 1234, 1167, 1108, 1041 and 998cm^{-1}. Ring out-of-plane vibrations of the imidazole ring are observed at 626cm^{-1} in FT-IT spectrum.

C-H vibrations

C-H vibrations can be divided into aromatic C-H vibrations and aliphatic side chain C-H vibrations.

The aromatic C-H stretching vibrations are normally found between 3100 and 3000cm^{-1}. Above 2500cm^{-1}, in the domain of C-H vibrations, the bands are quite low in intensity. The aromatic C-H stretching vibrations are recorded at 3145 and 3117cm^{-1}. The aromatic C-H in-plane bending modes are observed at 1512, 1453, 1288, 1234, 1108 and 1083cm^{-1}. The aromatic C-H out of plane bending modes are observed at 825 and 694cm^{-1}.

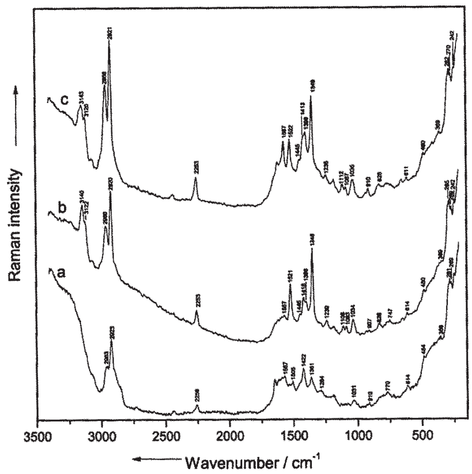

Fig. 7. SER spectra of N-(2-cyanoethyl)-imidazole containing KCl in different conditions: (a) acidic (b) neutral (c) basic

For the aliphatic side chain C_6-N_9 the C-H vibrations are observed as scissoring vibrations at 1453 and 1420cm^{-1}. The rocking vibrations are observed at 1041, 998 and 751 cm^{-1}. The wagging vibrations are observed at 1370cm^{-1}. The twisting vibrations are observed at 1288, 1234 and 1167cm^{-1}. The stretching vibrations occurred at 3145, 3117 and 2969cm^{-1} in FT-IR spectrum.

SER spectra and adsorption on the Silver surface

Overall, the SER spectra show clear and sharp bands. In order to investigate the adsorption mechanism of N-(2-cyanoethyl)-imidazole onto the surface of silver nanoparticule, SER spectra at different values of *p*H were recorded.

SER spectra of N-(2-cyanoethyl)-imidazole at different *p*H values are presented in figure 7.

As NaCl was added to the silver colloid, H_2SO_4 was used to achieve acidic conditions instead of HCl to avoid the influence of the chloride ion. The basic *p*H was achieved by adding NaOH.

Variations in the SER spectra with the change of *p*H values are attributed to a change in orientation of adsorbates in respect with the surface of metal surface. According to the selection rules [33, 34] the most intense bands are those given by vibrations which induce a polarization of the adsorbate electron cloud perpendicular to the metal surface [35]. When the molecule adopts a perpendicular orientation on the surface of silver nanoparticule, the in-plane vibrations would be increased, while out-of-plane vibrations would be decreased.

By looking at SER spectra recorded at different values of *p*H we can observe that new bands occurred in neutral and basic conditions while in acidic conditions the intensity of SER signal decreased.

The molecule of N-(2-cyanoethyl)-imidazole can be adsorbed onto the surface of silver nanoparticule in three ways: through the lone pair-electrons of nitrogen atom N3, through the π-system of the imidazole ring or through the unshared pair of electrons of nitrogen atom from nitrile group N_9. The nitrogen atom N_1 is sterically hindered by the side chain, therefore the molecule cannot be adsorbed onto the metal surface through this atom.

The signal of nitrile group at 2254cm^{-1} in all SER spectra of N-(2-cyanoethyl)-imidazole i.e. acidic, neutral and basic conditions as shown in figure 5 does not present shifts larger than 2cm^{-1}, therefore is unlikely that the molecule of N-(2-cyanoethyl)-imidazole is adsorbed via the nitrogen atom in nitrile group.

