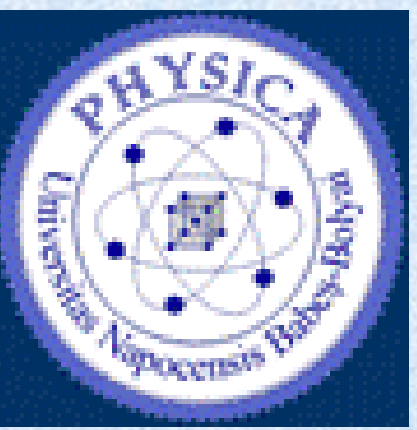# Surface-enhanced Raman scattering and DFT investigation of Eriochrome Black T metal chelating compound

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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 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 Eriochrome Black T (EBT) molecule and its complexes with Zn(II), Cu(II), Fe(III), Mn(II) and Pb(II). The surface-enhanced Raman scattering (SERS) spectra of Eriochrome Black T (EBT) and its Cu(II), Fe(III), Mn(II), Zn(II) and Pb(II). complexes were recorded using a hydroxylamine reduced silver colloid. Molecular geometry optimization, molecular electrostatic potential (MEP) distribution and vibrational frequencies calculation were performed at B3LYP/6-31G(d) level of theory for the EBT molecule and its Cu(EBT), Fe(EBT) and Mn(EBT) metal complexes. Differentiation between EBT complexes of Cu(II), Fe(III), Mn(II), Zn(II) and Pb(II) is shown by the SERS spectral features of each complex. The molecular electrostatic potential of the molecules has been calculated and used for predicting site candidates of electrophilic attack.

Key words: DFT; Eriochrome Black T (EBT); FTIR; FT-Raman; SERS.

