SERS, Raman, IR and DFT investigation of 1-(2-pyridylazo)-2-naphthol and its metal complexes

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Abstract

Metal ions determination represents an area of interest in several fields, like environmental protection, food safety or clinical diagnostics. Analytical methodologies for direct determination of metal ions were established over the last decades including atomic absorption or emission spectroscopy and mass spectrometry. Although these methods are sensitive and accurate, they require tedious sample pre-treatment and expensive equipment. Thus, a significant increase in the development of optical chemical sensors for heavy metals has been noted in the last years, aiming to their routinely production, low cost, high selectivity and sensitivity. In this work, IR, Raman and SERS spectroscopy is used in conjunction with quantum chemical calculations in order to characterize the molecular structure, electronic properties and vibrational energies of the 1-(2-pyridylazo)-2-naphthol (PAN) molecule and its complexes with Al(III), Ca(II), Mn(II), Fe(III), Cu(II), Zn(II) and Pb(II). Thus, IR, Raman and SERS spectra of PAN, as well as the SERS spectrum of the Al(III), Ca(II), Mn(II), Fe(III), Cu(II), Zn(II) and Pb(II) complex of PAN, were assigned using DFT calculations with the hybrid B3LYP exchange-correlation functional using the standard 6-31G(d) basis set. The experimental vibrational bands were assigned to the calculated normal modes and a very good correlation was achieved between the experimental and theoretical data. The SERS spectra of PAN and of its metal chelates were recorded using HeNe laser emitting at 633 nm and hydroxylamine reduced silver colloid [1]. PAN complexes with Al(III), Ca(II), Mn(II), Fe(III), Cu(II), Zn(II) and Pb(II) are differentiated by their SERS spectra, each metal complex showing a particular SERS spectral fingerprint. The molecular electrostatic potential of the molecules has been calculated and used for predicting site candidates of electrophilic attack.

Key words: Metal chelating compounds, heavy metal ion, FTIR, FT-Raman, SERS, DFT, 1-(2-pyridylazo)-2-naphthol (PAN).

Experimental techniques

FT-IR/ATR

The FTIR/ATR spectrum of PAN powder sample was recorded at room temperature on a conventional Equinox 55 (Bruker Optik GmbH, Ettlingen, Germany) FTIR spectrometer equipped with a DTGS detector.

FT-Raman

The FT-Raman spectrum of PAN was recorded in a backscattering geometry with a Bruker FRA 106/S Raman accessory equipped with a nitrogen cooled Ge detector. The 1064 nm Nd:YAG laser was used as excitation source, and the laser power measured at the sample position was 300 mW. The FT-Raman and FTIR/ATR spectra were recorded with a resolution of 4 cm^{-1} by co-adding 32 scans.

SERS

SERS spectra were recorded using a DeltaNu Advantage 633 Raman spectrometer (DeltaNu, Laramie, WY) equipped with a HeNe laser emitting at 633 nm. The laser power was 4 mW and the spectral resolution of 10 cm^{-1}. For all SERS measurements 25 μl of analyte were added to 0.5 ml silver colloid. All chemicals used were of analytical reagent grade. The silver colloid was prepared according to the previously reported procedure [1]. The pH value of the silver colloid, measured immediately after preparation, was found to be 8. PAN complexes with Al(III), Ca(II), Mn(II), Fe(III), Cu(II), Zn(II) and Pb(II) were prepared by adding 1 ml dilutions of 10^{-3} M metal salt solution to 2 ml 10^{-3} M PAN solution, up to obtaining finally 3 ml mixtures at 2:1 PAN:metal salt molar ratio, PAN chelating metal ions at 2:1 ratio.

