Vibrational spectroscopy analysis of the antraquinone pigment alizarin

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Alizarin (1,2-dihydroxyanthraquinone) (Fig.1), is extracted from the roots of madder, *Rubia tinctorum L.*, where it is the main coloring matter [1-3]. Madder has been cultivated as a source of dyestuff since antiquity in central Asia and Egypt to the 19th century when alizarin was synthetically reproduced [2,3]. As a dihydroxyquinone, alizarin belong to a prominent family of pharmaceutically active and biologically relevant chromophores [1].

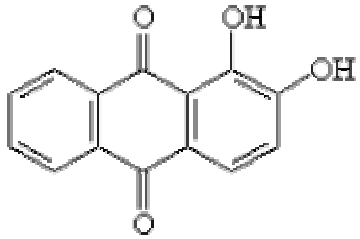

Fig.1: The structure of alizarin.

Alizarin is highly fluorescent and this property seriously limit the application of Raman spectroscopy (RS) to carry out a structural study and detect this molecule in plant or art samples [1, 4]. However, the Fourier transform-RS can be applied since the near-infrared excitation lines lie far from the absorption region of alizarin. The surface enhanced-RS (SERS) technique also makes the fluorescence quenching possible. It is performed by using of rough metal surfaces to enhance the Raman emission [1, 4].

The SERS spectra were collected from methanol solution of alizarin at the concentration of 10^{-5}M on rough Ag electrode with the wavelength excitation of 488 nm, 647 nm and 514.5 nm. Dependent on the excitation line the SERS or SERRS (surface-enhanced resonance Raman scattering) spectra of alizarin were observed. The FTRS spectra of alizarin as well as its complexes with Ag(I), Fe(III), Cr(III) metal ions in the solid state were also recorded. Additionally, alizarin was investigated directly in the roots of *Rubia tinctorum L.* To avoid the fluorescence, the radiation of 1064 nm was used for an excitation. As a complementary method for the investigation of alizarin structure and its interaction with metals FT-IR-ATR spectroscopy was applied. Experimental data were compared with theoretical study of alizarin molecular structure in order to support the assignment of vibrational bands. A quantum-chemical calculations of geometry optimization and vibrational frequencies were performed at DFT level with at least 6-31G** basis set.

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