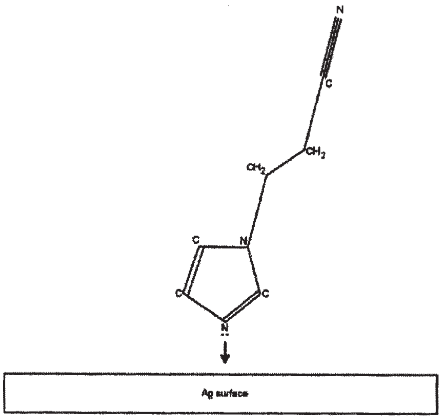

Fig. 8. Suggested adsorption geometry of N-(2-cyanoethyl)-imidazole on the surface of silver nanoparticles, via the unshared electrons of nitrogen atom N_3, in basic and neutral conditions

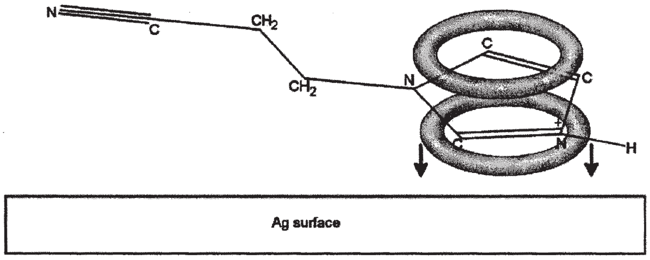

Fig. 9. Suggested adsorption geometry of N-(2-cyanoethyl)-imidazole on the surface of silver nanoparticles, via the delocalized aromatic electrons from imidazole ring, in acidic conditions

We assume that the molecule of N-(2-cyanoethyl)-imidazole in basic conditions is adsorbed on the surface of the silver nanoparticles via the unshared electrons from nitrogen atom N_3, perpendicular onto the surface as it can be seen in figure 8, as in neutral and basic conditions there are very strong bands corresponding to ring breathing at 1348cm^{-1}, while in acidic conditions this band is absent. The strong signal at 1521cm^{-1} in both neutral and basic conditions which correspond to C-H in-plane vibrations, is very weak and blue shifted to 1505cm^{-1} in acidic conditions. This orientation of the molecule of N-(2-cyanoethyl)-imidazole is furthermore supported by the presence of the in-plane medium to strong vibrations bands at 3140, 2960 and 1398cm^{-1} in both SER spectra recorded in neutral and basic conditions, while these bands are weak or are missing in acid conditions.

The molecule of N-(2-cyanoethyl)-imidazole may adopt a tilting position, with respect of imidazole ring against the metal surface, in neutral conditions, as the band at 1567 cm^{-1}, corresponding to in-plane C-H bending, is very strong in basic conditions, but weak in neutral conditions and very weak in acidic conditions.

In acidic conditions the molecule of N-(2-cyanoethyl)-imidazole is found under its imidazolium form [36]. The molecule is adsorbed on the surface of the silver nanoparticles via the delocalized aromatic electrons from imidazole ring, and the molecule lies flat, parallel with the surface, while the side chain C_6-C_7-C_8-N_9 is situated above the plane of the imidazole ring as it can be seen in figure 9. Beside the above arguments, the band at 1361cm^{-1} in acidic conditions, which correspond to out-of-plane H-C-H vibrations, is missing in both neutral and basic SER spectra.

The adsorbate-metal interactions are evidenced by the presence of some bands bellow 300cm^{-1}. The Ag-N stretching mode appears at 242cm^{-1} [25]. The bands at

269cm^{-1} and 285cm^{-1} are most probably due to the AgCl stretching vibrations [37].

Conclusions

An experimental and theoretical spectroscopic study (SERS, Raman and FT-IR) concerning the structure of N-(2-cyanoethyl)-imidazole have been performed. The fundamental vibrational frequencies of N-(2-cyanoethyl)-imidazole have been obtained from ab initio and DFT calculations. The FT-IR and SER spectra at different values of pH were recorded for N-(2-cyanoethyl)-imidazole. As this molecule present a very strong fluorescence at 532 nm, the SER spectroscopy is a very useful tool for detecting a very small amount of these components (10^{-3} M). The data obtained from quantum mechanical methods are in good agreement with the data obtained by experimental observed spectra. Both types of calculations are useful to explain vibrational spectra of N-(2-cyanoethyl)-imidazole, but we have found that *ab initio* calculations RF/6-31+G** level gives overestimated results, even after scaling, compared with DFT-B3LYP/6-31+G** and B3PW91/6-31+G**.

The N-(2-cyanoethyl)-imidazole molecule is adsorbed on the silver surface via the delocalized aromatic electrons from imidazole ring, parallel with the surface in acidic conditions. In neutral and basic conditions, the N-(2-cyanoethiy)-imidazole molecule is adsorbed on the surface of the silver nanoparticles via the unshared electrons from nitrogen atom N_3, perpendicular onto the surface.

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