UNIVERSITY ”ALEXANDRU IOAN CUZA” OF IAȘI

FACULTY OF CHEMISTRY

DOCTORAL SCHOOL OF CHEMISTRY AND LIFE SCIENCES

Study by infrared spectroscopy, Raman and SERS of imidazole derivatives

PhD THESIS SUMMARY

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Contents

Keywords

- IR, Raman, SERS
- vibrational analysis
- adsorption on the silver surface
- imidazole derivatives
- benzimidazole derivatives

General

Infrared spectroscopy (FT-IR), Raman and SERS are techniques commonly used to identify drugs and their precursors. Infrared spectroscopy and Raman spectroscopy provides detailed information on molecular vibrations. Raman spectroscopy is an analytical method used frequently in the analysis of pigments [1-3]. SERS (Surface-Enhanced Raman Spectroscopy) has become an extremely useful method used in determining the structure of bioorganic compounds [4].

In order to understand correctly the infrared spectra, Raman and SERS of molecules, it is required to identify the vibrational modes. Quantum mechanics methods *ab-initio* and DFT (Density Functional Theory) are used. These methods calculate the theoretical vibration modes and subsequently assigned to the results obtained experimentally.

The thesis is divided into three chapters. The first part briefly describes the techniques of infrared spectroscopy, Raman and SERS investigation of imidazole derivatives used in the experimental investigation of this thesis.

Section Two describes briefly the method of computational simulation used to determine the theoretical vibratory modes of the imidazole derivatives investigated in the experimental part of this thesis.

Personal researches are summarized in the third chapter of this thesis and present the FT-IR spectra, Raman and SERS.

II. Computational details

Theoretical calculations were investigated with Firefly [5, 6]. DFT calculations are made according to the method of Becke exchange functional [7] and Perdew-Wang 91 method (B3PW91) [8]. Also, B3LYP method was used. This method contains hybrid parameters using Lee-Yang-Parr correlation [9, 10].

DFT/B3LYP, DFT/B3PW91 methods were used, and *ab initio* HF with 6-31G basis set *.

III. Personal researches

Objectives

PhD thesis entitled “Study by infrared spectroscopy, Raman and SERS of imidazole derivatives“ aims vibrational spectroscopic investigation of a series of organic compounds, investigation in conjunction with computational methods of theoretical simulations.

The research presented in this paper had the following objectives:

1. Synthesis of imidazole derivatives by previously established methods.

2. The main objective was to investigate the synthesized imidazole derivatives by infrared spectroscopy, Raman and SERS. Raman spectroscopy provides complementary information, but due to fluorescence which may present some organic compounds, information may be limited. SERS technique can be used instead.

3. Calculation of vibrational modes of the compounds studied by computational methods. Interpretation of vibrational spectra (FT -IR , Raman and SERS) is a difficult task. Identification of vibrational modes is difficult in the case of complex spectra. The interpretation and identification of vibrational modes in the spectra may be facilitated by comparison of experimentally obtained data with computational simulation data.

4. Identification of functional groups involved in adsorption of molecules on the surface of the particle of colloidal silver.

5. Development of SERS technique for the class of compounds studied. This technique is highly sensitive. Spectra can be recorded with very small amounts of substance. The method can be used for the detection and identification of compounds present in traces. The identification can be used to create a database.

III.1 Experimental (Selective)

Infrared spectra were recorded with the Bruker VERTX 70, spectral resolution 2 cm^{-1} /pixel within 3500 – 300 cm^{-1}.

Raman and SERS spectra were recorded with Raman-Horiba Jobin Yvon RPA-HE 532 spectrometer.

The final concentration of analyte in the sol was approximately $1 \cdot 10^{-3}$ M. NaOH and H_2SO_4 were used to adjust the pH value.

III.1.1 Synthesis

The synthesis of imidazole derivatives (Fig. III.1 and Fig. III.2) [11, 12].

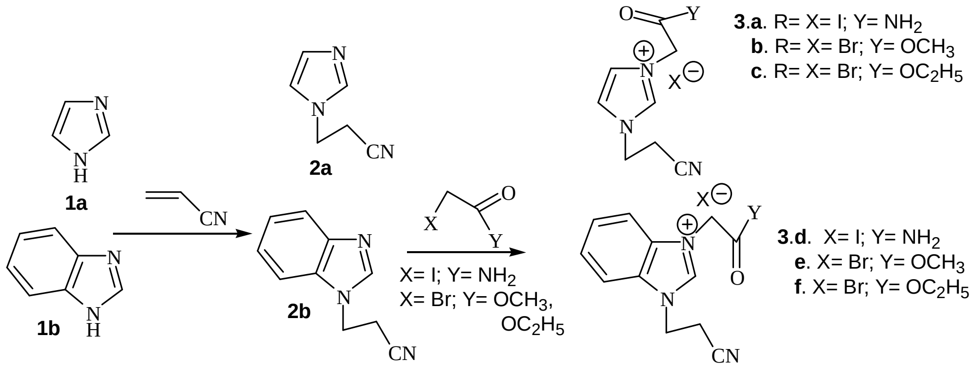


Fig.III.1 Synthesis of imidazole derivatives

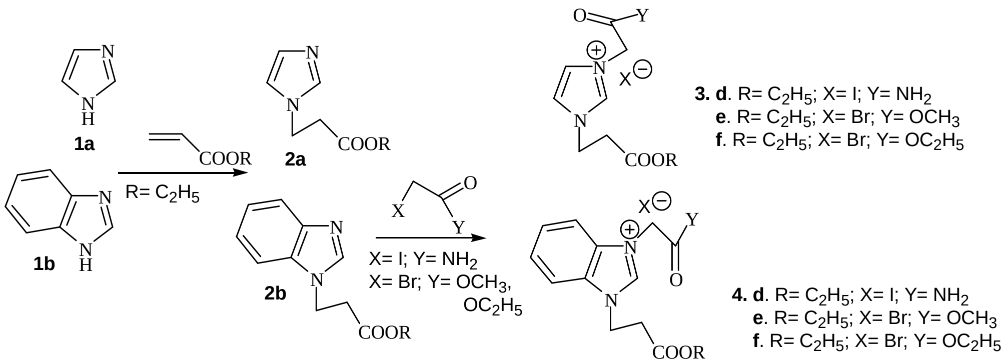


Fig.III.2 Synthesis of imidazole derivatives

In basic medium, the salts of imidazole derivatives formed the corresponding ylides. The characterization of ylide by SERS technique is scarce [13, 14].

III.1.2 Study by infrared spectroscopy, Raman and SERS of imidazole derivatives.Vibrational analysis. Adsorption on the silver surface.

