

# Adsorption behavior of 1 - and 2 - Naphthol species on Ag colloidal nanoparticles

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**Abstract.** Surface plasmon resonance of the Ag colloidal nanoparticles was employed for the investigation of the adsorbed geometry and the functional groups involved in adsorption on the nano-size surface. The study on the structure of naphthols is motivated by the excited-state-proton transfer. This reaction is found in many chemical and biological processes. The surface-enhanced Raman is very sensitive technique and has been used to evaluate the structure of the 1-and 2-naphthol in solid and solution phases. This technique is able to assess both organic and inorganic compounds. The SERS of 1- and 2-naphthol were obtained using citrate-reduced silver colloid at a final sample concentration of  $10^{-4}$  mol<sup>-1</sup>. The both forms are found to chemisorb on Ag colloidal nanoparticles exhibiting different SERS spectral pattern. The 1- or 2- position of the –OH group leads to large differences in the Raman spectra of the species. Different adsorption geometries of the species on the Ag colloidal nanoparticles are discussed.

**Key Words:** surface plasmon resonance, adsorbed geometry, Raman, SERS.

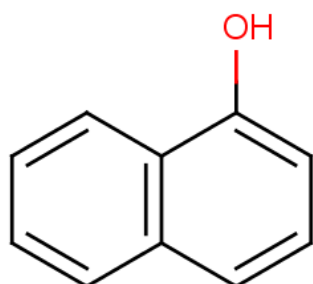
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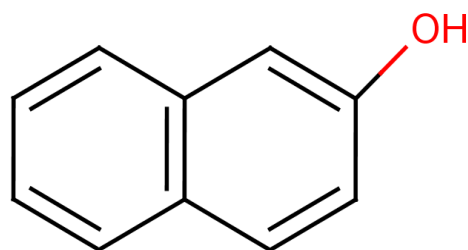
## Introduction

Naphthol (hydroxynaphthalene or naphthalenol) is a colorless crystalline solid with the molecular formula C<sub>10</sub>H<sub>8</sub>O. Naphthols (both 1 and 2 isomers) are fluorescent organic compounds and they can be used as biomarkers for livestock and human exposed to polycyclic aromatic hydrocarbons (Sreekanth et al 2013). 1-Naphthol consists of two fused benzene rings (naphthalene) with an OH group attached to position 1, whereas 2-Naphthol is the other structural isomer in which the OH is attached to position 2. Naphthol is the naphthalene homologue of phenol, with the hydroxyl group being more reactive than in the phenols (Meeker et al 2006).

The molecular structures of both isomers are shown in figure 1.



a)



b)

Figure 1. Molecular structures of 1- naphthol (a) and 2- naphthol (b).

Naphthols have recently attracted much interest due to their large nonlinear optical properties (NLOP). This fact raised a technological importance in various photonic technologies as optical switching, optical communications, computing, wave guiding, compact 3D data storage and micro fabrication, chemical and biological sensing, optical power limiting, bioimaging, signal and data processing, and many other current items in materials science (Janarthanan et al 2011).

The interest for 1 and 2-naphthols has increased in the last decade due to their use in chemical and plastics industry also in the manufacture of insecticides and fungicides. Naphthols are also used as moth repellents, air fresheners, deodorizers for nappy pails, and for production of dyes and further organic synthesis (Schreiner 2003).

Most studies found in literature on this material were carried by molecular modeling analysis based on molecular mechanics, semi-empirical and density functional theory DFT calculations (Chis *et al* 2006). The study has been carried out to provide information on the relative stability of naphthalene and its metabolites, and in this way useful in the understanding of naphthalene induced toxicity (Fazlul 2006).

Theoretical investigation on 2-naphthalenol, which was shown to be a potential organic non-linear (NLO) material (Marcinak *et al* 2003) has been by single crystal X-ray diffraction method. Raman spectroscopy is a powerful vibrational spectroscopic technique which has been applied in different biomedical applications. One of its disadvantages is the extremely poor efficiency because of the low cross section. Recently, there has been a renewed interest in Raman techniques due to the discovery of surface-enhanced Raman scattering (SERS) effect, which results in strongly increased Raman signals when molecules are adsorbed on nanometer-size metallic structures (Aroca 2006; Moskovits 2005). From the metallic structures silver is able to increase the Raman intensity enough to detect single molecules, since it can support plasmon resonance properties (Nie & Emory 1997; Qian & Nie 2008).

