Interpretation of Vibrational Spectra of DNA Fragments Interacting with Metal Ions

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Metal ions play an important role in structure and in vivo functioning of nucleic acids. They can stabilize or destabilize native double-helical DNA, participate in replication and transcription as well as metallo-enzymatic and some metabolic processes, mutagenesis, carcinogenesis, and DNA packing in a living cell [1]. Therefore, the interaction with metal ions has been widely studied by a number of techniques, including vibrational spectroscopy [2].

Traditionally, infrared (IR) and Raman vibrational spectra were used for investigating nucleic acid secondary structure. However, recent development of chiral vibrational methods, such as vibrational circular dichroism (VCD) and Raman optical activity (ROA), significantly broadened the structural information, which could be obtained from these experiments. Additionally, due to advances in computer technologies and quantum chemistry tools, it became possible to apply high level calculations to relatively large molecular systems, allowing reasonably accurate simulations and reliable interpretations of the vibrational spectra [3]. However, systems with metals are difficult to model due to the relativistic and spin effects, and the weak metal-DNA bond.

Therefore, we calibrate the methodology on both theoretical and experimental IR analyses of model DNA fragments interacting with metal ions. Complexes of one of the main DNA building blocks, deoxyguanosine monophosphate (dGMP), with various metal ions, such as Cu, Cd, Zn, Ni, Ca, Mg and Na are studied. Owing to the theoretical computations most of the spectral features observed experimentally could be assigned to simulated spectra and explained. In many cases a correlation between the spectral changes occurring upon the dGMP interaction with the metal ions and the geometry of the complexes could be established. Differences in the interactions of alkaline, alkaline earth and transition metal ions with several distinct binding sites of dGMP are analysed.

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[3] P. Bour, V. Andrushchenko, M. Kabelac, V. Maharaj, H. Wieser, J. Phys. Chem. B 109 (2005) 20579-20587.