

# Raman and surface-enhanced Raman studies of the food additive sodium benzoate

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Raman spectroscopy was used for the study of sodium benzoate, in the solid state, as well in different acid and basic aqueous solutions. The surface-enhanced Raman scattering (SERS) spectra of sodium benzoate solutions in the 4.5–7 pH range were also recorded. Both, Raman and SERS pH dependent spectra reveal the transition of sodium benzoate from the undissociated to the anionic molecular form. The SERS spectra prove a chemical interaction of benzoate molecules with the silver colloidal particles through the lone pair electrons of the oxygen atoms of the carboxylate functional group. The orientation of the molecules on the silver surface was discussed.

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## 1. Introduction

Sodium benzoate is the sodium salt of benzoic acid (known as E 211 in Europe). Sodium benzoate is widely used in many food products and medicinal syrups. Also, sodium benzoate is therapeutically used in high doses for the treatment of some rare diseases such as hyperammonemia and non-ketotic hyperglycinemia [1,2]. In most cases children affected by these inherited metabolic disorders refuse the oral uptake of sodium benzoate as a powder or in solution due to its bad taste. Therefore coated granules with lipophilic [3] and hydrophilic [4] binders have been developed.

Benzoates, in vitro, possess antibacterial properties similar to those of fluoride and in combination with fluoride could affect caries development [5]. The molecular structure of sodium benzoate, as well of benzoic acid and its deprotonated molecular form are shown in Fig. 1.

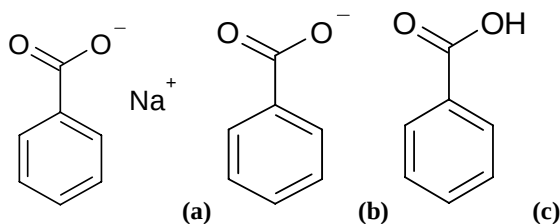


Fig. 1. (a) molecular structure of sodium benzoate; (b) anionic form of benzoate; (c) molecular structure of benzoic acid (benzoate).

Benzoate exists in a pH-dependent equilibrium between unchanged acid molecules and charged anions. The pK<sub>a</sub> of benzoate is 4.2 [6,7]. Weak acid preservatives

are more effective at lower pH values where solutions contain increased concentrations of undissociated acids. Optimum functionality occurs when the pH is between 2.5 and 4.0 [8]. Vibrational spectroscopic methods present an increased interest, as showed by a high number of publications in the last years [9]. Also, by applying density functional theory calculations the assignment of the vibrational spectra becomes easier [10].

In this study, sodium benzoate is investigated by means of Raman and SERS spectroscopy to examine the molecular structure of the molecule in solid state, in aqueous solution, at different concentrations as well in solutions with different pH.

## 2. Experimental

Sodium benzoate (purity 99 %) was purchased from Aldrich. The pure and commercially available sodium benzoate were used in our measurements. On behalf of the commercially available sodium benzoate no analytical purity certificate was accessible. In most cases, impure ingredients are used by many companies. Many times the raw materials may contain only 90% or less of the listed ingredients along with 10% or more corn starch and lactose. Lactose and corn are known as allergens for some people and these items have been known to cause digestive disturbances and weaken the immune system. The sodium benzoate solutions were prepared using distilled water.

As metallic substrate for the SERS measurements silver colloid prepared according to the literature [11] was used. The SERS samples were obtained by adding 0.1 ml of sodium benzoate solutions at different concentrations into 3.5 ml silver colloid, getting the final SERS concentrations ( $2.8 \times 10^{-3}$  –  $2.8 \times 10^{-4}$  mol l<sup>-1</sup>). The acid or

basic pH values were adjusted by adding HCl or NaOH solutions ( $10^{-1}$  mol  $l^{-1}$ ), respectively.

The FT-Raman spectrum was obtained by using a Bruker IFS 120HR spectrometer with an integrated FRA106 Raman module and a resolution of  $1\text{ cm}^{-1}$ . The 1064 nm radiation from a Nd-YAG laser with an output of 1 W was employed for the excitation. A Ge detector operating at liquid nitrogen temperature was used and the number of scans was 1000.