Experimental techniques

FT-IR
The FTIR/ATR spectrum of EBT powder sample (room temperature) 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 EBT 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.
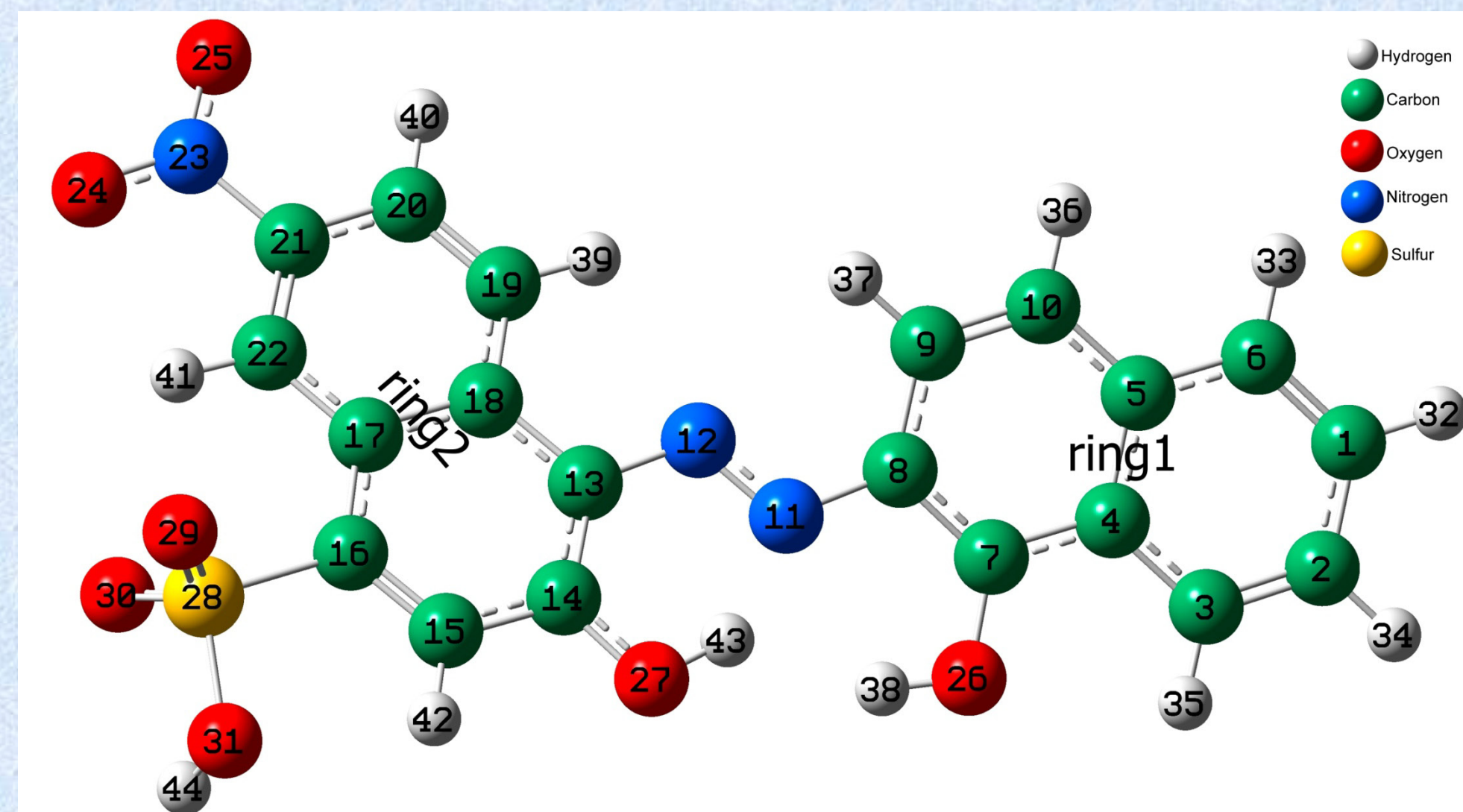
SERS
SERS spectra were recorded using a DeltaNu Advantage 532 Raman spectrometer (DeltaNu, Laramie, WY) equipped