The aim of this work was to investigate the adsorption of naphthols species on Ag colloidal nanoparticles.

The naphthol does not easily adsorb onto conventional silver surfaces.

The SERS analysis of 1- and 2-naphthol is important since they are considered the relevant biomarkers for livestock and human exposed to polycyclic aromatic hydrocarbons.

Surface enhanced Raman spectroscopy was employed for the investigation of the adsorbed geometry of the 1- and 2-naphthol and the functional groups involved in adsorption on the nanometer colloidal surface. In this respect, vibrational spectroscopic techniques have been applied to investigate the adsorption ability of the title species on Ag colloidal nanoparticles.

## Experimental

In this study the 1- and 2-naphthol were used as crystalline solids dissolved in distilled water at room temperature.

As a SERS surface, the silver colloid was employed by reduction of silver nitrate with sodium citrate, using the Lee-Meisel method (Lee & Meisel 1982). Small quantities of 1-naphthol and 2-naphthol aqueous solutions were added to 3 mL sodium citrate reduced Ag colloid to obtain the SERS sample with a final concentration of  $10^{-4}$  mol l<sup>-1</sup>.

The micro-Raman and the SERS spectra of the 1 and 2-naphthol on silver colloid were recorded with a Raman microspectrometer (Horiba-Jobin-Yvon, model LabRam) using the 514.5 nm excitation line from an argon ion laser (Spectra Physics, model 2016). The spectra were collected in the backscattering geometry using an optical microscope equipped with an Olympus LMPlanFL 50x objective. The spectral resolution was 2 cm<sup>-1</sup>. The detection of Raman signal was carried out with a Peltier-cooled

CCD camera and for the signal acquisition the LabSpec software package was employed. The laser power output used in our measurements was 200 mW.

## Results and discussion

The both species of naphthols in solid state, aqueous solution and adsorbed on Ag colloidal particles have been analyzed by Raman spectroscopy. The vibrational assignments of the title species is given based on the DFT calculation. Surface-enhanced Raman scattering is an extremely sensitive molecular fingerprinting technique. It requires sample preparation (Kasera *et al* 2012) and can be used successfully in detection of naphthols species onto conventional silver surfaces. In aqueous solution, such molecular species can behave as an acid and lose a proton, and as result the naphthol is in equilibrium with its conjugate base in water. Negative charge generated is not favorable to the O-adsorption. In SERS spectra any bands attributable to the O-Ag stretching are absent.

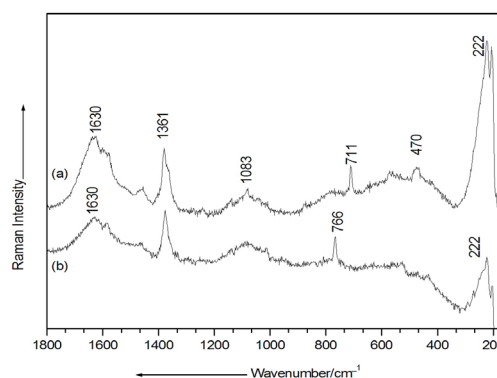


Figure 2. Raman spectra of 1-naphthol (a) and 2-naphthol (b) in aqueous solution state. Excitation: 514.5 nm, 200 mW.

By comparing Raman spectra of 1-naphthol and 2-naphthol in solution state minimal differences in bands intensity were observed (Figure 2).

Differences found between Raman spectra of 1 and 2 naphthol are showed in Figure 2.

One difference has been found in the case of band with wavelength 766 cm<sup>-1</sup>. This band is shifted at 711 cm<sup>-1</sup> in Raman spectrum of 1-naphthol. The second difference has been observed at 470 cm<sup>-1</sup> wavelength. The band at 470 cm<sup>-1</sup> appear only in Raman spectrum of 1-naphthol.