The micro-Raman and SERS spectra on silver colloid were recorded with a Dilor Labram spectrometer using the 514.5 nm excitation line from a Spectra Physics argon ion laser. The spectra were collected in back-scattering geometry with a resolution of  $2\text{ cm}^{-1}$ . The detection of Raman signal was carried out with a CCD camera (Photometric model 9000), while the laser power varied from 100 to 250 mW as it is indicated in each figure caption.

### 3. Results and discussion

The vibrational fundamentals from the FT-Raman (Fig. 2a) and the micro-Raman (Fig. 2b) spectra of sodium benzoate were analyzed by comparing the experimental vibrational modes with the previously published Raman data [12-14].

Comparing the FT-Raman spectrum (Fig. 2a) of industrial sodium benzoate with both micro-Raman spectra of impure (industrial) (Fig. 2b) and pure (Fig. 2c) sodium benzoate, respectively, one can observe close similarities in the band positions and relative intensities. Only a weak background, most probably due to the fluorescent impurities of the commercial benzoate, is shown by the micro-Raman spectrum of impure sodium benzoate (Fig. 2b).

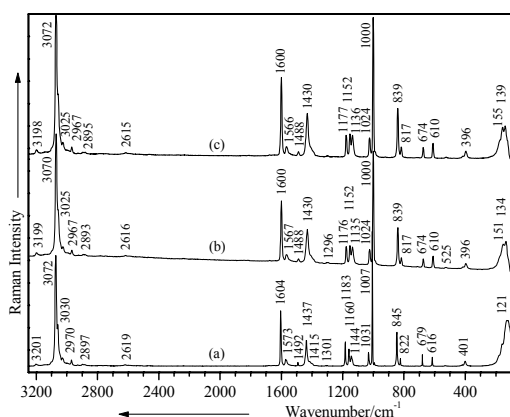


Fig. 2. (a) FT-Raman spectrum of industrial (impure); (b) micro-Raman spectrum of industrial; (c) micro-Raman spectrum of pure sodium benzoate. Excitation: (a) 1064 nm, 1 W; (b) 514.5 nm, 25 mW; (c) 514.5 nm, 100 mW.

All bands may be divided into two groups: bands connected with the carboxylate anion vibrations and bands

associated with the aromatic ring vibrations. The medium strong band at  $1604\text{ cm}^{-1}$  was attributed to the asymmetrical stretching mode of the carboxylate anion  $\nu_a(\text{COO}^-)$ , whereas the medium peak at  $1415\text{ cm}^{-1}$  was assigned to the symmetrical stretching mode of the carboxylate anion  $\nu_s(\text{COO}^-)$ .

The medium band at  $845\text{ cm}^{-1}$  is due to the carboxylate anion symmetrical in plane deformation, while the asymmetrical in plane deformation is absent. According to the literature [12] the out of plane deformation modes of the  $\text{COO}^-$  functional group exhibit a strong band in the  $720\text{--}705\text{ cm}^{-1}$  spectral range.

Bands attributed to the aromatic ring vibrations are the very weak band at  $3201\text{ cm}^{-1}$  and the very strong band at  $3072\text{ cm}^{-1}$ , which were attributed to the aromatic C-H stretching modes. Also, the bands of the FT-Raman spectrum at 1183, 1160, 1144, and  $1031\text{ cm}^{-1}$  are due to the in plane C-H deformation of the benzene ring. The very strong band at  $1007\text{ cm}^{-1}$  is attributed to the breathing mode of the aromatic ring [13, 20]. The weak peak at  $822\text{ cm}^{-1}$  was assigned to the in plane C-H deformation mode of the benzene ring, while the peak at  $679\text{ cm}^{-1}$  is due to the out of plane bending mode of the benzene ring, whereas the band at  $616\text{ cm}^{-1}$  is due to the plane bending mode of the benzene ring.

Concluding, the FT-Raman and/or the micro-Raman spectra of the pure and impure sodium benzoate can be used to give-away the marker bands of the sodium benzoate molecule.