with a doubled frequency NdYAG laser emitting at 532 nm. The laser power was 6 mW and the spectral resolution of 10 cm^{-1}. For all SERS measurements 25 μl of analyte were added to 0.5 ml silver colloid, the final concentration of the metal-complexes in the colloidal solution was 4.8x10^{-5} M.
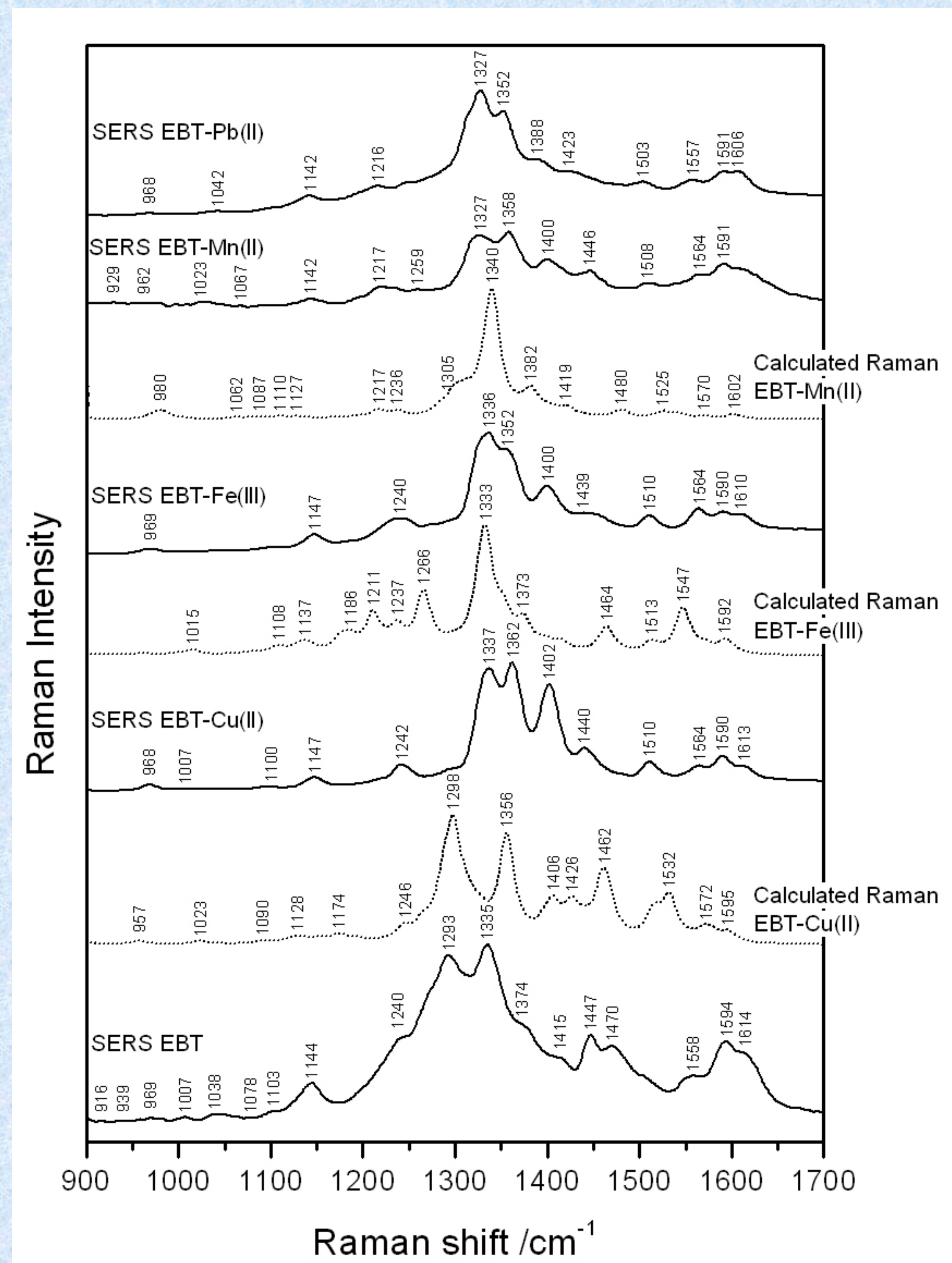
Computational methods