III.2 Study by infrared spectroscopy, Raman and SERS of N-(2-cyanoethil)-imidazole. Adsorption on the silver surface.

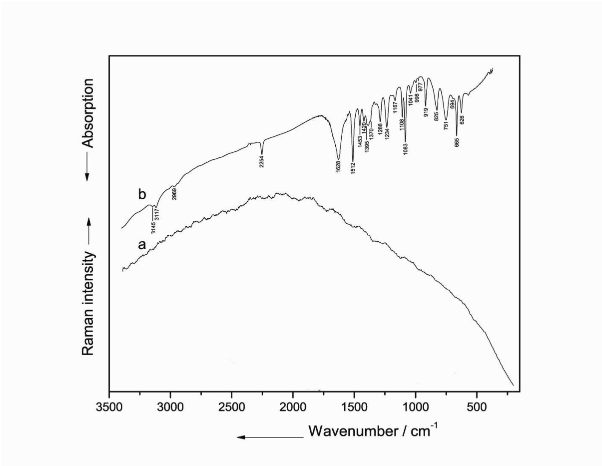


Fig.III.2.1 FT-IR (b) and Raman (a) spectra of N-(2-cyanoethil)-imidazole

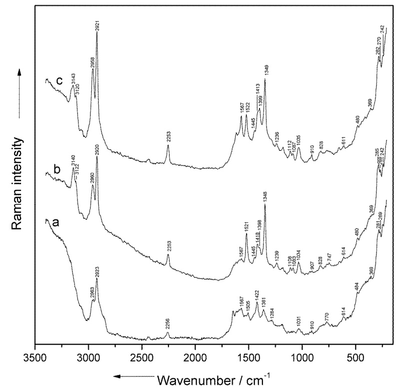


Fig. III.2.2 SERS spectra of N-(2-cyanoethil)-imidazole in different media: (a) acidic, (b) neutral and (c) basic

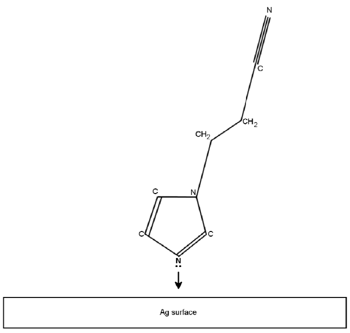


Fig. III.2.3 Molecule adsorption in neutral and basic medium

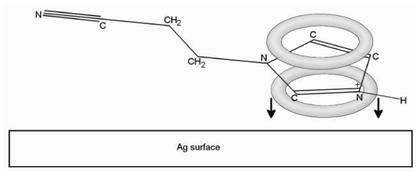


Fig. III.2.4 Molecule adsorption in acidic medium

Conclusions

In neutral and basic medium the molecule is adsorbed via nitrogen atom N_3.
In acidic medium the molecule is adsorbed via the electronic cloud of imidazole.

III.3 Study by infrared spectroscopy, Raman and SERS of N-(2-cyanoethil)-benzimidazole. Adsorption on the silver surface.

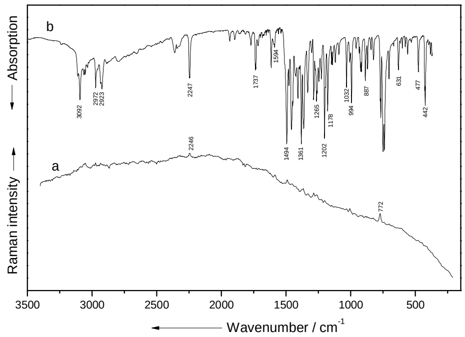


Fig. III.3.1 Raman (a) and FT-IR (b) spectra of N-(2-cyanoethil)-benzimidazole

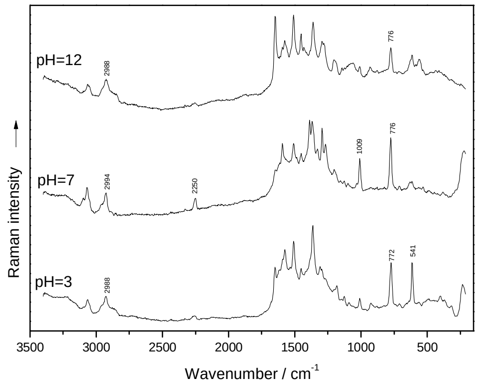


Fig. III.3.2 SERS spectra of N-(2-cyanoethil)-benzimidazole at different pH values

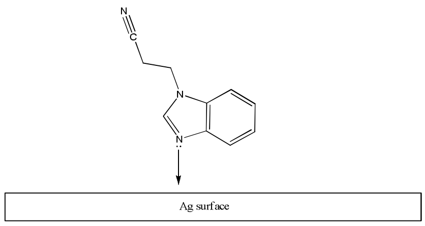


Fig. III.3.3 Molecule adsorption in neutral medium

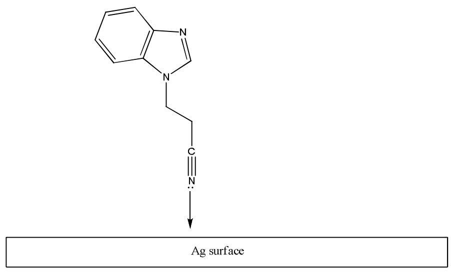


Fig. III.3.4 Molecule adsorption in acidic and basic medium

Conclusions

The molecule is adsorbed via nitrogen atom N_3 in neutral medium.
The molecule is adsorbed via nitrogen atom N_{13} in acidic and basic medium

III.4 Study by infrared spectroscopy, Raman and SERS of 3-(2-amino-2-oxoethyl)-1-(2-cyanoethyl)-1*H*-imidazol-3-ium iodide. Adsorption on the silver surface.