On passing from the FT-Raman spectrum of powder to the micro-Raman spectrum of the sodium benzoate solution, several changes in the band positions and relative intensities can be observed (Fig. 3).

Small red shifts in wavenumbers and the broadening of the bands were observed in solution probably due to the well-known solvent effects. An increased relative intensity for the asymmetrical stretching mode of the carboxylate anion (the band at  $1598\text{ cm}^{-1}$  in the Raman spectrum of the solution) can be observed (Fig 3).

The shoulder at  $1415\text{ cm}^{-1}$  in the FT-Raman spectrum of the sodium benzoate powder becomes an intense peak at  $1383\text{ cm}^{-1}$  and it is significantly red shifted ( $32\text{ cm}^{-1}$ ) in the Raman spectrum of solution (Fig. 3b) suggesting changes in the electron distribution of the carboxylate anion that makes possible a protonation of this group.

Mainly, the benzoate anion can interact through hydrogen bonds with the water molecules. As a result, these interactions will furnish an important contribution to the sum of all interactions in the benzoate molecule as showed in the spectral shape [14]. This finding is further asserting from the band corresponding to the symmetrical in plane deformation of the carboxylate anion ( $845\text{ cm}^{-1}$  in the FT-Raman spectrum—Fig 3a), which slowly increases in relative intensity and becomes broader in the Raman spectrum of sodium benzoate solution ( $834\text{ cm}^{-1}$ ) (Fig 3b). Moreover, the three bands connected to the aromatic ring vibrations, namely the in plane C-H deformation modes of the aromatic ring (1183, 1160,  $1144\text{ cm}^{-1}$  in the FT-Raman spectrum) are changed in the relative intensities in the Raman spectrum of the solution ( $1172$ ,  $1153$ ,  $1135\text{ cm}^{-1}$ ).

Additionally, the band corresponding to the in plane C-H deformation mode of the benzene ring ( $1031\text{ cm}^{-1}$  in the FT-Raman spectrum) increases in the relative intensity in the Raman spectrum of the solution ( $1020\text{ cm}^{-1}$ ).

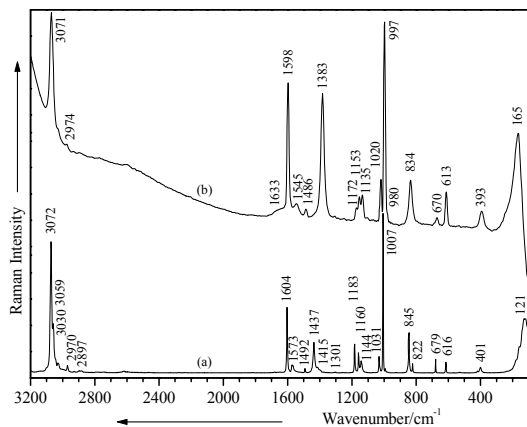


Fig. 3. (a) FT-Raman spectrum of the sodium benzoate powder; (b) Raman spectrum of  $1\text{ mol l}^{-1}$  sodium benzoate solution. Excitation: (a)  $1064\text{ nm}$ ,  $1\text{ W}$  (a); (b)  $514.5\text{ nm}$ ,  $200\text{ mW}$  (b).

On the other hand, the two weak peaks corresponding to the in plane and out of plane deformation of the benzene ring ( $616$ ,  $401\text{ cm}^{-1}$  in the FT-Raman spectrum) are importantly increased in relative intensities and become broader ( $613$ ,  $393\text{ cm}^{-1}$ ) in the Raman spectrum of the solution.

Comparing the micro-Raman spectra of the pure and industrial sodium benzoate solutions (Fig. 4) at the same concentration ( $1\text{ mol l}^{-1}$ ), we notice that the bands are slightly blue shifted in the case of the industrial sample.