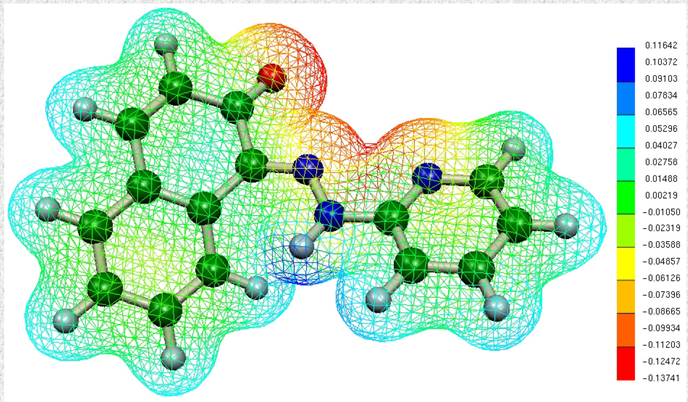
[1] *N. Leopold, B. Lendl, J. Phys. Chem. B 107 (2003) 5723.*

Computational methods

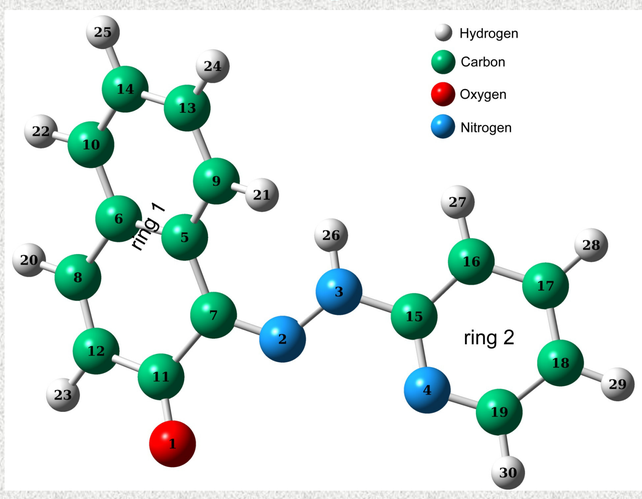
DFT

exchange-correlation functionals: B3LYP & BLYP, basis sets: "spectroscopic" 6-31G(d)

B3LYP/6-31G(d) calculated 3D electrostatic potential contour map of PAN, in atomic units.



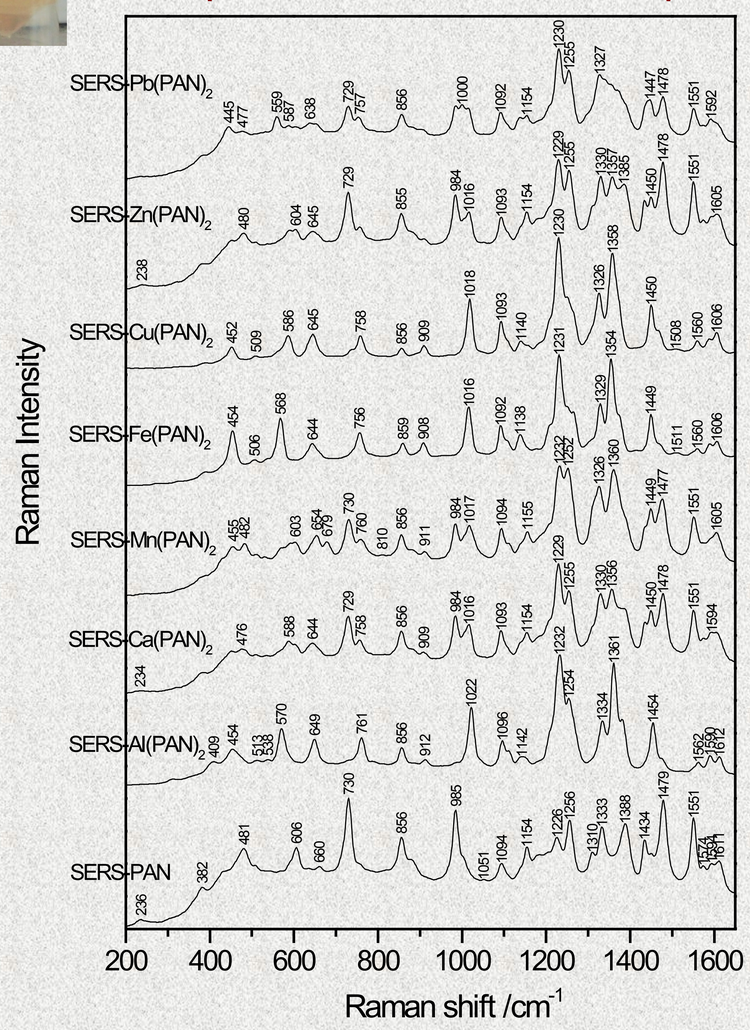
Optimized chemical structure of PAN with atom numbering scheme.