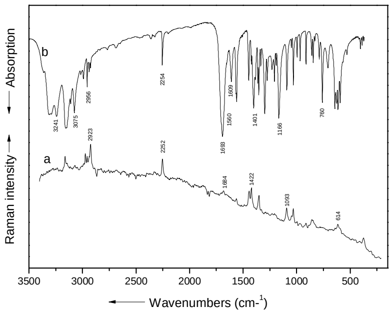


Fig. III.4.1 Raman (a) and FT-IR (b) spectra of 3-(2-amino-2-oxoethyl)-1-(2-cyanoethyl)-1*H*-imidazol-3-ium iodide

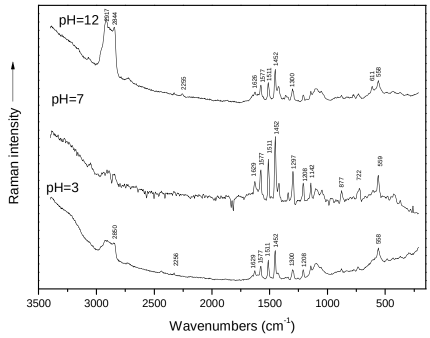


Fig. III.4.2 SERS spectra of 3-(2-amino-2-oxoethyl)-1-(2-cyanoethyl)-1*H*-imidazol-3-ium iodide at different pH values

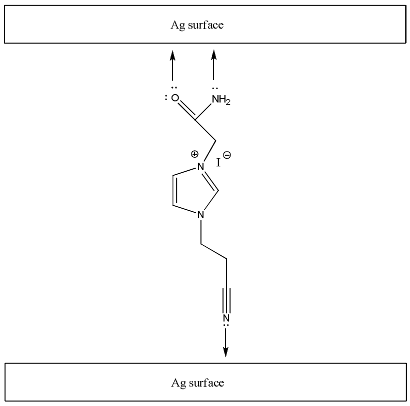


Fig. III.4.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via nitrile and amide groups.

III.5 Study by infrared spectroscopy, Raman and SERS of 3-(2-amino-2-oxoethyl)-1-(2-cyanoethyl)-1*H*-benzo[d]imidazol-3-ium iodide. Adsorption on the silver surface.

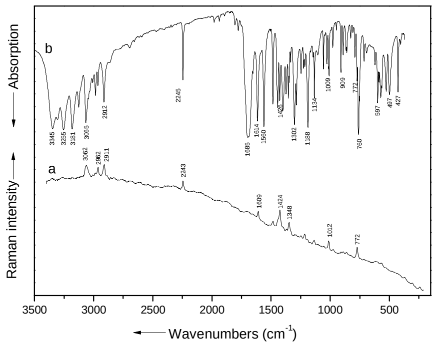


Fig. III.5.1 Raman (a) and FT-IR (b) spectra of 3-(2-amino-2-oxoethyl)-1-(2-cyanoethyl)-1*H*-benzo[d]imidazol-3-ium iodide

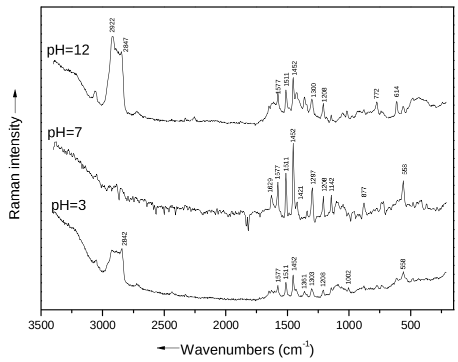


Fig. III.5.2 SERS spectra of 3-(2-amino-2-oxoethyl)-1-(2-cyanoethyl)-1*H*-benzo[d]imidazol-3-ium iodide at different pH values

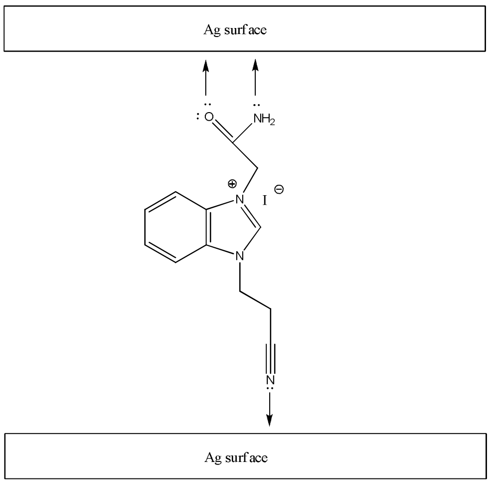


Fig. III.5.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via nitrile and amide groups.

III.6 Study by infrared spectroscopy, Raman and SERS of 1-(2-cyanoethyl)-3-(2-methoxy-2-oxoethyl)-1*H*-imidazol-3-ium bromide. Adsorption on the silver surface.

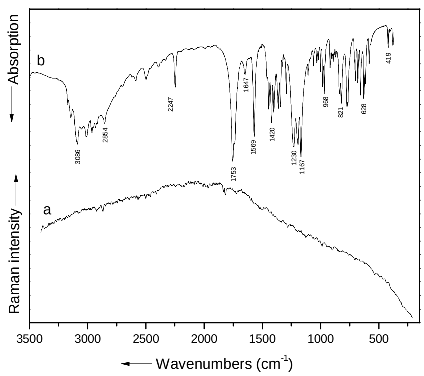


Fig. III.6.1 Raman (a) and FT-IR (b) spectra of 1-(2-cyanoethyl)-3-(2-methoxy-2-oxoethyl)-1*H*-imidazol-3-ium bromide

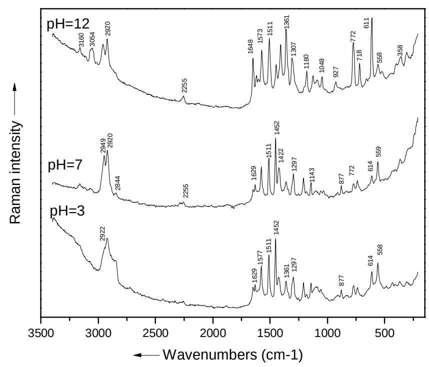


Fig. III.6.2 SERS spectra of 1-(2-cyanoethyl)-3-(2-methoxy-2-oxoethyl)-1*H*-imidazol-3-ium bromide at different pH values

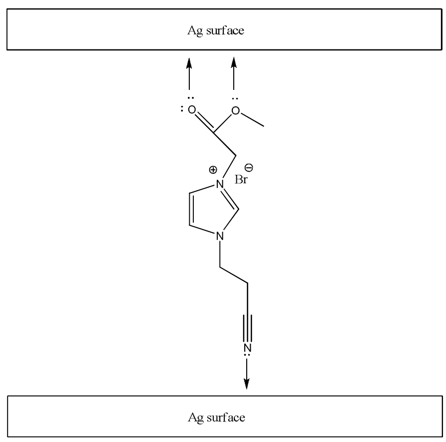


Fig. III.6.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via nitrile and ester groups.

III.7 Study by infrared spectroscopy, Raman and SERS of 1-(2-cyanoethyl)-3-(2-methoxy-2-oxoethyl)-1*H*-benzo[d]imidazol-3-ium bromide. Adsorption on the silver surface.

