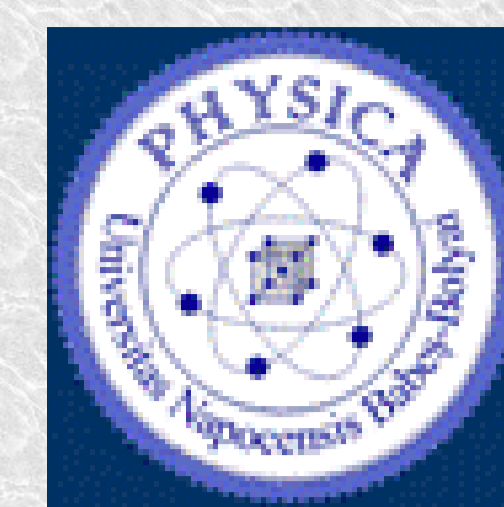


Zn (II) DETERMINATION IN CONTAMINATED SOIL BY SERS SPECTROSCOPY



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Abstract

The surface-enhanced Raman scattering (SERS) spectra of 4-(2-pyridylazo)resorcinol (PAR) and its Zn(II) and Cu(II) complexes were recorded using a hydroxylamine reduced silver colloid. Molecular geometry optimization, molecular electrostatic potential (MEP) distribution and vibrational frequencies calculation were performed by density functional theory (DFT) computations for the PAR molecule and its Zn(PAR)₂ complex. The SERS spectra of the samples prepared at PAR:metal salt 3:1 molar ratio, show mainly the spectral features of Zn(PAR)₂ or Cu(PAR)₂ complexes, but also spectral features of PAR molecules adsorbed to the silver surface, whereas the SERS spectra of the 1:1 molar ratio samples show exclusively the spectral features of the PAR-metal complex. Differentiation between PAR complexes with Zn(II), Cu(II), Fe(III), Mn(II) and Pb(II) is shown by the SERS spectral features of each complex.

Motivation

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.

4-(2-pyridylazo)resorcinol (PAR), with the structure shown in Fig.1, is a non-selective azo dye, widely used as colorimetric reagent for metal ions because of forming very stable, water-soluble and highly colored complexes with the vast majority of transition metals.