From another point of view, several bands present approximately the same relative intensities, whereas the band corresponding to the symmetrical stretching mode of the carboxylate anion ( $1383\text{ cm}^{-1}$  in the Raman spectrum of the pure sodium benzoate solution—Fig. 4a) becomes weaker in the Raman spectrum of the industrial benzoate ( $1389\text{ cm}^{-1}$ —Fig. 4b), as well as the band assigned to the symmetrical in plane deformation of the carboxylate functional group ( $835\text{ cm}^{-1}$  in the Raman spectrum of the pure probe); the peak attributed to the in plane bending mode of the aromatic ring ( $613\text{ cm}^{-1}$  in the Raman spectrum of the pure sodium benzoate) are also weaker ( $840$ ,  $613\text{ cm}^{-1}$  Fig. 4b) in the case of the impure sodium benzoate spectrum.

The micro-Raman spectrum of impure sodium benzoate solution shows a fluorescent background, probably due to the impurity molecules, which are present in the commercial substance.

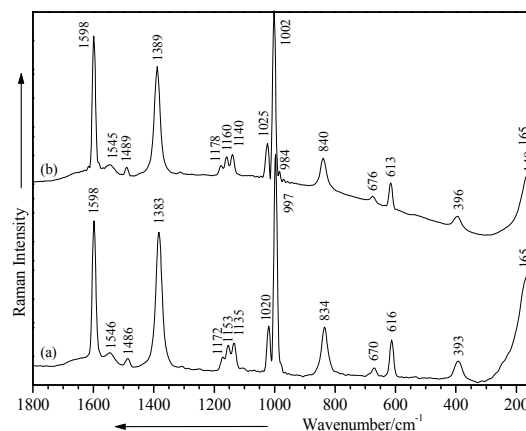


Fig. 4. Micro-Raman spectrum of: (a) pure sodium benzoate  $1\text{ mol l}^{-1}$ ; (b) impure sodium benzoate  $1\text{ mol l}^{-1}$ . Excitation: (a)  $514.5\text{ nm}$ ,  $200\text{ mW}$ , (b)  $100\text{ mW}$ .

The Raman spectra of the sodium benzoate solution have been recorded in the concentration range of  $1$  to  $10^{-2}\text{ mol l}^{-1}$  when the Raman signal becomes very weak (Fig. 5).

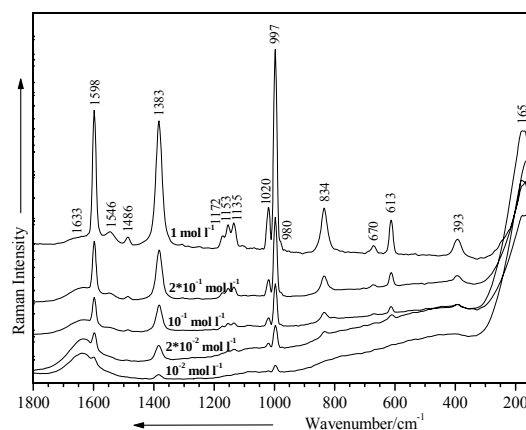


Fig. 5. Micro-Raman spectra of pure sodium benzoate solution at different concentrations. Excitation:  $514.5\text{ nm}$ ,  $200\text{ mW}$ .

Analyzing the micro-Raman spectra of sodium benzoate solutions at different basic (Fig. 6) and acidic (Fig. 7) pH values, we can point out that the spectra show the transition from the anionic molecular form to the undissociated molecular form of the benzoate molecule.

At basic pH values no important structural changes can be observed in the pH range  $7$ – $13$ , the spectra being attributed to the anionic molecular form of benzoate.

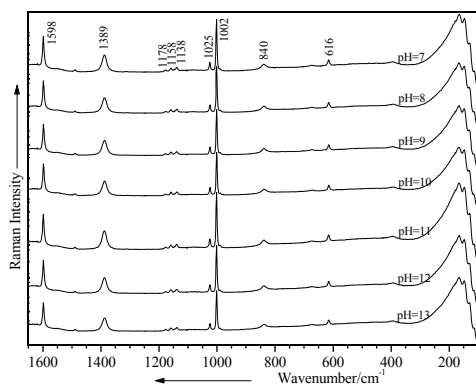


Fig. 6. Micro-Raman spectra of  $10^{-1}$  mol  $l^{-1}$  sodium benzoate solution at different basic pH values. Excitation: 514.5 nm, 100 mW.