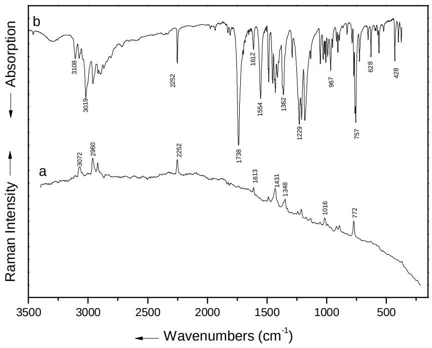


Fig. III.7.1 FT-IR (b) and Raman (a) spectra of 1-(2-cyanoethyl)-3-(2-methoxy-2-oxoethyl)-1*H*-benzo[d]imidazol-3-ium bromide

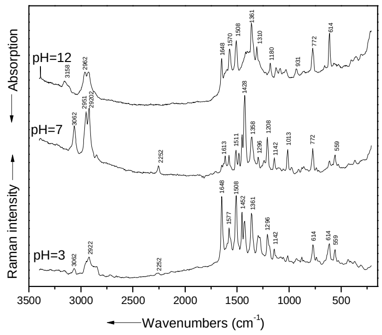


Fig. III.7.2 SERS spectra of 1-(2-cyanoethyl)-3-(2-methoxy-2-oxoethyl)-1*H*-benzo[d]imidazol-3-ium bromide at different pH values

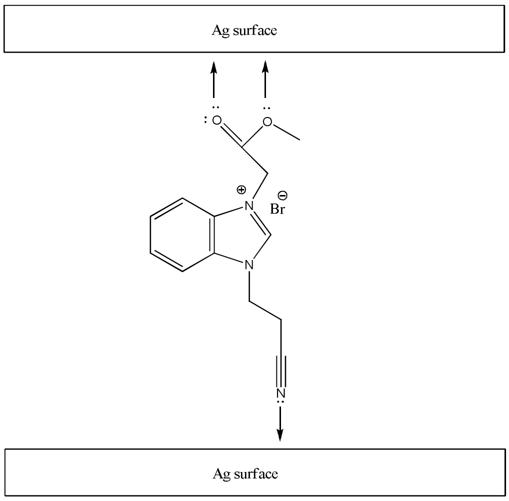


Fig. III.7.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via nitrile and ester groups.

III.8 Study by infrared spectroscopy, Raman and SERS of ethyl 3-(1*H*-imidazol-1-yl)propanoate. Adsorption on the silver surface.

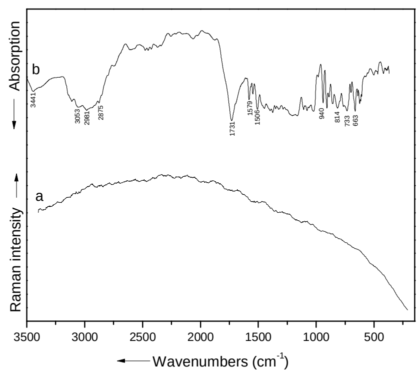


Fig. III.8.1 Raman (a) and FT-IR (b) spectra of ethyl 3-(1*H*-imidazol-1-yl)propanoate

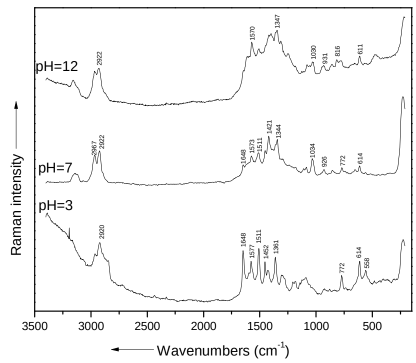


Fig. III.8.2 SERS spectra of ethyl 3-(1*H*-imidazol-1-yl)propanoate at different pH values

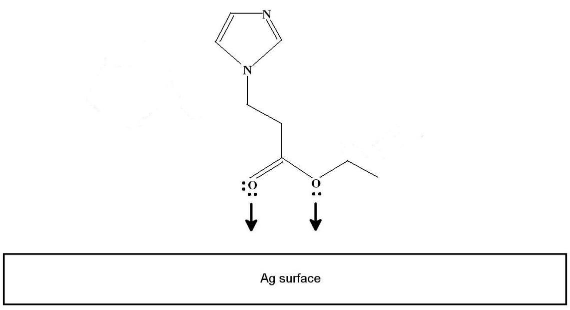


Fig. III.8.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via ester group.

III.9 Study by infrared spectroscopy, Raman and SERS of methyl 3-(1*H*-imidazol-1-yl)propanoate. Adsorption on the silver surface.

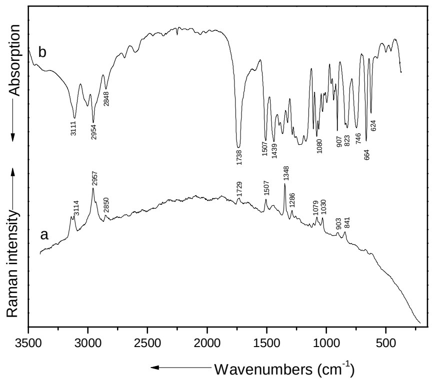


Fig. III.9.1 Raman (a) and FT-IR (b) spectra of methyl 3-(1*H*-imidazol-1-yl)propanoate

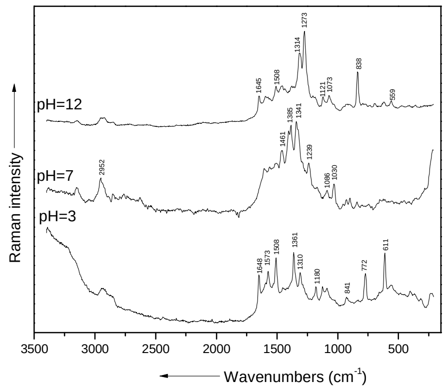


Fig. III.9.2 SERS spectra of methyl 3-(1*H*-imidazol-1-yl)propanoate at different pH values

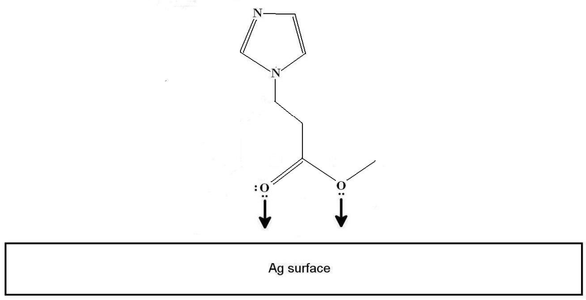


Fig. III.9.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via and ester group.

III.10 Study by infrared spectroscopy, Raman and SERS of 3-(1*H*-imidazol-1-yl)propanamide. Adsorption on the silver surface.