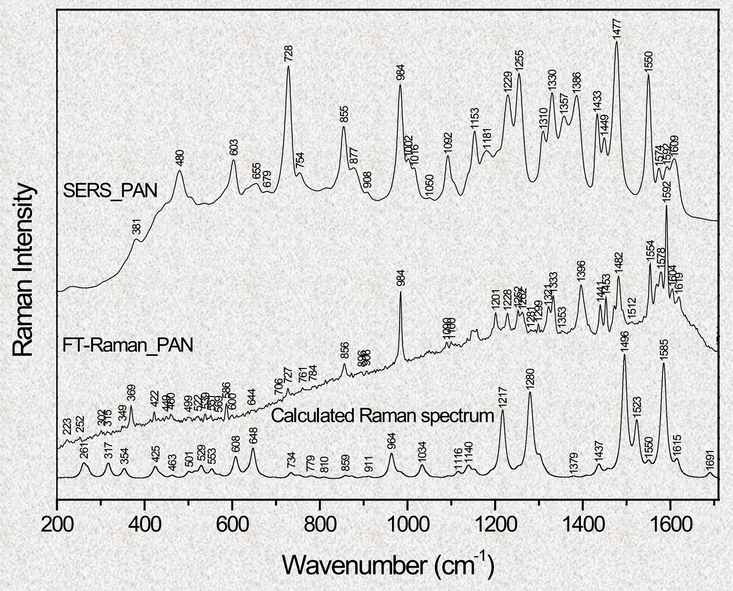
Picture of solutions of different PAN-metal complexes:

PAN $Al(PAN)_2$ $Ca(PAN)_2$ $Mn(PAN)_2$ $Fe(PAN)_2$ $Cu(PAN)_2$ $Zn(PAN)_2$ $Pb(PAN)_2$

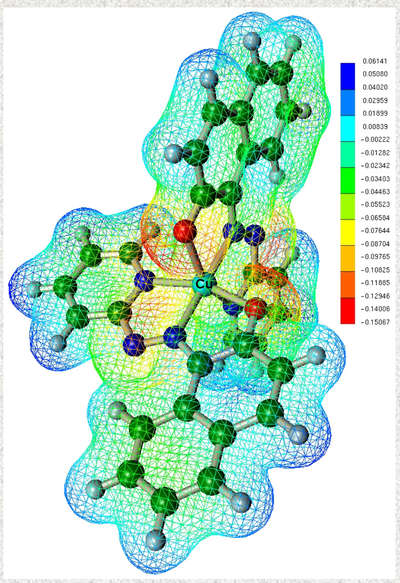
SERS spectra of PAN and PAN-metal complexes