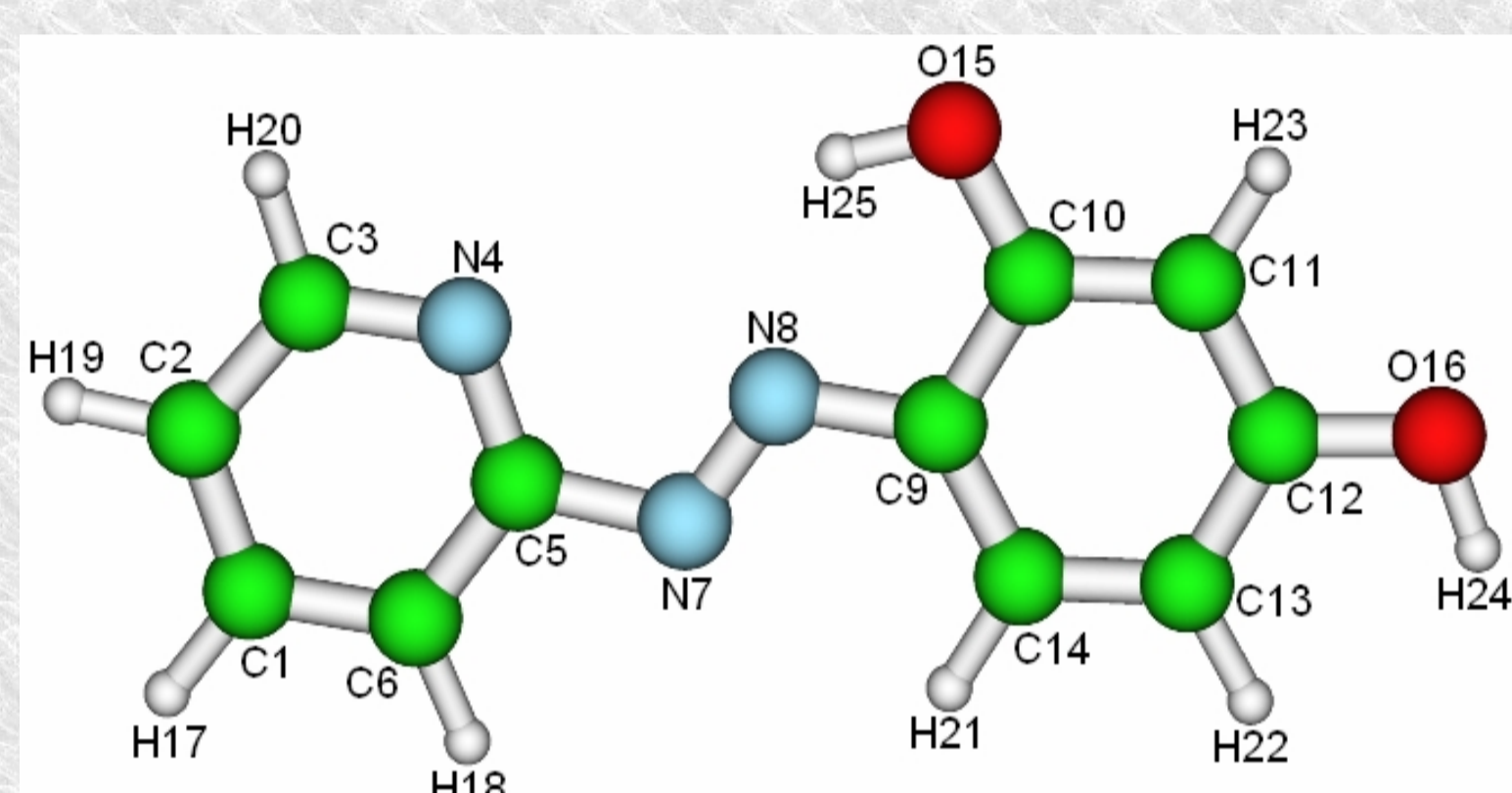


Fig.1. Chemical structure of PAR with atom numbering scheme.