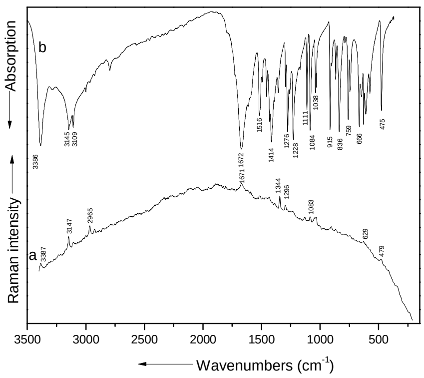


Fig. III.10.1 Raman (a) and FT-IR (b) spectra of 3-(1*H*-imidazol-1-yl)propanamide

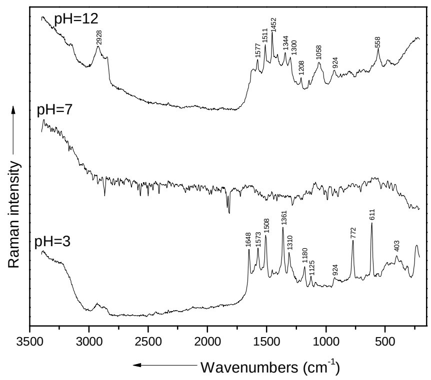


Fig. III.10.2 SERS spectra of 3-(1*H*-imidazol-1-yl)propanamide at different pH values

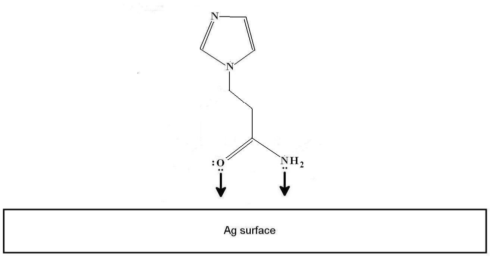


Fig. III.10.3 Molecule adsorption on silver surface in basic medium

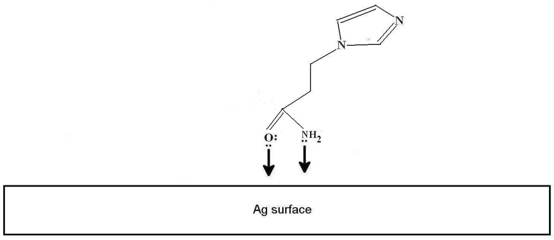


Fig. III.10.4 Molecule adsorption on silver surface in acidic medium

Conclusions

The molecule is adsorbed via amide group. The molecule is vertical on surface in basic medium. In acidic medium the molecule adopts a tilted position relative to the surface.

III.11 Study by infrared spectroscopy, Raman and SERS of 3-(1*H*-benzo[d]imidazol-1-yl)propanamide. Adsorption on the silver surface.

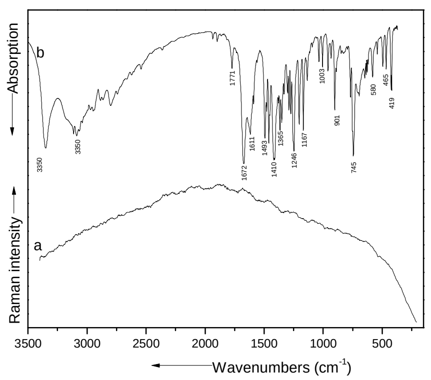


Fig. III.11.1 Raman (a) and FT-IR (b) spectra of 3-(1*H*-benzo[d]imidazol-1-yl)propanamide

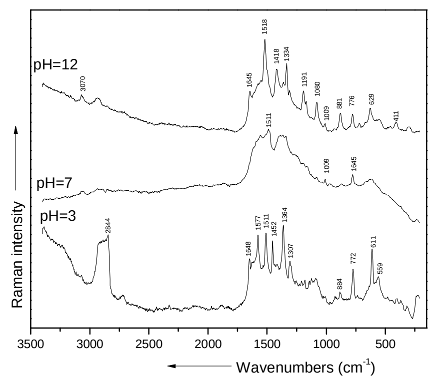


Fig. III.11.2 SERS spectra of 3-(1*H*-benzo[d]imidazol-1-yl)propanamide at different pH values

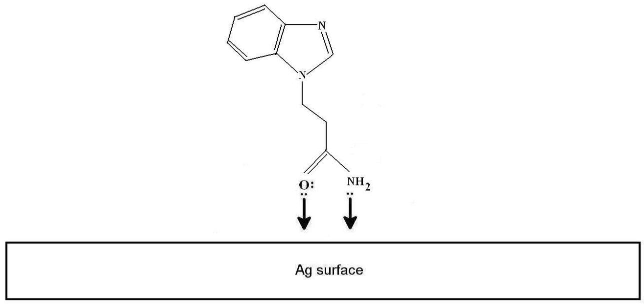


Fig. III.11.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via amide group.

III.12 Study by infrared spectroscopy, Raman and SERS of 3-(2-amino-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium iodide. Adsorption on the silver surface.

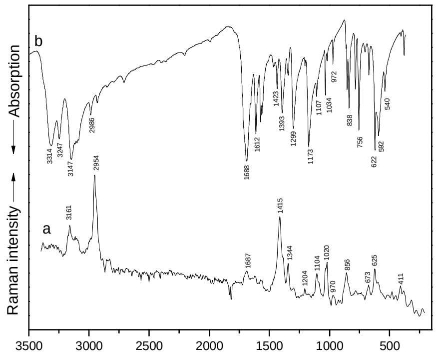


Fig. III.12.1 Raman (a) and FT-IR (b) spectra of 3-(2-amino-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium iodide

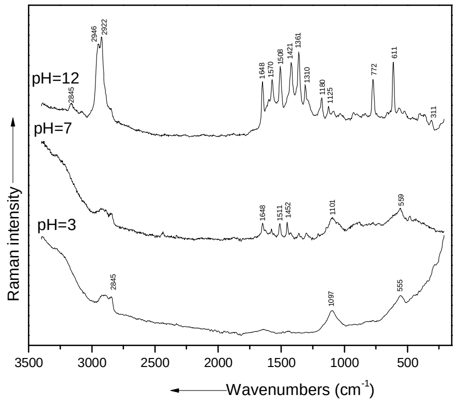


Fig. III.12.2 SERS spectra of 3-(2-amino-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium iodide at different pH values

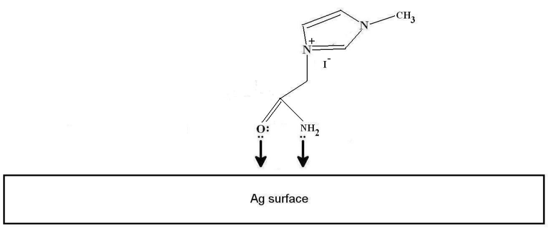


Fig. III.12.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via amide group. The molecule adopts a tilted position relative to the surface.

