

Dynamics of ordered counterions in the ion-hydrate shell of DNA double helix

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The DNA double helix is known to be formed in presence of water molecules and metal counterions. Positively charged counterions neutralize the negatively charged phosphate groups of the double helix backbone reducing the electrostatic repulsion. The counterions and water molecules form the ion-hydrate shell of DNA stabilizing the structure of the double helix. The localization of counterions in different compartments of the double helix (grooves of the double helix, phosphate groups) determines physical properties of the macromolecule that are responsible for the mechanisms of DNA biological functioning. Due to the regular structure of the double helix the counterions tethered to DNA may form an ordered system around macromolecule. The dynamics of such system should be modulated by the macromolecule structure and dynamics. In the present work the dynamics of ordered metal counterions around DNA double helix has been studied at different timescales of the system.

Considering the structure of double helix with counterions tethered to the phosphates as the lattice of ionic type (ion-phosphate lattice), the dynamics of DNA has been studied using the developed phenomenological model [1-4]. As the result the frequencies and Raman intensities of the vibrational modes for right-handed *B*- and *D*-, *A*-forms, and left-handed *Z*-form of the double helix with Na^+ , K^+ , Rb^+ , Cs^+ , and Mg^{2+} counterions and hydrogen peroxide molecule were calculated. The modes of ion-phosphate vibrations have been found in the low-frequency spectra range ($<200 \text{ cm}^{-1}$). In the case of alkali metals the frequencies of ion-phosphate vibrations decrease from 180 to 100 cm^{-1} , and Raman intensities increase as the counterion mass increases. In the case of *Z*-DNA the mode of ion-phosphate vibrations (near 150 cm^{-1}) appear due to the motions of Mg^{2+} counterions in the minor groove of the double helix. The calculations of the spectra for DNA in complex with Na^+ counterions and H_2O_2 molecule in the hydration shell of the ion show the low-frequency shift of the modes of ion-phosphate vibrations [5,6]. The obtained results give the interpretation of the experimental low-frequency Raman spectra of DNA.

To study the dynamics of ordered counterions in different interaction sites of the double helix the classical molecular dynamics calculations have been performed for the DNA fragment d(CGCGAATTCGCG) in water solution with the metal ions Na^+ , K^+ , Cs^+ and Mg^{2+} [7]. The computer simulations were performed using NAMD software package [8]. The results show that the Na^+ counterions interact with the phosphate groups directly from outside of the double helix and via water molecules at the top edge of DNA minor groove. The potassium ions interact with the phosphate groups (directly and via water molecules) and with the atoms of nucleic bases from the minor groove of the double helix. The cesium ions penetrate deeply inside the minor groove and directly bond to the atoms of nucleic bases. Cs^+ counterions form a structured system of charges in the DNA minor groove that may be considered as a specific case of ionic lattice. The magnesium ions interact with the atoms of DNA only via water molecules of the hydration shell. The considered ions in the major groove of the double helix do not have a defined interaction site and are not ordered.

- [1] Perepelytsya S.M., Volkov S.N. *Eur. Phys. J. E.* 24, 261 (2007).
- [2] Perepelytsya S.M., Volkov S.N. *Eur. Phys. J. E.* 31, 201 (2010).
- [3] Perepelytsya S.M., Volkov S.N. *J. Molec. Liq.* 164, 113 (2011).
- [4] Perepelytsya S.M., Volkov S.N. *J. Phys.: Conf. Ser.* 438, 012013 (2013).
- [5] Piatnytskyi D.V., Zdorevskyyi O.O., Perepelytsya S.M., Volkov S.N., *Eur. Phys. J. D.* 69,255 (2015).
- [6] Piatnytskyi D.V., Zdorevskyyi O.O., Perepelytsya S.M., Volkov S.N., *Ukr.J. Phys.* 61,219 (2016).
- [7] Liubysh O.O., Vlasiuk A.O., Perepelytsya S.M. *Ukr. J. Phys.* 60, 433 (2015).
- [8] Phillips J.C. *et al. J. Comp. Chem.* 26, 1781 (2005).