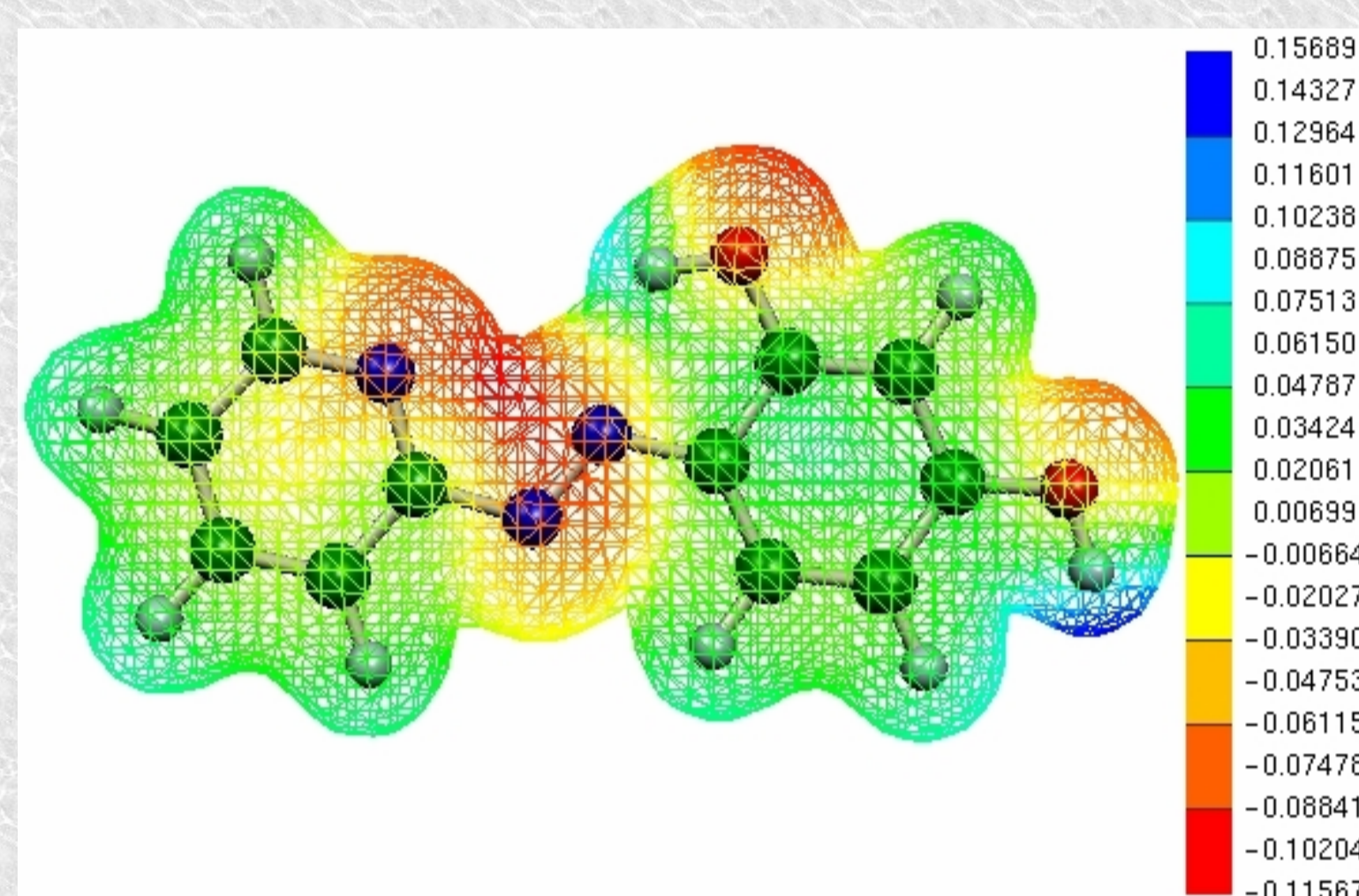


Fig.2. B3LYP/6-31G(d) calculated 3D molecular electrostatic potential of PAR (in a.u.).