III.13 Study by infrared spectroscopy, Raman and SERS of 3-(2-ethoxy-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium iodide. Adsorption on the silver surface.

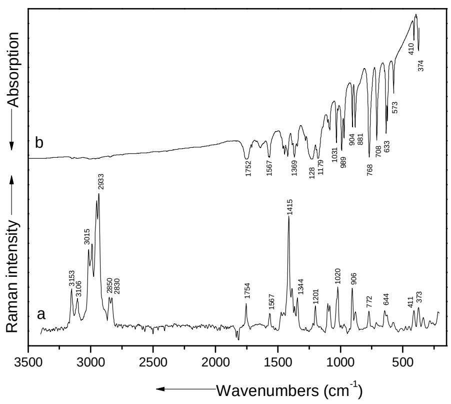


Fig. III.13.1 Raman (a) and FT-IR (b) spectra of 3-(2-ethoxy-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium iodide

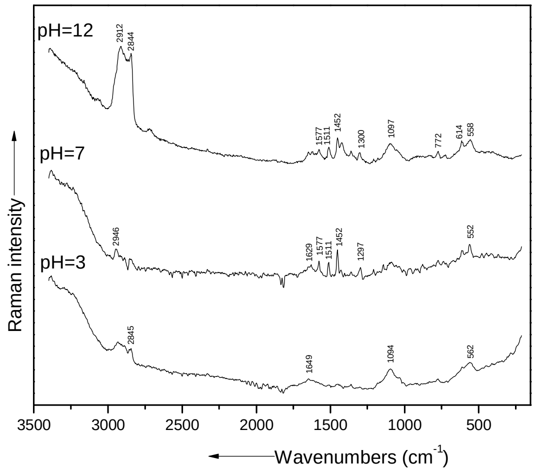
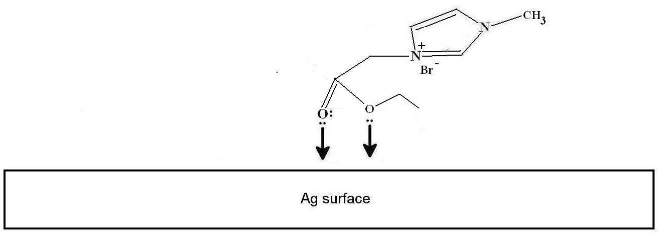


Fig. III.13.2 SERS spectra of 3-(2-ethoxy-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium iodide at different pH values



III.13.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via ester group. The molecule adopts a tilted position relative to the surface.

III.14 Study by infrared spectroscopy, Raman and SERS of 1-(2-cyanoethyl)-3-(2-ethoxy-2-oxoethyl)-1*H*-imidazol-3-ium bromide. Adsorption on the silver surface.

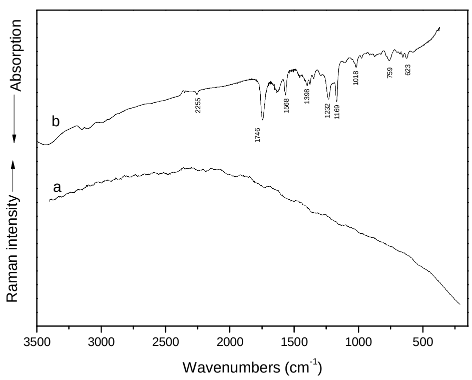


Fig. III.14.1 Raman (a) and FT-IR (b) spectra of 1-(2-cyanoethyl)-3-(2-ethoxy-2-oxoethyl)-1*H*-imidazol-3-ium bromide

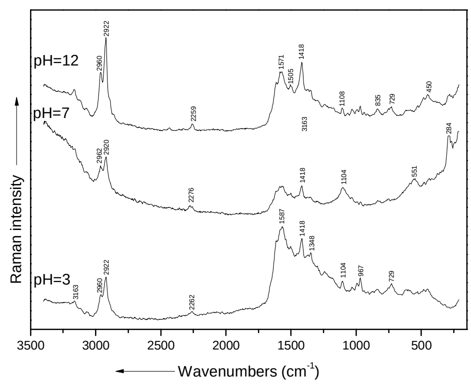
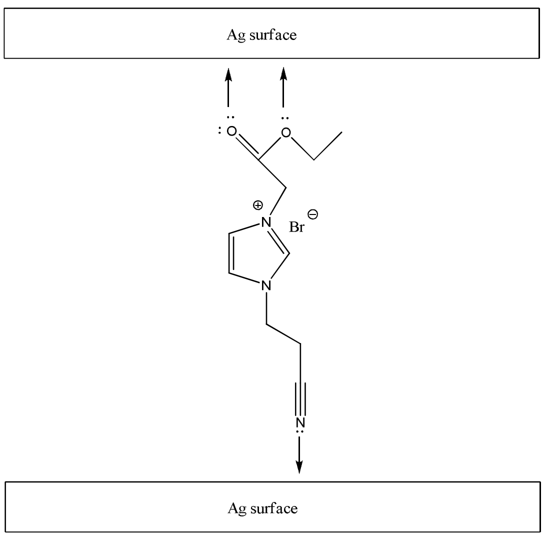


Fig. III.14.2 SERS spectra of 1-(2-cyanoethyl)-3-(2-ethoxy-2-oxoethyl)-1*H*-imidazol-3-ium bromide at different pH values



III.14.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via ester and nitrile groups.

III.15 Study by infrared spectroscopy, Raman and SERS of 1-(2-cyanoethyl)-3-(2-ethoxy-2-oxoethyl)-1*H*-benzo[d]imidazol-3-ium bromide. Adsorption on the silver surface.