The major changes in band profiles and relative intensities appear below pH 5. On passing from neutral to acidic pH values, the bands due to the carboxylate anion stretching modes decrease in relative intensity and become broader (1598, 1387  $cm^{-1}$ ). At pH 4 appears a new band at 792  $cm^{-1}$ , which can be due to the symmetrical out of plane deformation mode of the carboxylate anion (Fig. 7). This band is absent in the FT-Raman spectrum of the sodium benzoate powder (Fig. 2a) and the Raman spectra of the sodium benzoate solution in the normal pH range (Figs. 4 and 5). Most probably at pH 4 anionic molecular forms of benzoate coexist in the solution with neutral molecular forms of benzoate.

The Raman spectrum at pH 3 is mainly due to the undissociated molecular form of the sodium benzoate (Fig. 1c). Characteristic for this molecular form of benzoate are the benzene ring breathing vibration at 1002  $cm^{-1}$  and the asymmetrical carboxyl stretching mode  $\nu_a(COOH)$  at 1600  $cm^{-1}$ . Also, for pH 3 the peak at 1387  $cm^{-1}$  shows a decreased intensity compared to higher pH values, indicating a reduced number of benzoate molecules in the anionic form.

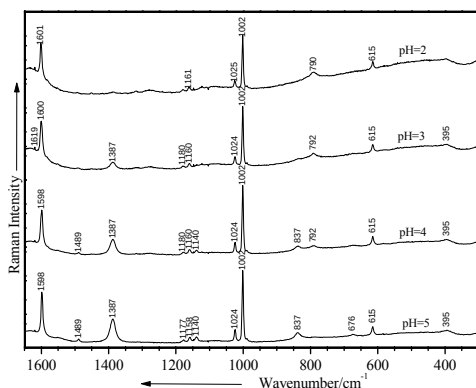


Fig. 7. Micro-Raman spectra of  $10^{-1}$  mol  $l^{-1}$  sodium benzoate solution at different acidic pH values. Excitation: 514.5 nm, 100 mW.

The SERS spectrum of sodium benzoate is presented in Fig. 8 in comparison with the Raman spectrum of the sodium benzoate solution at micro-molar concentration and pH 7.

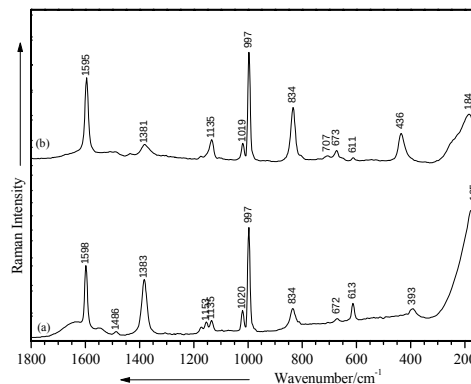


Fig. 8. Comparison between (a) micro-Raman ( $2 \times 10^{-1}$  mol  $l^{-1}$ ) and (b) SERS ( $2.8 \times 10^{-3}$  mol  $l^{-1}$ ) spectrum of sodium benzoate (pH 7). Excitation: 514.5 nm, 200 mW (a,b).

Going from Raman to SERS spectrum at micro-molar concentration, large differences were observed in the band positions and relative intensities.

Since the SERS signal is concentration sensitive, in order to discuss the adsorption behavior of the benzoate to the silver particles, the SERS spectrum at micro-molar concentration was chosen here for the adsorption geometry proposed.

Theoretically, the benzoate molecule could interact with the silver colloidal surface through the carboxylate functional group, or through the  $\pi$  electrons of the benzene ring.

The latter supposition is excluded because the breathing vibrational mode of the benzene ring has high relative intensity in the SERS spectra, so that a flat orientation to the silver surface is excluded by the SERS selection rules. Also the benzene ring C-H stretching vibration was demonstrated to be an unambiguous probe in the determination of surface orientation of aromatics. In accordance to the electromagnetic selection rules proposed by Creighton [15], and Moskovits and Suh [16], the C-H stretching mode should be relatively enhanced when the C-H bond is perpendicular to the metal surface plane as compared to the case in which the C-H bond lies parallel to the surface.