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

Experimental FTIR/ATR (top) and B3LYP/6-31G(d) (bottom) calculated IR spectra of EBT.

Molecular electrostatic potential of EBT-Cu(II) and schematically view of EBT-Cu(II) complex adsorption geometry on the silver surface.

Chemical structure of EBT with atom and ring numbering scheme numbering scheme.

B3LYP/6-31G(d) calculated Raman spectra and SERS spectra of EBT, EBT- Cu(II), -Fe(III), -Mn(II) and -Pb(II) complexes, prepared at EBT:metal salt molar ratio of 1:1

B3LYP/6-31G(d) calculated 3D molecular electrostatic potential contour map of EBT (in atomic units) and schematically view of EBT adsorption geometry on the silver surface.

Experimental FT-Raman spectrum (middle) of polycrystalline EBT, SERS spectrum (top) of EBT and B3LYP/6-31G(d) calculated Raman spectrum of EBT (bottom) in gas-phase

Conclusions

Optimized geometries, molecular electrostatic potential and normal modes of EBT and EBT-metal complexes of Cu(II), Fe(III) and Mn(II) were calculated by theoretical DFT B3LYP/6-31G(d) methods.
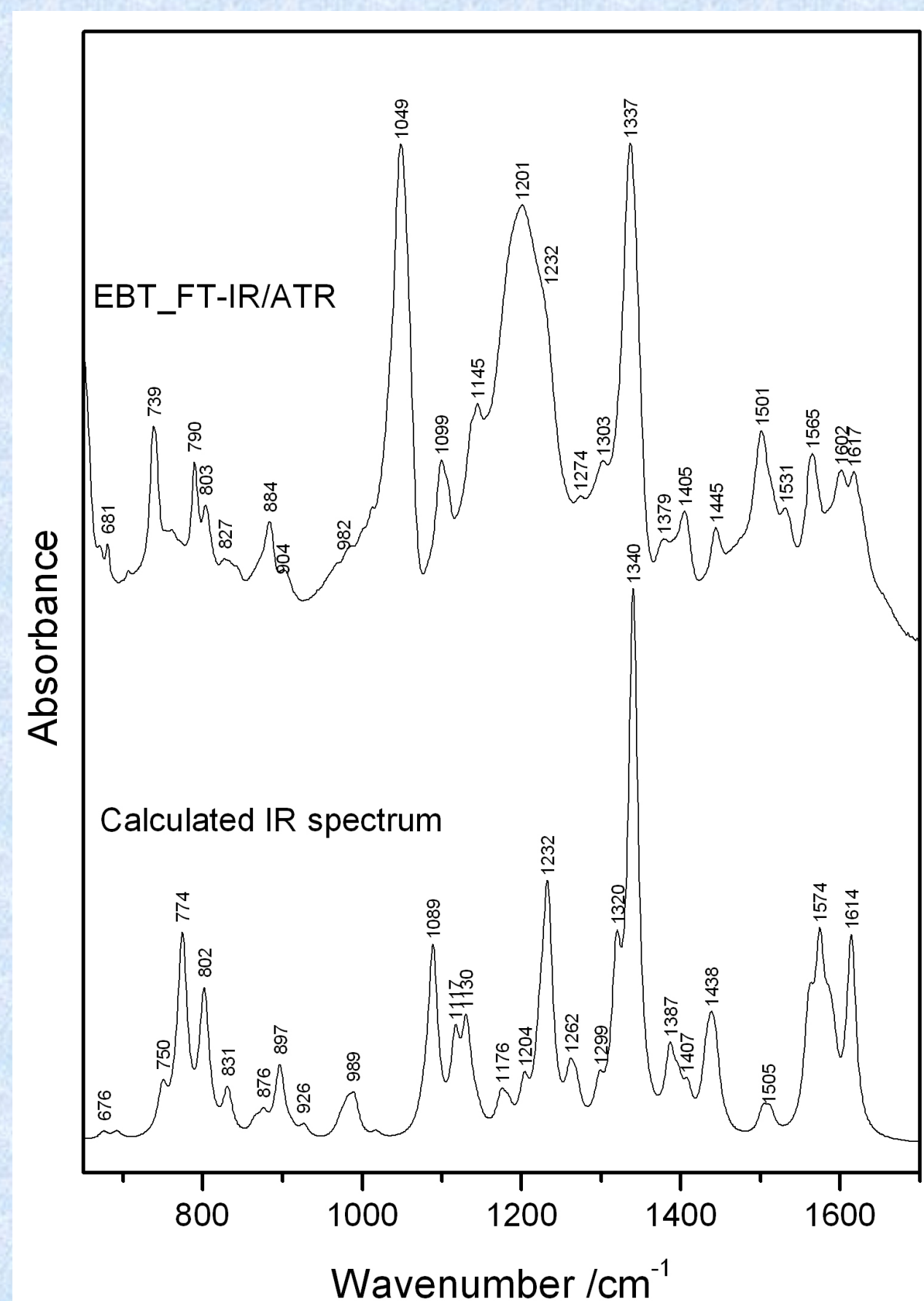
The FT-Raman and SERS spectra of EBT and EBT-metal complexes were safely assigned, due to a good match between experimental and DFT calculated vibrational modes.

