SERS, IR and DFT investigations of some metal-chelating compounds

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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 (ErBT) and Calcon molecules and its complexes with Zn(II), Cu(II), Fe(III), Mn(II) and Pb(II). Thus, IR and SERS spectra of ErBT and Calcon, as well as the SERS spectrum of the Zn(II), Cu(II), Fe(III), Mn(II) and Pb(II) complex of ErBT and Calcon, 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. ErBT and Calcon complexes with Zn(II), Cu(II), Fe(III), Mn(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, SERS, DFT, Calcon, Eriochrome Black T(ErBT).

Experimental techniques

FT-IR

powder samples, room temperature,
Bruker Equinox 55 FT-IR spectrometer, ZnSe ATR, DTGS detector

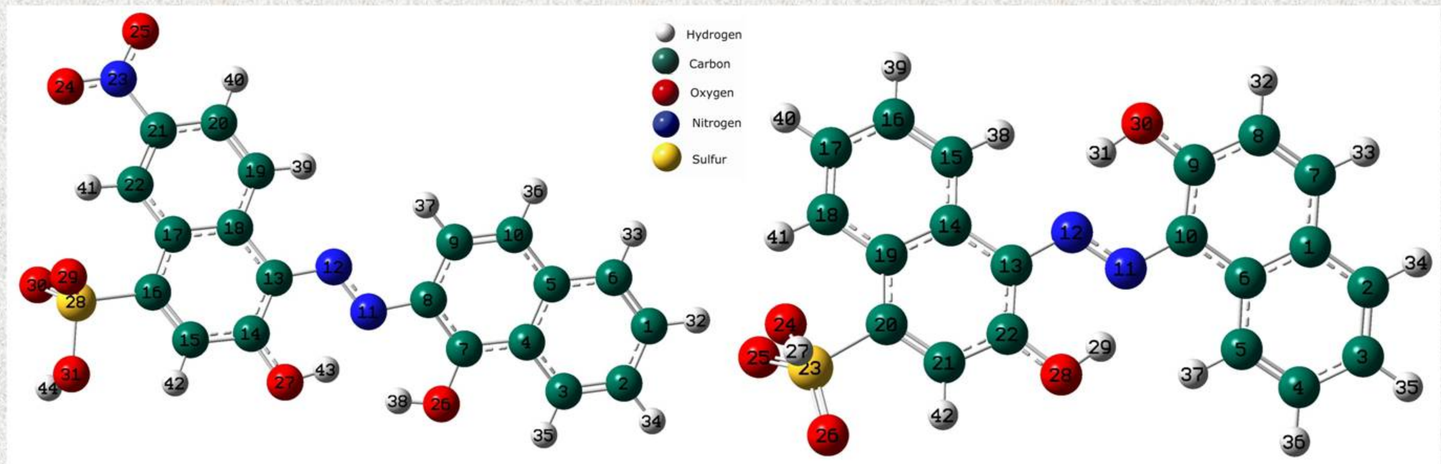
SERS

Advantage 532 spectrometer (DeltaNu USA). 532 nm frequency doubled NdYAG laser, 40 mW, resolution ~8 cm^{-1}. For SERS measurements 50 µl of analyte were added to 0.5 ml silver colloid. The silver colloidal SERS substrate, was prepared by reducing Ag+ with hydroxylamine. Briefly, 0.017g silver nitrate were solved in 90 ml distilled water. In a separate recipient, 0.011 g of hydroxylamine hydrochloride were solved in 10 ml water, followed by the addition of 0.1 ml sodium hydroxide solution, 2 mol/l (v). The hydroxylamine / sodium hydroxide solution was then added rapidly to the silver nitrate solution under vigorous stirring. After a few seconds a grey brown colloidal solution resulted, with pH value 9, and was further stirred for 10 minutes.