On the other hand, the possibility for benzoate to chemisorb is provided by the presence of the lone electron pairs of oxygen atom from the carboxylate (Fig. 1). In this case, according to the surface selection rules [15] the stretching modes of the carboxylate are expected to be enhanced.

The observed bands in the SERS spectrum (Fig. 8) support our consideration. Furthermore, the intense band at 1595  $cm^{-1}$  assigned to the symmetrical stretching mode of the carboxylate seems to be in the close vicinity of the

silver particles with a perpendicular orientation of the ring. Moreover, the very strong band observed in the SERS spectrum at  $997\text{ cm}^{-1}$  is due to the ring breathing mode. A bending of the  $\text{COO}^-$  functional group near the surface is supported by the medium band at  $834\text{ cm}^{-1}$  (Fig. 8b), which can be assigned to the symmetrical in plane  $\text{COO}^-$  deformation mode. By comparing the SERS spectrum with the Raman spectrum (Fig. 8a), the mode at  $834\text{ cm}^{-1}$  is significantly enhanced, which is due to the symmetrical in plane deformation of the carboxylate perpendicularly adsorbed. The new band at  $436\text{ cm}^{-1}$  is due to the in plane bending mode of the carboxylate. Other bands with medium or weak intensities from the SERS spectrum are attributed to different bending modes of the structure.

The shoulder at  $242\text{ cm}^{-1}$  was assigned to the well-known Ag-O stretching mode [17] whereas the band at  $184\text{ cm}^{-1}$  can be attributed to the O-Ag-O deformation mode [18]. The structures of the carboxylate anion and aromatic ring influence each other. This might be revealed in exclusive physical-chemical or biological properties of the molecule. The metal affects the carboxylate anion as well as the aromatic ring structure. The ionic potential of the metal is the most important parameter responsible for the influence of the metal on the rest of the molecule [12, 19]. The monocarboxylic acids is chemisorbed to silver surfaces as symmetric [20, 21], bidentate carboxylate anions and both oxygen atoms of the carboxylate are symmetrically bonded to the surface [22].

By lowering the concentration (Fig. 9) several bands decrease in the SERS intensity and also strong chemical interaction of sodium benzoate with the silver colloidal particles through the carboxylate anion was observed.

SERS spectra of the sodium benzoate at different acidic pH values (Fig. 10) show dramatic changes in the band positions and relative intensities. The SERS signal in the case of acidic pH range was recorded just for two values, namely 4.5 and 6.5. At more acidic pH as 3.5, the SERS signal is very weak or absent. In the case of more basic pH values as 6.5, the SERS signal is very noisy (spectra not showed here).

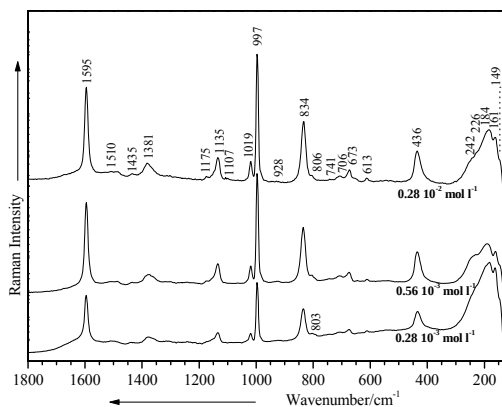


Fig. 9. SERS spectra of sodium benzoate at different concentrations. Excitation:  $514.5\text{ nm}$ ,  $200\text{ mW}$ .

In contrast with the SERS measurements at pH 7 (Fig. 8b), beginning with pH 6.5, the band corresponding to the  $\text{COO}^-$  asymmetrical stretching mode ( $1595\text{ cm}^{-1}$  in SERS spectrum at pH 7–Fig. 8b) is shifted to  $1603\text{ cm}^{-1}$ .