The calculated MEP distributions indicate for the EBT molecule and EBT-Cu(II) complex the highest electronegativity localized on the NO$_2$ and SO$_3$H groups, thus, the adsorption to the silver surface occuring by these groups.
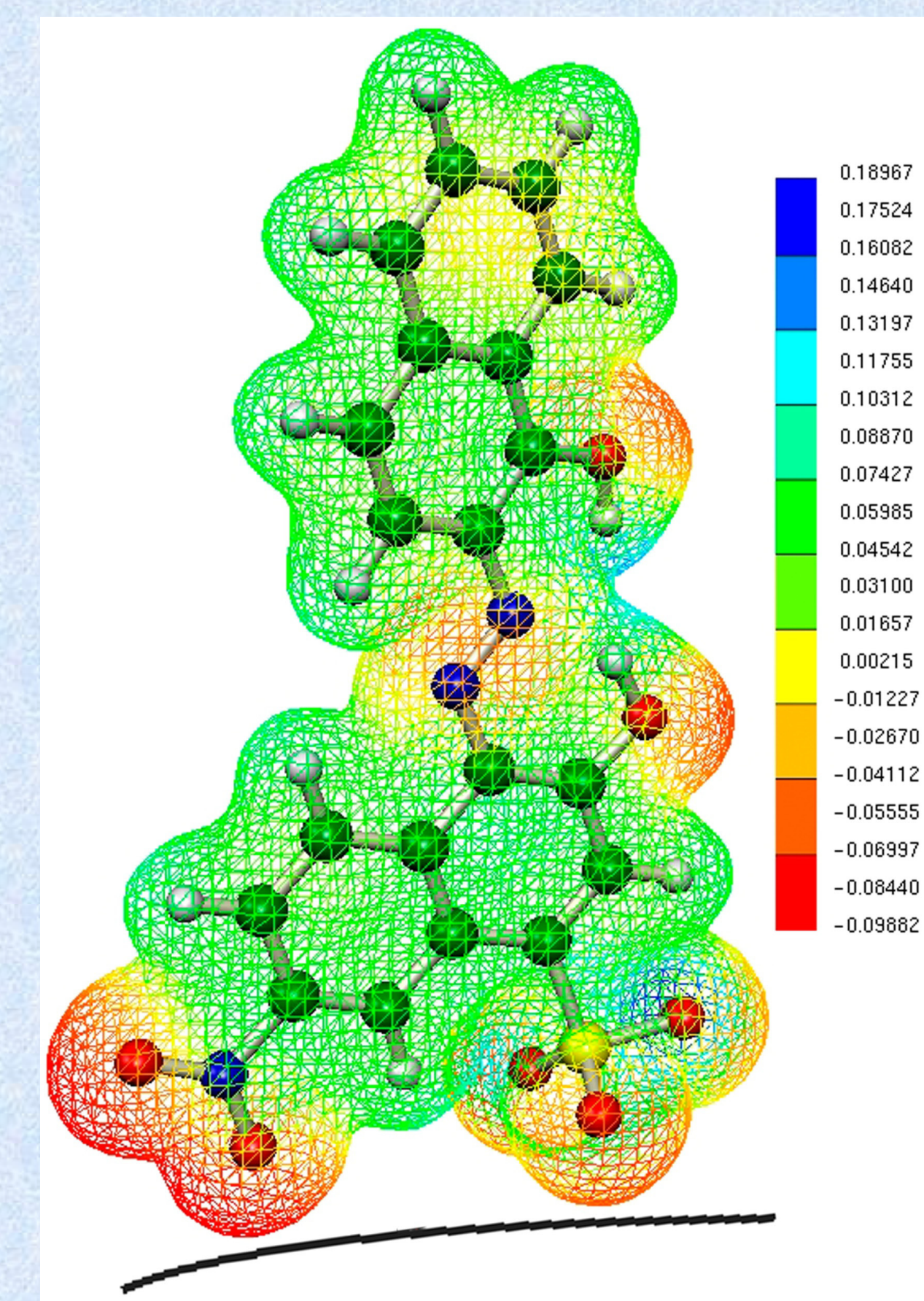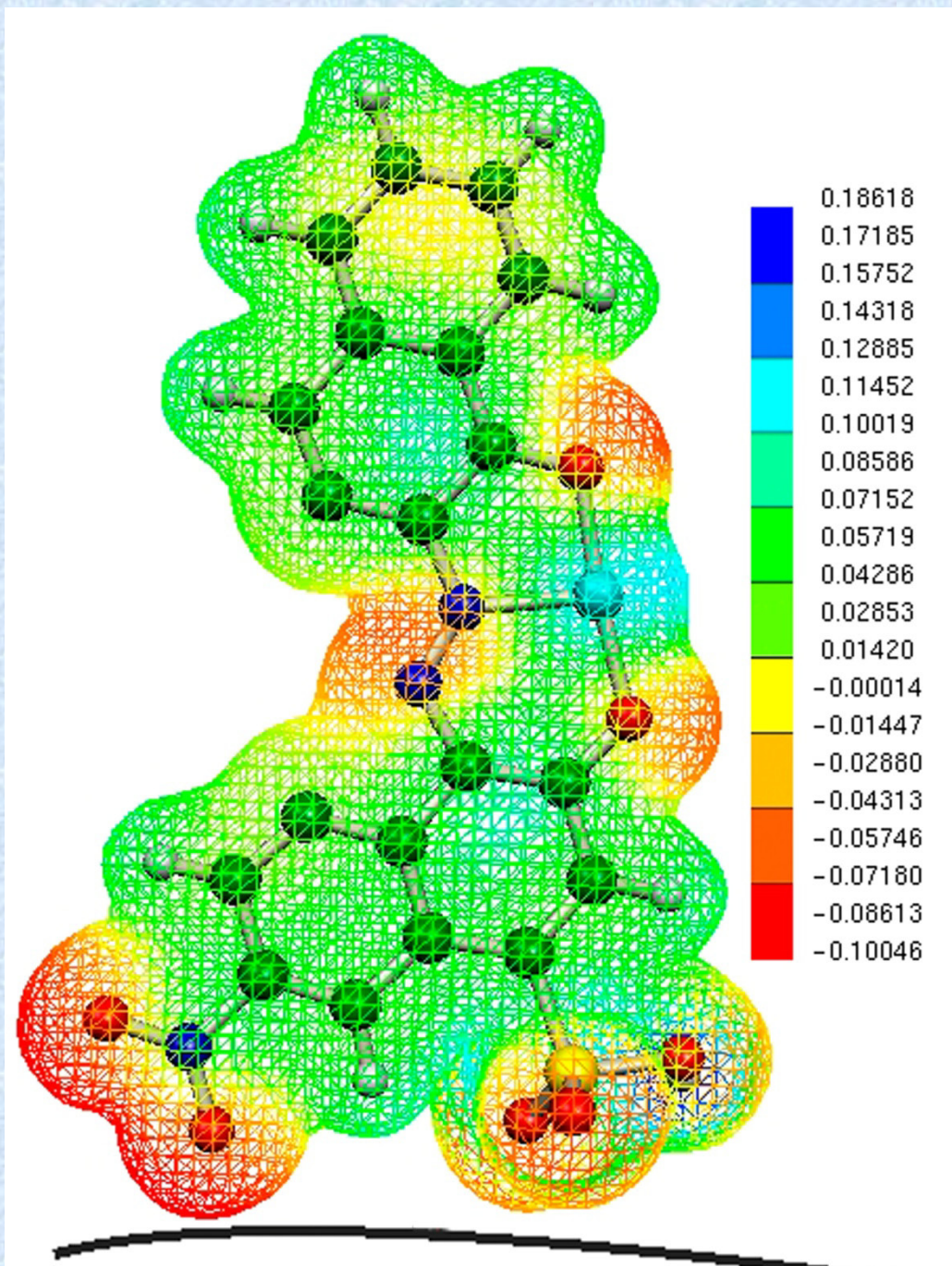
Each EBT-metal complex SERS spectrum shows a characteristic spectral fingerprint, permitting thus discrimination between EBT-metal ion complexes.