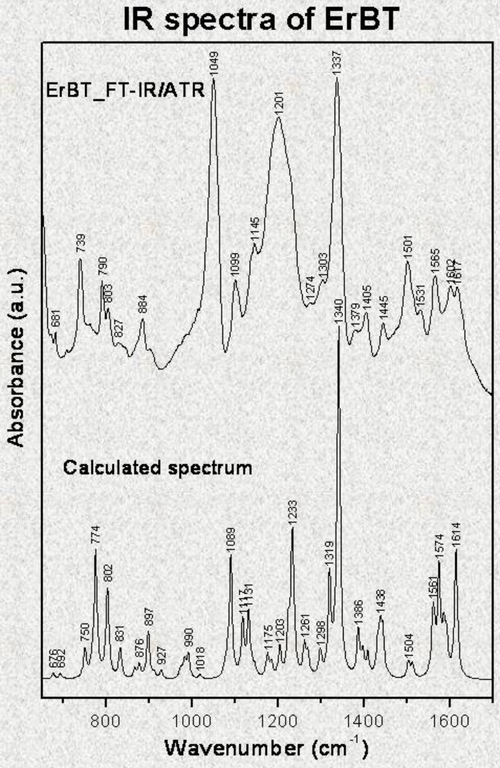
Computational methods

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

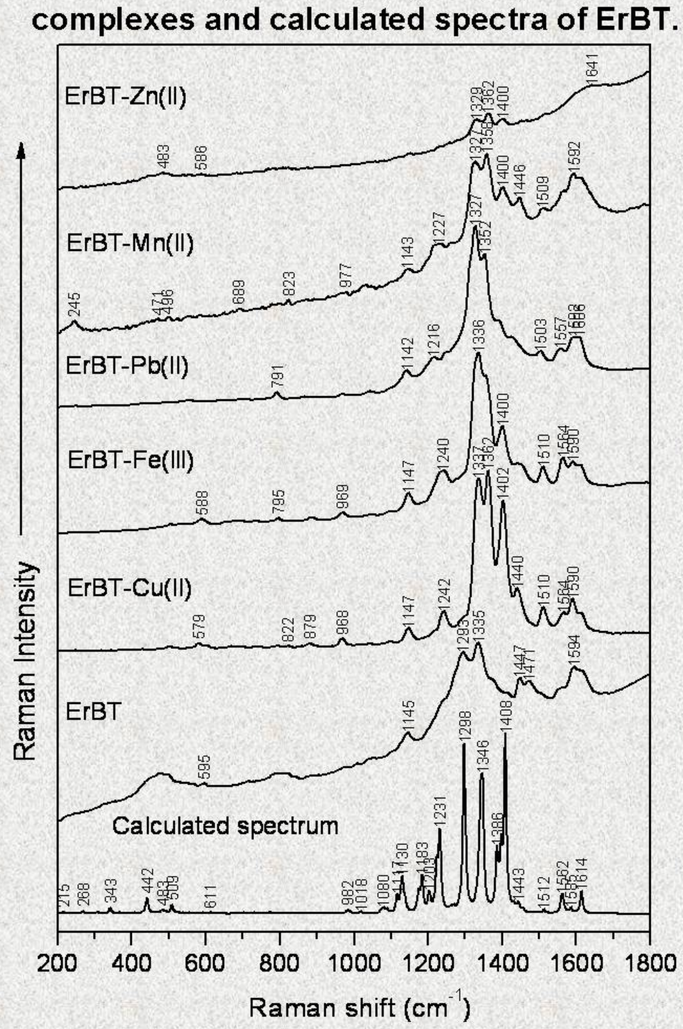
Chemical structure of ErBT (left) and Calcon (right) with atom numbering scheme.



