Synthetic Research Report

on project achievement in the period December 16th, 2015 - September 30th, 2016

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In this work, we present an ultrasensitive Raman (surface - enhanced Raman spectroscopy, SERS) spectroscopic study, based on the full widths at half-maximum and on the corresponding global relaxation times, characteristic to molecular subgroups of different types of genomic DNAs from plant species. The dependence of dynamical parameters on the structure of DNA molecular subgroups and also on the source of the investigated nucleic acid has been identified.

Particularly, SERS spectra of genomic DNA molecules isolated from leaf tissues of two plants species, obtained on a mixture silver colloid-graphene, at different pH values were registered. In these cases, molecular relaxation processes for different vibrational modes of nucleic acids were investigated. Also, spectra-structure correlations, corresponding to the SERS profiles for which dynamical parameters were identified, were established.

Besides, we report an UV resonance Raman spectroscopic (UVRR) study on double-stranded and single-stranded DNA oligomers dynamics. Particularly, investigation of subpicosecond dynamical changes induced in a natural DNA recognition site (LacDNA), in the presence and absence of some divalent metal ions, at two pH values, respectively, providing data about changes in the half bandwidths and in the global relaxation times of LacDNA subgroups UVRR vibrations, is of interest.

Also, 2’ - deoxyadenosine - 5’ - monophosphate (dAMP) compound was investigated from the molecular dynamics point of view, as a function of its concentration in aqueous solution, by using UV resonance Raman spectroscopy.

We have demonstrated, that the ultrasensitive Raman spectroscopy (surface - enhanced Raman spectroscopy and UV resonance Raman spectroscopy) represents

useful methods for monitoring the (sub)picosecond dynamics of DNA molecular subgroups, in the case of relaxation processes which take place in the proximity of a metallic surface or in solution, respectively.

In the case of surface dynamics and solution dynamics, respectively, we can suppose for the investigated DNA molecules, that the dominant relaxation mechanism is the vibrational one. The values of the global relaxation time suggest also the existence of a vibrational relaxation time, because the reorientational movement is much more slower for nucleic acids molecules.

We have found experimentally, that the surface dynamics of molecular subgroups of *in vitro* - grown plant genomic DNA includes, in some cases, rapid relaxation processes. Reduced dimensionality and the suppression of rotational degrees of freedom, upon the interaction of the molecule with the metallic surface are mainly responsible for this experimental observation.

Besides, theoretical aspects related with the molecular dynamics, characterizing some DNA constituents in the proximity of a metallic surface are discussed.

Our theoretical studies indicate, that the translation of DNA bases on a metallic surface (Ag) is expected to be an important component of the molecular dynamics at room temperature. It is also natural to assume that this will lead to relaxation mechanisms completely different to those present in solution. A second feature of our theoretical analysis regarding these systems is that, similar energetic landscapes can occur for the DNA bases paired in a nucleic acid chain, respectively. Indeed, for the A and T, the dynamics on the surface is expected to take place along lines placed at 60 degrees in our representation, while for the C and G is suggested a dynamics along vertical lines.

Also, the vibrational properties of DNA bases adsorbed on metallic surfaces were investigated by ab-initio molecular dynamics. By using a Verlet type algorithm and the 300 K temperature, the densities of the vibrational states of the adsorbed molecules, at room temperature were put into evidence.

Results clearly indicate the vibrational bands with maximum intensity, in the case of each molecule - surface complex, in the spectral range 0 - 3500 cm^{-1}. These could be used as a data base for experimental data assignation, in the case of adsorbed DNA

bases on gold surfaces.

As perspectives for new developments within the framework of approached thematic area in this project, we identify the investigation of some DNA - exogenous agents interactions (of physical and chemical nature, respectively) and also using a new SERS detection platform, within ultrasensitive spectroscopic studies of DNA molecules.

In addition to this synthetic research report, full length research report (55 pages) is submitted to the beneficiary.

Project manager,

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