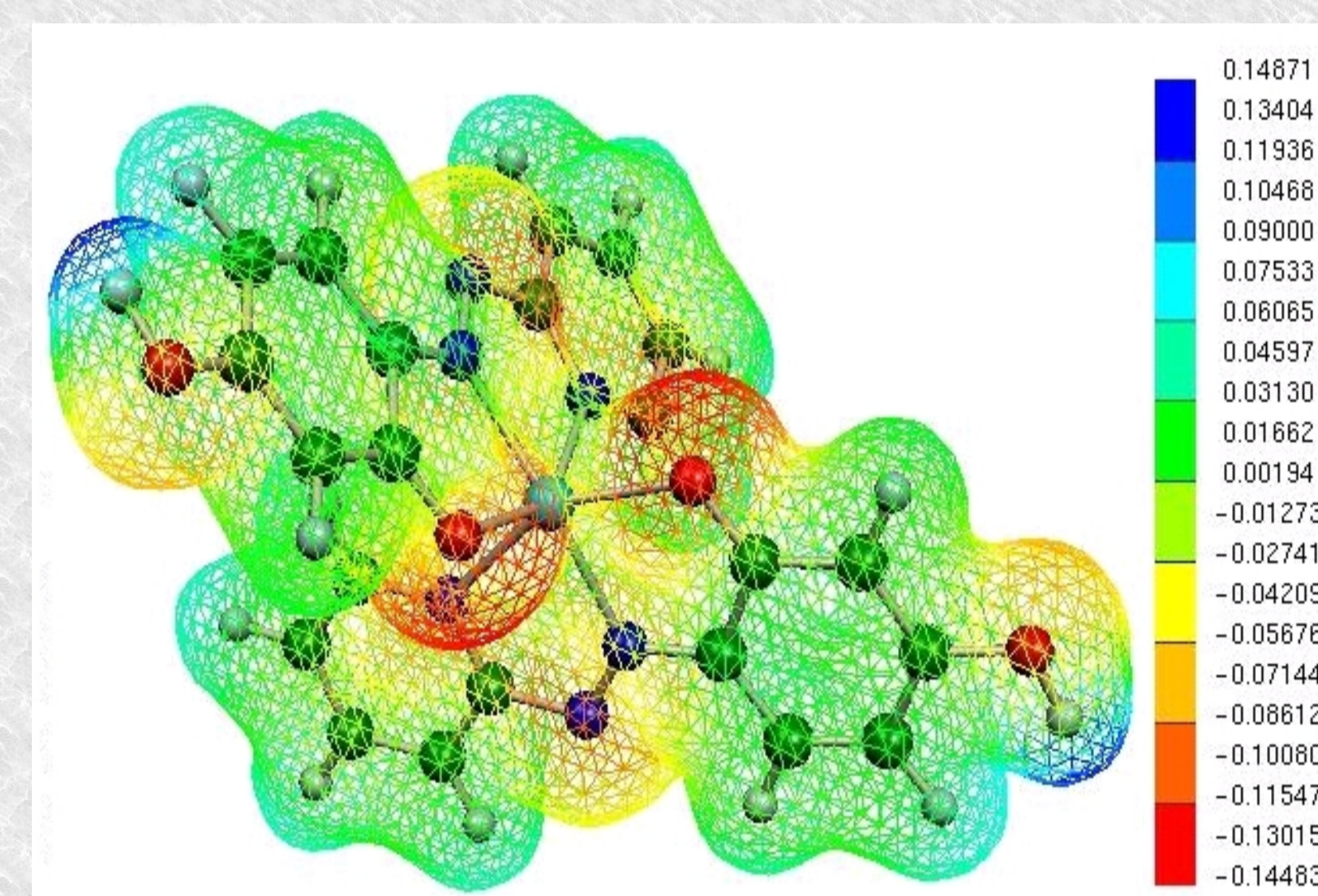


Fig.3. B3LYP/6-31G(d) calculated 3D molecular electrostatic potential of Zn(PAR)₂ complex (in a.u.).