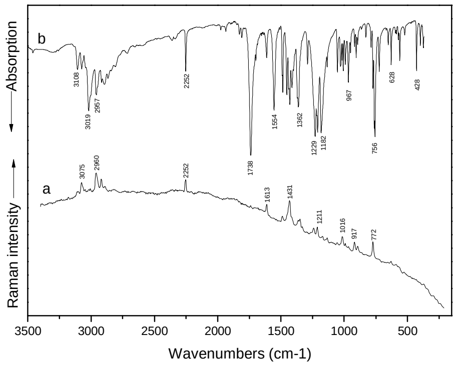


Fig. III.15.1 Raman (a) and FT-IR (b) spectra of 1-(2-cyanoethyl)-3-(2-ethoxy-2-oxoethyl)-1*H*-benzo[d]imidazol-3-ium bromide

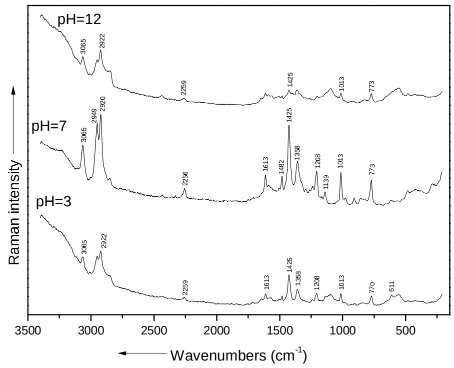


Fig. III.15.2 SERS spectra of 1-(2-cyanoethyl)-3-(2-ethoxy-2-oxoethyl)-1H-benzo[d]imidazol-3-ium bromide at different pH values

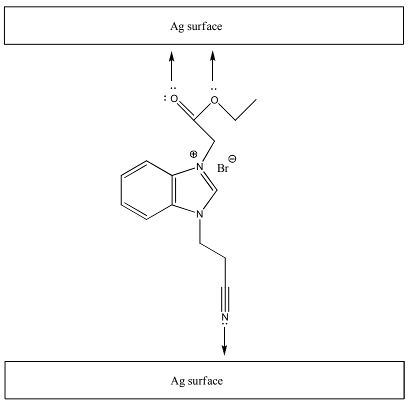


Fig. III.15.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via ester and nitrile groups.

III.16 Study by infrared spectroscopy, Raman and SERS of 3-(2-ethoxy-2-oxoethyl)-1-(3-ethoxy-3-oxopropyl)-1*H*-imidazol-3-ium bromide. Adsorption on the silver surface.

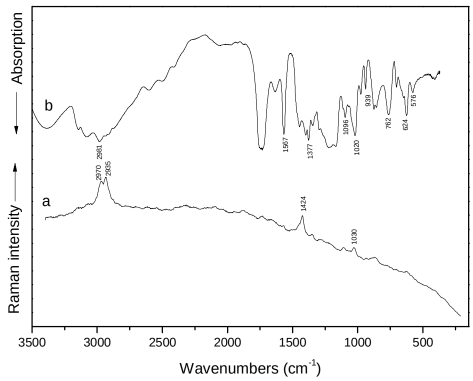


Fig. III.16.1 Raman (a) and FT-IR (b) spectra of 3-(2-ethoxy-2-oxoethyl)-1-(3-ethoxy-3-oxopropyl)-1*H*-imidazol-3-ium bromide

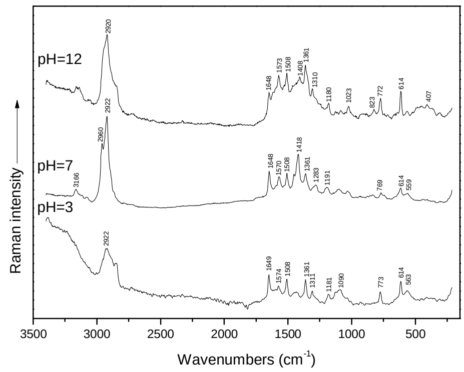


Fig. III.16.2 SERS spectra of 3-(2-ethoxy-2-oxoethyl)-1-(3-ethoxy-3-oxopropyl)-1*H*-imidazol-3-ium bromide at different pH values

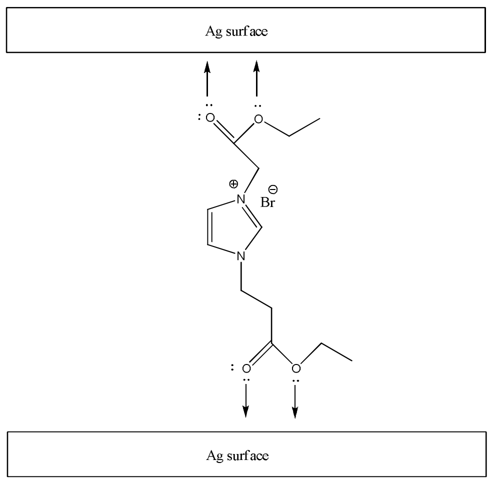


Fig. III.16.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via ester groups.

III.17 Study by infrared spectroscopy, Raman and SERS of 1-(3-ethoxy-3-oxopropyl)-3-(2-methoxy-2-oxoethyl)-1*H*-imidazol-3-ium bromide. Adsorption on the silver surface.

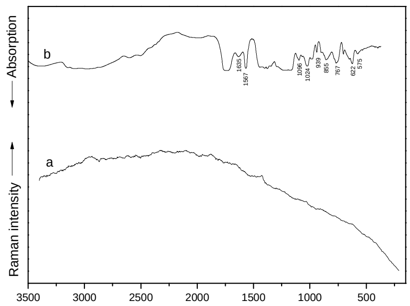


Fig. III.17.1 Raman (a) and FT-IR (b) spectra of 1-(3-ethoxy-3-oxopropyl)-3-(2-methoxy-2-oxoethyl)-1*H*-imidazol-3-ium bromide

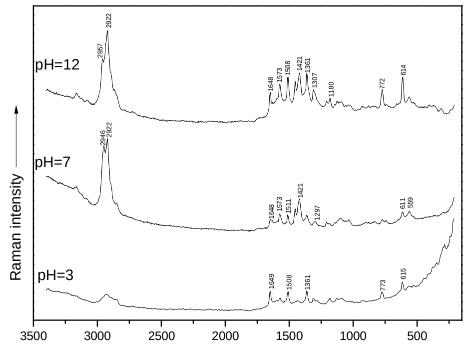
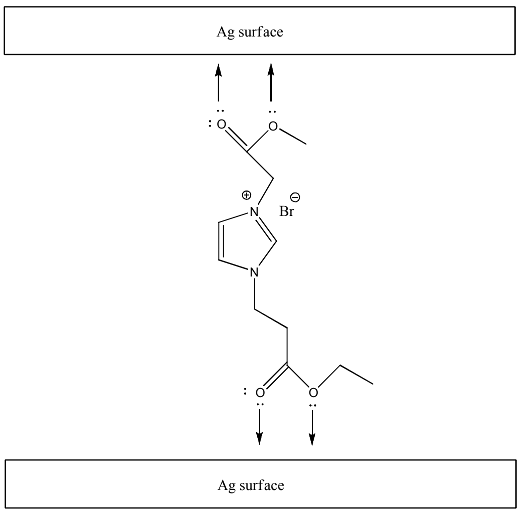


Fig. III.17.2 SERS spectra of 1-(3-ethoxy-3-oxopropyl)-3-(2-methoxy-2-oxoethyl)-1*H*-imidazol-3-ium bromide at different pH values



III.17.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via ester groups.