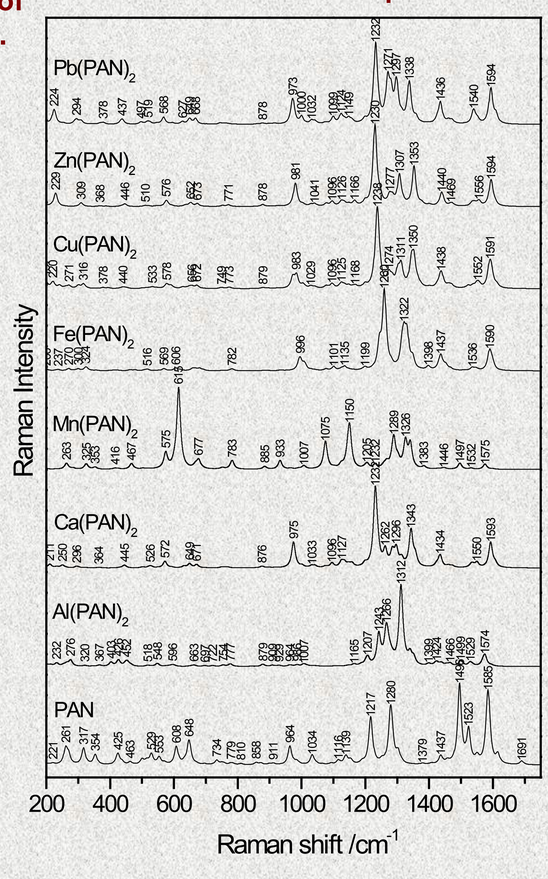
SERS, FT-Raman and Calculated Raman spectra of PAN



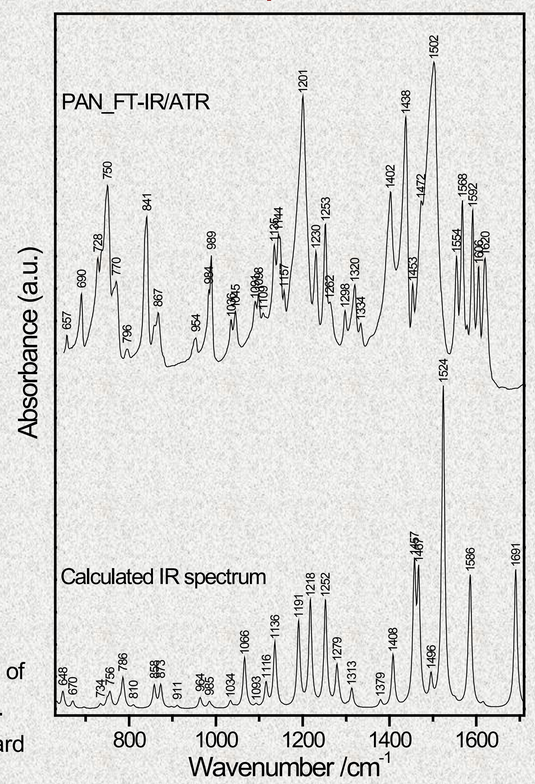
B3LYP/6-31G(d) calculated 3D electrostatic potential contour map of $Mn(PAN)_2$ complex, in atomic units.



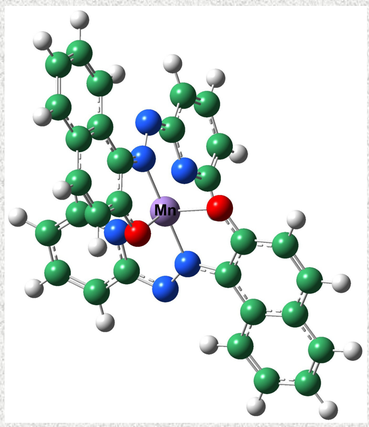
Calculated Raman spectra of PAN and PAN-metal complexes



FTIR/ATR spectra of PAN



Optimized chemical structure of $Mn(PAN)_2$ complex



Conclusions

PAN was investigated by experimental (FT-IR, FT-Raman and SERS) techniques in conjunction with DFT quantum chemical calculations.

In order to assess the detection potential of different metal ions PAN as chelating agent and SERS as detection method, SERS spectra of different metal complexes of this ionophores were recorded (Al(III), Ca(II), Mn(II), Fe(III), Cu(II), Zn(II), Pb(II)) using a silver colloid substratum.

Each PAN-metal complex SERS spectrum shows a characteristic spectral fingerprint. Because all PAN-metal compounds indicated standard marker bands, SERS method may be a new detection technique for Al(III), Ca(II), Mn(II), Fe(III), Cu(II), Zn(II) and Pb(II).

For PAN, DFT calculation were made for a good geometric optimization, for the molecular electrostatic potential determination and also for band assignment.

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