The vibrational fundamentals from the micro-Raman spectra, presented in figure 3 for 1- and 2-naphthol were analyzed by comparing the experimental vibrational modes with the previous published data (Trevor *et al* 2004). Based on recently reported DFT calculation on 2-naphthol (Chis *et al* 2006), the complete vibrational assignments of the two species is given.

The micro-Raman spectrum of 1-naphthol is increased in relative intensity in comparison with the micro-Raman spectrum of 2-naphthol, and the signal to noise ratio is different. 2-naphthol is presenting higher background under visible excitation. Comparing micro-Raman spectra of both naphthol compounds, is observed that they band positions and relative intensities with only small differences. The strong bands were observed for 1-naphthol at 3075, 1576, 1452, 1379 and 708 cm<sup>-1</sup>. In the

case of 2-naphthol, the main important bands were observed at 3056, 1579, 1466, 1378, 1010, 766, and 522 cm<sup>-1</sup>.

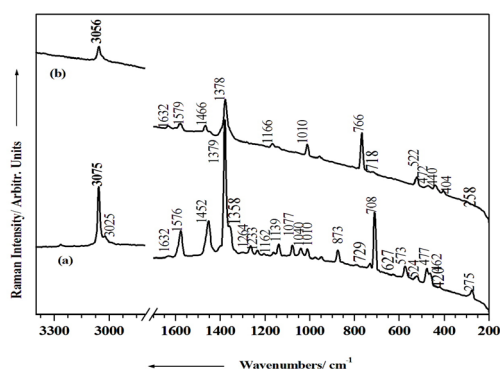


Figure 3. Micro-Raman spectra of 1-naphthol (a) and 2-naphthol (b). Excitation: 514.5 nm, 200 mW.

The strong bands at 3075 cm<sup>-1</sup> (1-naphthol) and 3056 cm<sup>-1</sup> (2-naphthol) were assigned to the C-H stretching modes. The medium strong band at 1576 cm<sup>-1</sup> and 1452 cm<sup>-1</sup> (1-naphthol) were assigned to the C-C stretching and C-H in-plane bending modes. The same attribution is available for the weak peaks at 1579 and 1466 cm<sup>-1</sup> (2-naphthol). The most intense band observed at 1378 cm<sup>-1</sup> for both species was assigned to the ring C-C and C-O stretching mode. New weak peaks appearing at 1264 and 1233 cm<sup>-1</sup> for 1-naphthol were assigned to the C-C stretching mode and in-plane bending of C-H. The following bands 1166 and 1139 cm<sup>-1</sup> was attributed to the OH and C-H in-plane bending modes (Helena *et al* 2000). The 1077 and 1010 cm<sup>-1</sup> bands were assigned to the C-H and C-C-C in-plane bending modes, respectively. The Raman signal observed at 1040 cm<sup>-1</sup> was assigned to the C-C out-of-plane bending mode and the medium peak at 873 cm<sup>-1</sup> corresponds to the out-of-plane deformation C-H. The very strong peak at 766 cm<sup>-1</sup> correspond to the OH out-of-plane deformations, whereas the Raman signal at 708 cm<sup>-1</sup> was assigned to C-C-C in-plane bending mode. Other peaks for the C-C-C in-plane deformation appear at 729, 718, 524, and 522 cm<sup>-1</sup>. The band at 573 cm<sup>-1</sup> was assigned to in-plane bending mode of the C-O group, while the bands at 627, 275, 258 cm<sup>-1</sup> correspond to C-C in-plane bending mode. The in-plane C-OH deformation and C-C-C deformation modes appear at 477, 472, 462, and 440 cm<sup>-1</sup>.

In the case of SERS spectra of naphthol species, large differences in band positions and relative intensities were observed compared to Raman spectra can be observed for both species (Figure 4). Thus chemisorption of each molecular specie to the silver nanoparticles is assumed.