At pH 4.5, this band is shifted to  $1594\text{ cm}^{-1}$ , is decreased in relative intensity, and exhibits a weak shoulder at about  $1573\text{ cm}^{-1}$ . Further, a new band at  $1646\text{ cm}^{-1}$  is present, due to a quadrant deformation mode of the benzene ring. The weak shoulder at  $1573\text{ cm}^{-1}$  is due to the CC aromatic bonds stretching mode. The very weak band at about  $1500\text{ cm}^{-1}$  in the SERS spectra at pH 7 (Fig. 8b) and 6.5 (Fig. 10) increases in relative intensity at pH 4.5 and was assigned to the symmetrical tangential stretching mode of the aromatic ring.

Furthermore, the symmetrical stretching mode of  $\text{COO}^-$  anion increases in relative intensity and is shared out into two bands at  $1375$  and  $1359\text{ cm}^{-1}$ , respectively. Also the following bands at  $1170$ ,  $1153$ ,  $1133$ , and  $1022\text{ cm}^{-1}$  bands corresponding to the in plane C-H deformation of the benzene ring, decrease in relative intensities. The very strong band in the SERS spectrum of sodium benzoate at pH 7 (Fig. 8b:  $997\text{ cm}^{-1}$ ) (breathing mode of the benzene ring) becomes weaker at pH 4.5.

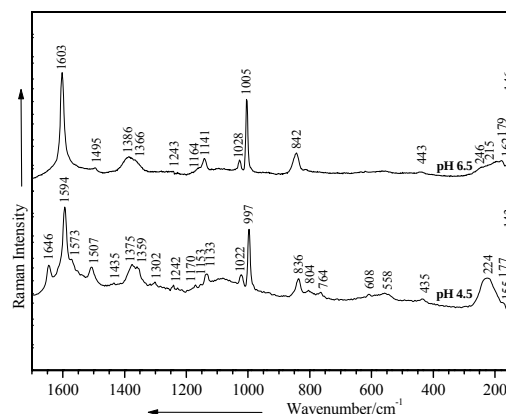


Fig. 10. SERS spectra of sodium benzoate at different acidic pH values. Excitation:  $514.5\text{ nm}$ ,  $250\text{ mW}$ .

The acidic pH adjustment was performed with  $10^{-1}\text{ mol l}^{-1}$  of HCl solution. An intense band, which can be observed in the presence of  $\text{Cl}^-$ , is the  $\nu(\text{Ag-Cl})$  stretching one that appears at about  $200\text{ cm}^{-1}$  and can be very useful in the study of the adsorption of the molecule on the silver surface [23]. In our spectra, we can observe this band at  $224\text{ cm}^{-1}$ . The band increases in relative intensity with the added quantity of HCl solution [24]. In addition to this band, other weaker bands or shoulders could be seen. These shoulders appear at  $113$  and  $177\text{ cm}^{-1}$  and are assigned to vibrations of smaller silver particles or adatoms, produced by the oxidation-reduction action of  $\text{Cl}^-$  on the surface of the silver colloid [25].

#### 4. Conclusions

The FT-Raman and micro-Raman spectra of sodium benzoate powder were recorded and the marker bands of characteristic functional groups were identified. The Raman signal for the industrial sodium benzoate shows a fluorescent background, probably due to the presence of the impurities.

The micro-Raman spectra of sodium benzoate solutions could be recorded down to micro-molar level. A weak fluorescence background was observed in the case of the industrial probe.

Analyzing the Raman spectra of sodium benzoate solutions, the transition from anionic to undissociated form of the sodium benzoate the on going from basic to acidic pH values could be evidenced.

SERS spectra of sodium benzoate could be recorded even at low concentrations with a conventional SERS setup ( $2.8 \times 10^{-4} \text{ mol l}^{-1}$ ).

The surface selection rules, along with literature data, have reasonably explained the adsorbed structures on the metal surface at different concentrations and pH values. A strong chemical interaction of sodium benzoate with the silver colloidal particles was observed under micro-molar concentrations through the lone pair electrons of the oxygen atoms of the carboxylate anion in a perpendicular orientation. The SERS spectra of sodium benzoate at acidic pH values were recorded and revealed the same orientation through the carboxylate anion.

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