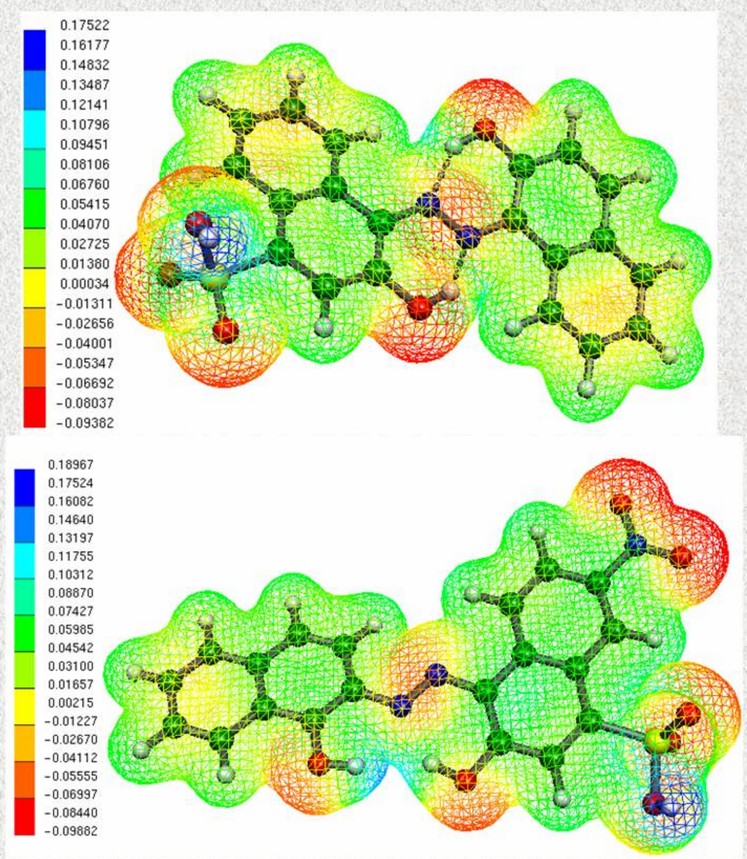
IR spectra of ErBT



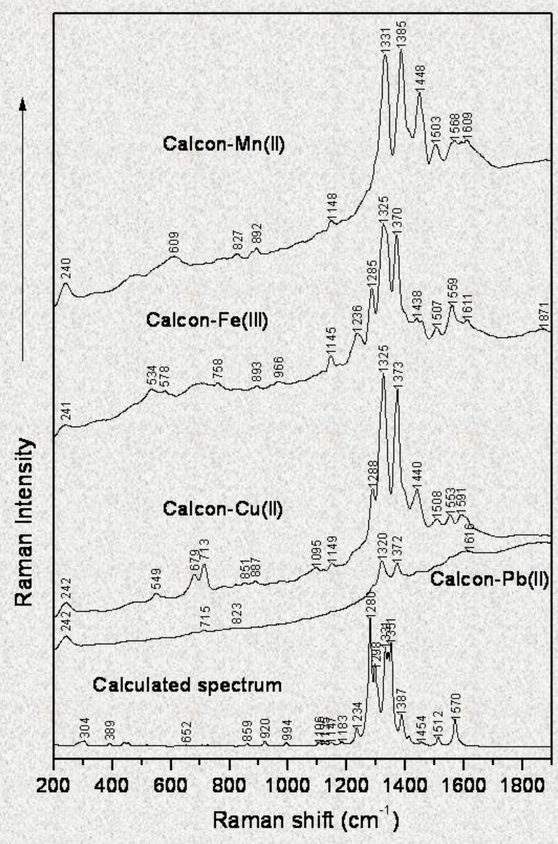
SERS spectra of ErBT, ErBT- Cu(II), Fe(III), Pb(II), Mn(II), Zn(II) complexes and calculated spectra of ErBT.



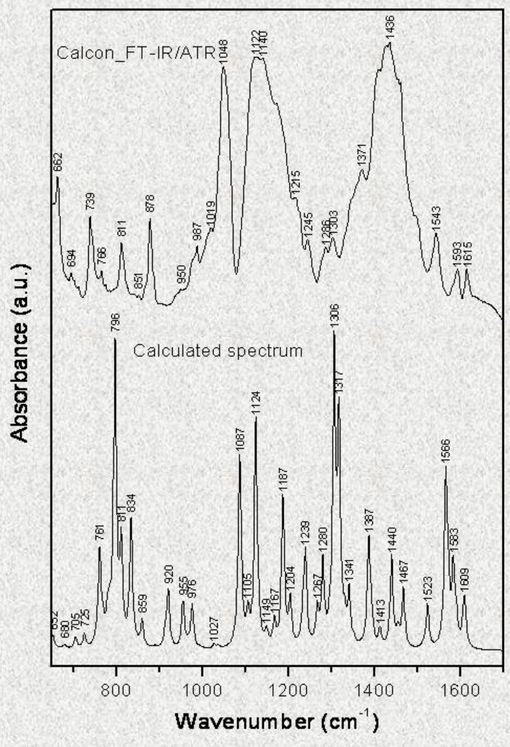
B3LYP/6-31G(d) calculated 3D electrostatic potential contour map of ErBT (top) and Calcon (bottom), in atomic units.



SERS spectra of Calcon, Calcon- Pb(II), Cu(II), Fe(III), Mn(II) complexes and calculated spectra of Calcon.



IR spectra of Calcon



Conclusions

ErBT and Calcon were investigated by experimental (FT-IR and SERS) techniques in conjunction with DFT quantum chemical calculations.

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

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

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

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