The SERS spectra shown in the figure 4 are dominated by aromatic ring vibrations. The band at 1619 cm<sup>-1</sup> characteristic for 1-naphthol is increased in intensity in comparison with 1615 cm<sup>-1</sup> band characteristic for 2-naphthol. This band was assigned to the C-C stretching mode. The medium strong band at 1590 cm<sup>-1</sup> in the spectrum of 1-naphthol was assigned to C-C stretching mode. The same attribution is available for the band at 1586 cm<sup>-1</sup> for 2-naphthol.

The most prominent features in the SERS spectrum for 1-naphthol are 1520, 1436 cm<sup>-1</sup> bands assigned to C-C stretching

vibrations and 1476 cm<sup>-1</sup> band assigned to the C-H in plane bending mode. The position of the band seen at 1378 cm<sup>-1</sup> is shifted to 1389 cm<sup>-1</sup> for the 1-naphthol and from 1378 to 1375 cm<sup>-1</sup> for the 2-naphthol in the SERS spectrum. The very strong peaks at 1389 and 1375 cm<sup>-1</sup>, respectively correspond to C-C and C-O stretching vibrations (Helena *et al* 2000).

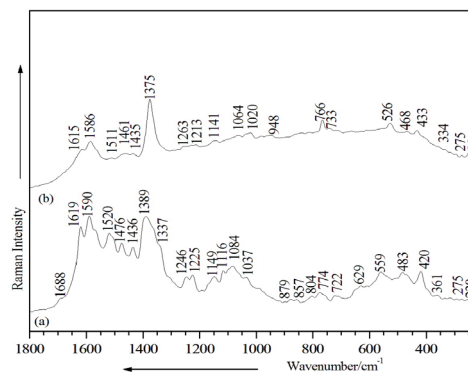


Figure 4. SERS spectra of 1-naphthol (a) and 2-naphthol (b). Excitation: 514.5 nm, 200 mW.

The position of the band corresponding to C-O stretching mode in SERS spectrum indicates that the molecule binds to the silver nanoparticles through the deprotonated hydroxyl group. If the C-O vibrational mode was perpendicular to the surface, the C-O stretching band should be strongly enhanced and the intensity relative to the other bands should not decrease (Helena *et al* 2000).

Comparing the SERS spectra for both naphthol species, many differences are observed in the bands position and the relative intensities. The bands at 1246 cm<sup>-1</sup> and 1225 cm<sup>-1</sup> are attributed to the C-C stretching mode and C-H in plane bending mode for 1-naphthol. The same attribution is available for the medium band at 1263 cm<sup>-1</sup> from SERS spectra of 2-naphthol. The very weak band at 1213 cm<sup>-1</sup> is attributed to the OH in plane bending mode. The weak peak at 1149 and very weak one at 1141 cm<sup>-1</sup> is assigned to the out of plane C-H vibrations. The out of plane C-H mode appears also at 774 cm<sup>-1</sup>, while the out of plane OH mode appears at 766 cm<sup>-1</sup>.

The 559 and 526 cm<sup>-1</sup> were attributed to the C-C-C in plane bending vibrations. The 420 and 433 cm<sup>-1</sup> were attributed to the C-OH and C-C-C in plane bending modes. The both forms are found to chemisorbed on Ag colloidal nanoparticles exhibiting different SERS spectral pattern. SERS of 1,1'-bi-2 naphthol has also been reported (Helena *et al* 2000; Trevor *et al* 2004) and it was found to be detectable within a titled geometry orientation with respect to the surface, O atom being involved into adsorption. The 1- or 2-position of the -OH group leads to large differences in the Raman spectra of naphthols. Based on the above vibrational characterization and on the DFT calculations accomplished so far as a concluding remark (Marcinak *et al* 2003) the two distinct species were found to be slightly different chemisorbed on the silver surface, 1-naphthol having a perpendicular orientation to the Ag surface, whereas 2-naphthol is parallel to the Ag surface.

## Conclusion

Raman spectra of 1- and 2-naphthol in solid state and SERS spectra of the aqueous solution of the same species have been obtained and discussed. The vibrational assignments of the title species is given based on the DFT calculation. Good quality SERS spectra on silver colloidal particles show large differences in the band positions and relative intensities in comparison to their Raman spectra. Therefore, one can conclude a strong chemisorption of both species with respect to the Ag surface.

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