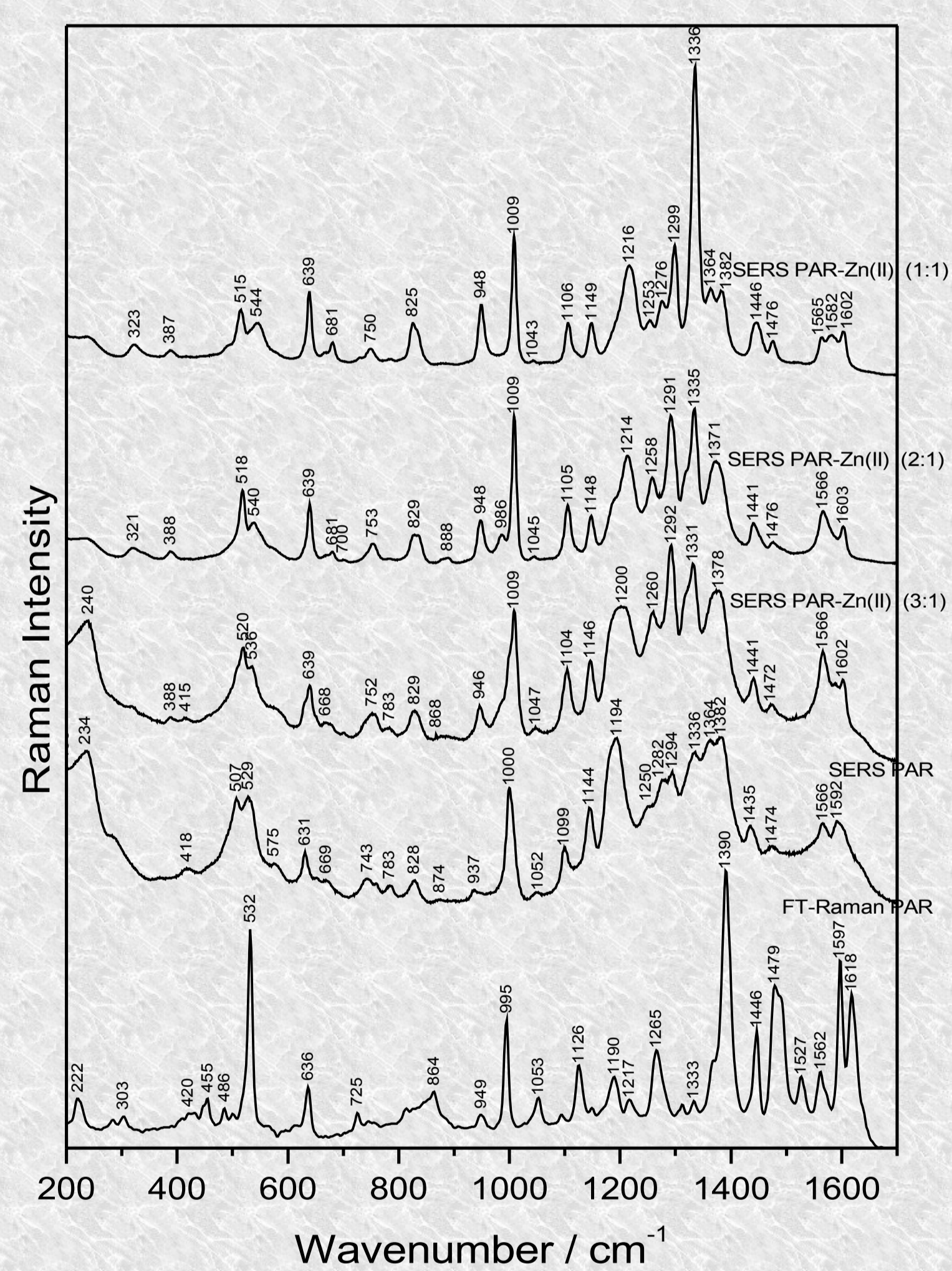


Fig.4. FT-Raman spectrum of PAR. SERS spectra of PAR and Zn(PAR)₂ complex, prepared at PAR:ZnSO₄ 3:1, 2:1 and 1:1 molar ratios.