III.18 Study by infrared spectroscopy, Raman and SERS of 3-(2-ethoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl)-1*H*-imidazol-3-ium bromide. Adsorption on the silver surface.

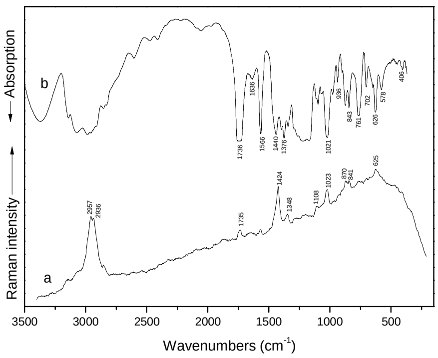


Fig. III.18.1 Raman (a) and FT-IR (b) spectra of 3-(2-ethoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl)-1*H*-imidazol-3-ium bromide

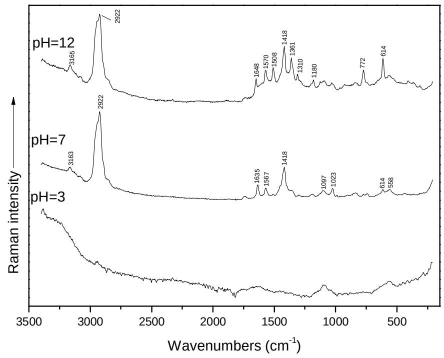
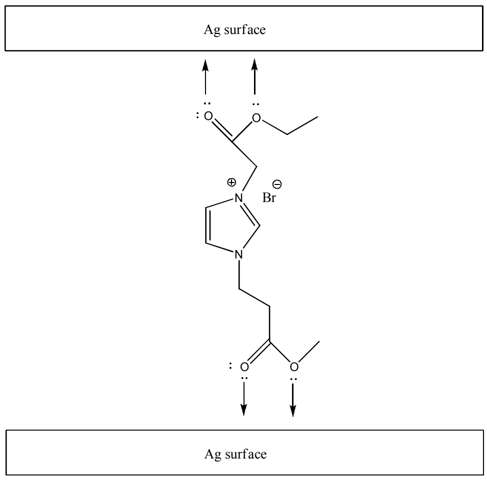


Fig. III.18.2 SERS spectra of 3-(2-ethoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl)-1*H*-imidazol-3-ium bromide at different pH values



III.18.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via ester groups.

III.19 Study by infrared spectroscopy, Raman and SERS of 3-(2-methoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl)-1*H*-imidazol-3-ium bromide. Adsorption on the silver surface.

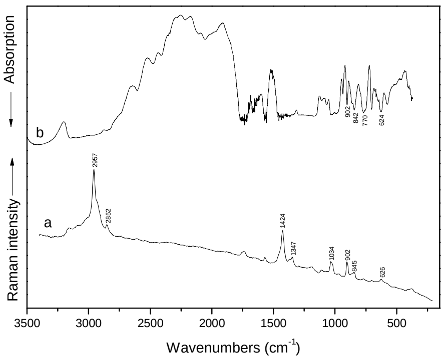


Fig. III.19.1 Raman (a) and FT-IR (b) spectra of 3-(2-methoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl)-1*H*-imidazol-3-ium bromide

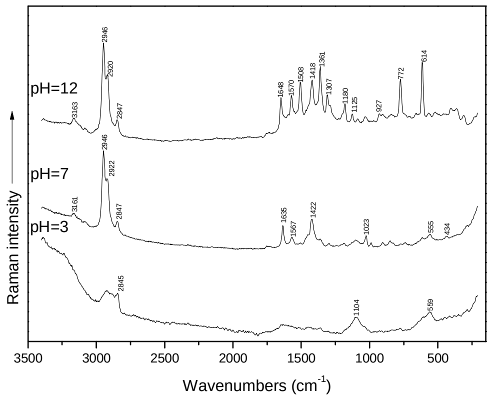
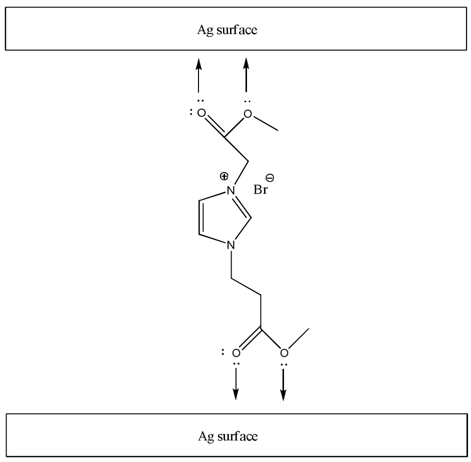


Fig. III.19.2 SERS spectra of 3-(2-methoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl)-1*H*-imidazol-3-ium bromide at different pH values



III.19.3 Molecule adsorption on silver surface

Conclusions

The molecule is adsorbed on the silver surface via ester groups.

Final conclusions

• In this thesis nineteen imidazole derivatives were synthesized and studied by infrared spectroscopy, Raman and SERS.

• Twelve imidazole derivatives were evaluated and optimized by computational methods type *a- initio* (HF) and DFT methods B3PW91/6-31G* and B3LYP/6-31G*.

• The theoretical vibrational modes were corrected according to the literature; for *ab-inito* method has been applied a correction factor of 0.8953; for DFT methods (B3LYP and B3PW91) has been applied a correction factor of 0.9614

• The theoretical data are consistent with the experimental values.

• The FT- IR spectra of the imidazole derivatives studied (with some exceptions) are clear and sharp.

• Raman spectra show a strong fluorescence. In some cases no useful information occurs. In other cases, on the contrary, complete the FT -IR spectra.

• The adsorption mechanisms on classes of compounds in SERS spectra were elucidated. Imidazole derivatives with amide or ester groups are strongly adsorbed on the particle surface of the colloidal silver. The band corresponding to the vibration of $C=O$ in amide and ester groups is shifted towards lower wave numbers.

• The nitrile group of imidazole derivatives studied is involved in the adsorption process. Imidazole derivatives containing only nitrile functional group can be adsorbed on the silver surface through the electronic cloud of the imidazole nucleus.

• These results can provide a basis for building a database to allow rapid identification of imidazole derivatives from various materials.

• The results of this study were published in two papers in ISI journals.

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