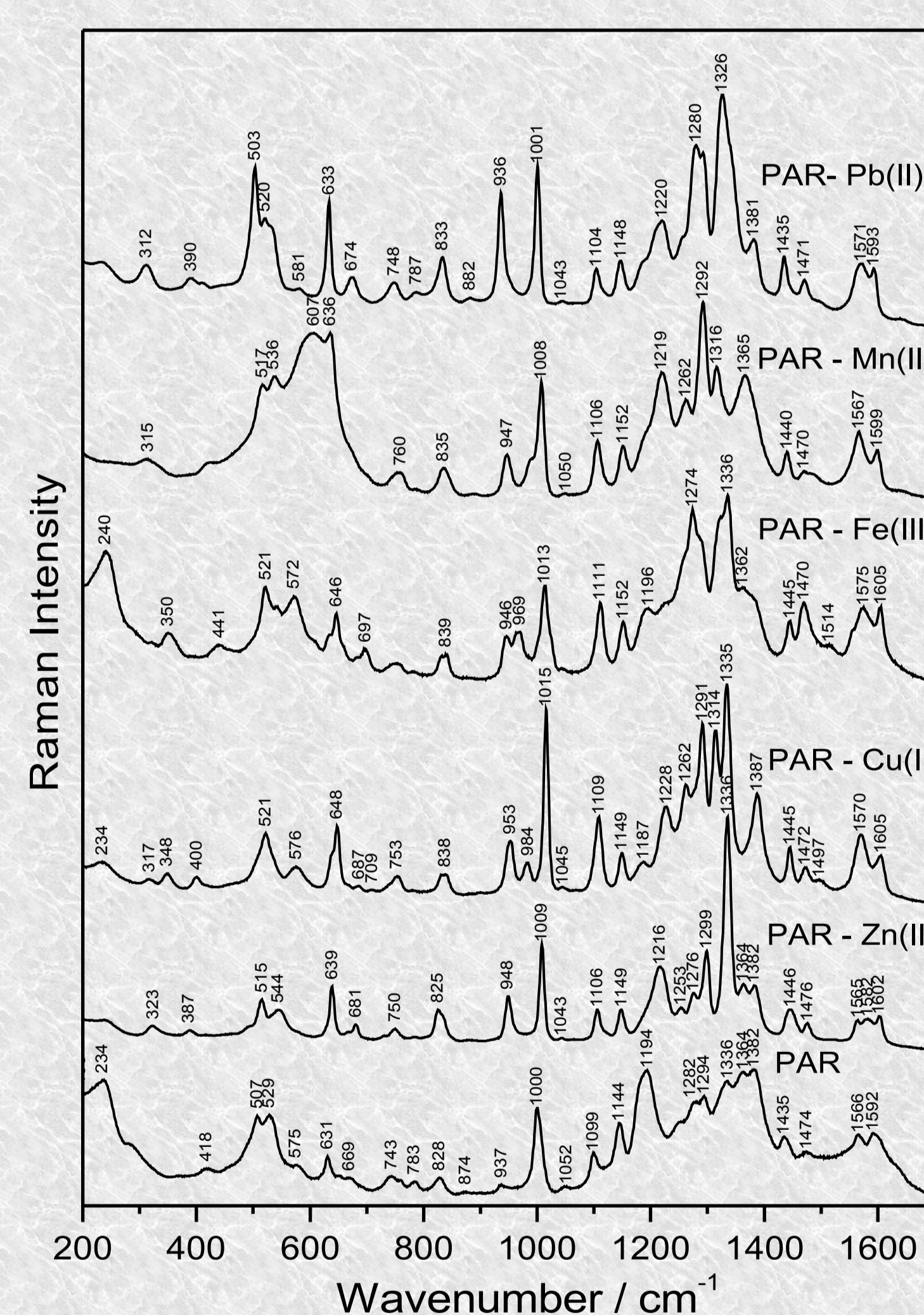


Fig.5. SERS spectra of PAR- Zn(II), Cu(II), Fe(III), Mn(II) and Pb(II) complexes, prepared at PAR:metal salt 1:1 molar ratio.

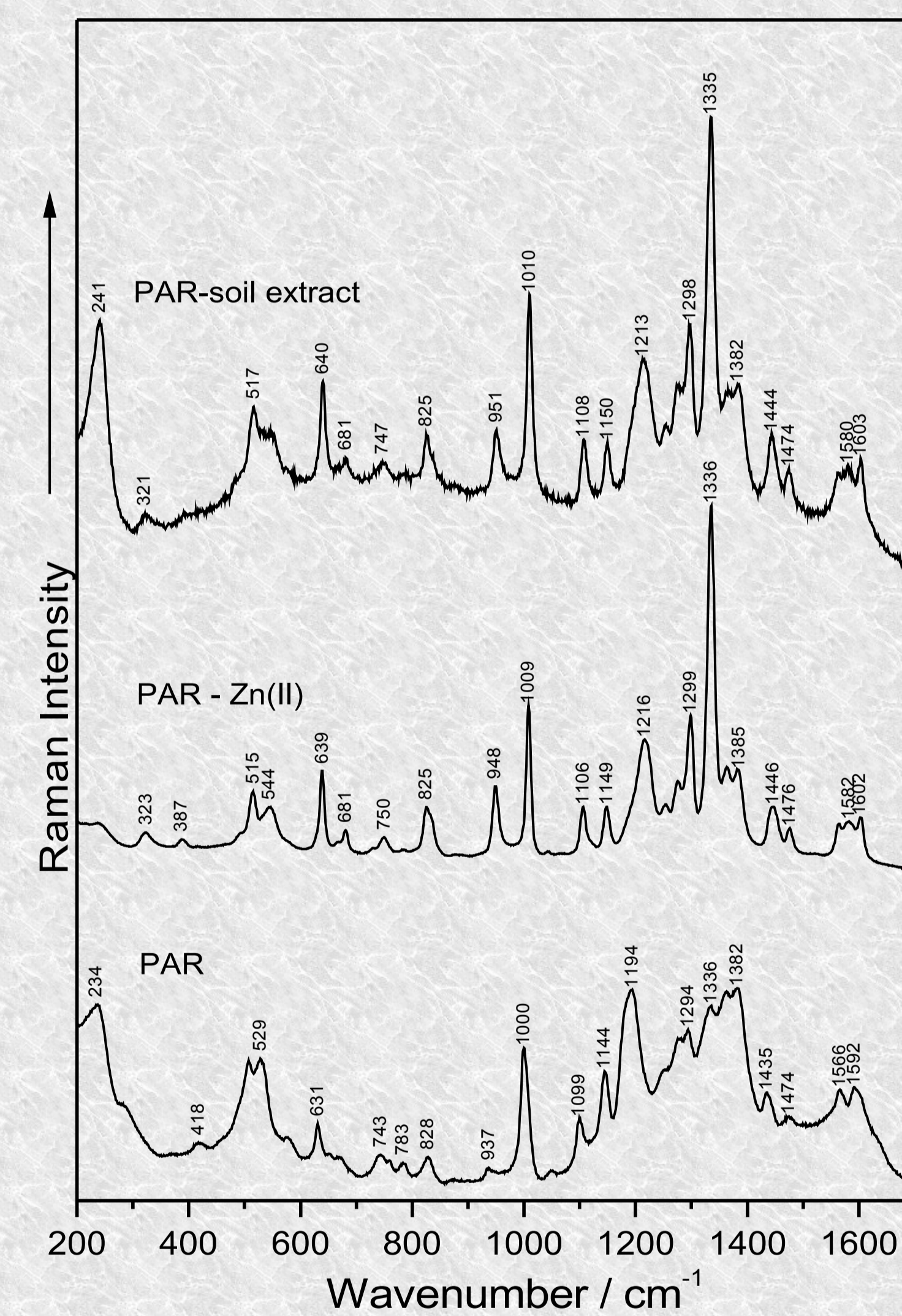


Fig.6. SERS spectra of PAR, Zn(PAR)₂ and PAR-soil water extract. In all SERS experiments a hydroxylamine reduced silver colloid was used.

Conclusions

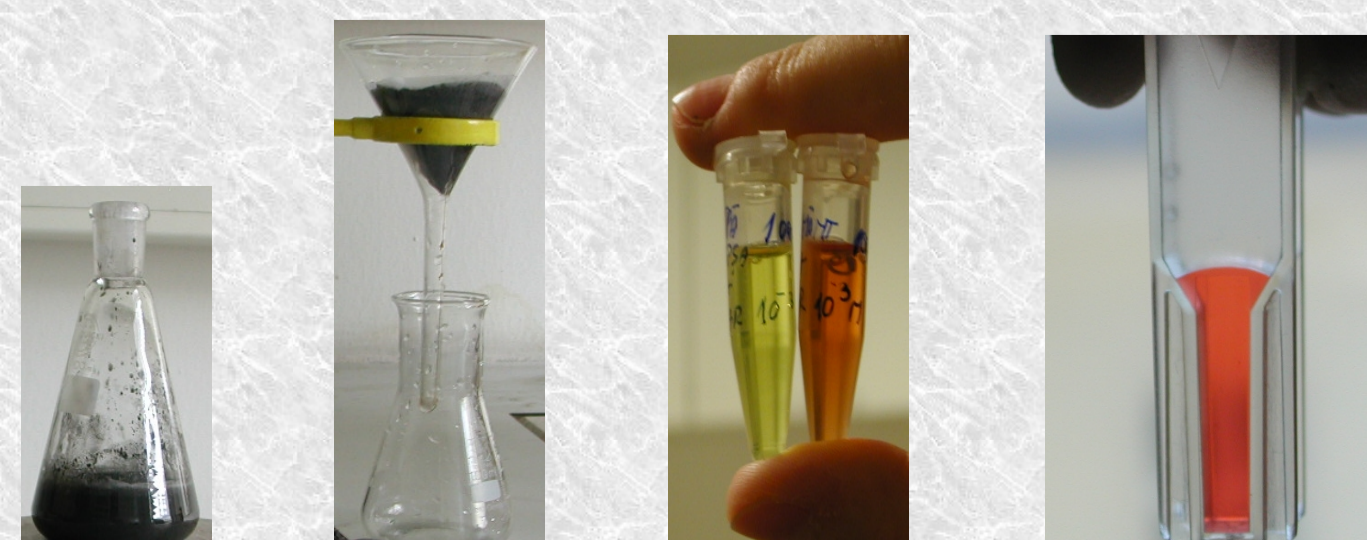
The FT-Raman and SERS spectra of PAR, as well as the SERS spectrum of Zn(PAR)₂ complex were safely assigned, due to a good match between experimental and DFT calculated vibrational modes. The SERS band assignment of the Cu(PAR)₂ complex was supposed to be similar to that of Zn(PAR)₂ complex, due to the similitude in band position between the two spectra.

The calculated MEP distributions indicate for the PAR molecule the highest electronegativity localized on the nitrogen and oxygen atoms. For the Zn(PAR)₂ complex the negative charge is localized mainly on the oxygen atoms involved in the metal ion coordination, as expected from the deprotonated character of these atoms.

The SERS spectra of the 3:1 molar ratios show mainly spectral features of the Zn(PAR)₂ or Cu(PAR)₂ complex, but also spectral features of PAR molecules adsorbed to the silver surface, whereas the SERS spectra of the 1:1 molar ratios show exclusively PAR-metal complex spectral features.

As several marker bands are characteristic to each PAR-metal complex, SERS could represent a prospective method for detection of metal ions, like Zn(II), Cu(II), Fe(III), Mn(II) and Pb(II).

The good match between the Zn(PAR)₂ and PAR-soil water extract SERS spectra represents a qualitative assessment for Zn(II) in contaminated soil.



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