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Conformational vibrations of ionic lattice in DNA
Manifestation in the low-frequency Raman spectra

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ABSTRACT

Conformational vibrations of DNA with counterions neutralizing the phosphate groups of the double helix backbone are studied within the framework of phenomenological approach developed. The counterions are considered to be localized in two possible positions: near the phosphate groups of the double helix backbone, and between the phosphate groups in DNA minor groove. For the description of DNA conformational vibrations the structure of counterions tethered to the phosphate groups of double helix backbone is represented as an ionic lattice. Using the developed approach the frequencies and Raman intensities for DNA with Na^+, Cs^+, and Mg^{2+} counterions in different positions are calculated. As a result the manifestations of influence of counterion type and their position on the low-frequency Raman spectra ($<200\ cm^{-1}$) are determined. The obtained spectrum of DNA with Na^+ counterions near phosphate group is characterized by intensive modes of internal conformational vibrations of the double helix (from 60 to 110 cm^{-1}), while modes of ion-phosphate vibrations (near 170 cm^{-1}) have low intensity. In case of DNA with Cs^+ counterions near phosphate groups the mode of ion-phosphate vibrations (near 115 cm^{-1}) is the most prominent, with other modes of DNA conformational vibrations being low-intensive. The spectra of DNA with Mg^{2+} counterions between phosphate groups are described by the high intensity of the internal modes of the double helix (from 60 to 120 cm^{-1}) that was found to be essentially dependent on the minor groove width. The obtained low-frequency Raman spectra provide a way to determine the type of counterions and its position with respect to phosphate groups.

1. Introduction

The DNA double helix is a polyelectrolyte macromolecule with a negatively charged phosphate backbone. Under the natural conditions the phosphate groups are neutralized by metal counterions that form an ion-hydrate shell around the double helix [1]. The concentration of counterions, their type and position with respect to the DNA phosphate groups determine the mechanical properties of macromolecule, such as, twisting and bending of the double helix, and interaction of DNA with biologically active compounds [2–6]. The development of methods for determination of the type of counterions and their position in DNA is of paramount importance for understanding the mechanisms of counterion influence on DNA biological functioning.

For solid DNA samples the position of counterions may be determined by X-ray and NMR methods [7–13]. In the case of water solutions only the distribution of counterions in DNA ion-hydrate shell may be determined within the framework of these methods [14–17]. In this respect the methods of vibrational spectroscopy are very effective [2,18–22]. In order to determine the local contacts of counterions with the atoms of DNA structural elements the frequency modes of atom vibrations on chemical bonds are used. The influence of counterions on the conformational dynamics of the whole double helix should be the most prominent in low-frequency range of vibrational spectra ($<200\ cm^{-1}$), where the vibrations of DNA structural elements (conformational vibrations) occur.

The low-frequency spectra of DNA is characterized by modes of transverse vibrations of the masses of structural elements of nucleosides, phosphates, and bases [23–26]. The modes near 20 cm^{-1} characterize vibrations of the double helix backbone, and the vibrations within 50–120 cm^{-1} concern to the H-bond stretching in the base pairs and intranucleoside mobility. The modes of this spectra range should be interdependent with the vibrations of counterions with respect to the phosphate groups (ion-phosphate vibrations). The previous study of counterion influence on conformational dynamics of DNA [27–30] has shown that counterions affect the frequencies of internal vibrations of the double helix, but the mode of ion-phosphate vibrations have not been determined. The determination of interrelation between ion-phosphate vibrations and internal

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dynamics of the double helix may provide a way to determine the counterion type and their position in DNA double helix by vibrational spectra.

In our previous works the approach to the description of the ion-phosphate vibrations has been developed [31–34]. To obtain frequencies of vibrational modes and their Raman intensities the structure of DNA double helix with counterions is considered as an ionic lattice. The calculated frequencies of ion-phosphate vibrations for DNA with Na^+, K^+, Rb^+, and Cs^+ counterions are localized within the low-frequency spectra range from 90 to 180 cm^{-1} and decrease as counterion mass increases which agrees with the experimental data [27,35–40]. Thus, our study has shown that counterion type influences essentially the low-frequency spectra of DNA. At the same time, the influence of counterion position in the double helix on the conformational vibrations of DNA has not been studied yet.

The goal of the present work is to study conformational vibrations of the double helix with counterions and to find features of DNA low-frequency Raman spectra determining the position of counterions with respect to the phosphate groups. To calculate the frequencies of vibrations the model for the conformational vibrations of DNA with counterions [31,32] is extended for the case of counterions inside the double helix minor groove. The intensities of the modes of DNA conformational vibrations are calculated within the framework of semiclassical approach for DNA [33,34]. Using the calculated frequencies and intensities the low-frequency Raman spectra for DNA with Na^+, Cs^+, and Mg^{2+} counterions are plotted. The obtained spectra show that both counterion type and counterion localization essentially influence the spectra shape.

2. Modeling DNA ion-phosphate lattice dynamics

The experimental data [7–13] and molecular dynamics simulations [41–48] show that the counterions may be localized with respect to the phosphate groups in different ways. Under the natural conditions the counterions are usually localized outside the double helix, because the chemical bonds between phosphorus and free oxygen atoms in the double helix are directed outward from the double helix (Fig. 1a). In this case one counterion neutralizes one phosphate group (single-strand neutralization).

Under certain conditions when the minor groove of DNA macromolecule is narrow (the case of an overtwisted or untwisted double helix) the counterions may neutralize the phosphate groups of different strands of the double helix [8,11,41–43]. In the solution the overtwisted (*D*-form) and untwisted (*Z*-form) double helixes may be realized under the influence of counterion concentration [1,2,5,6]. The helical twist of DNA may be also changed essentially during the processes of biological functioning. In the case of untwisted double helix (Fig. 1b) the counterion may be coordinated by the phosphates of the same nucleotide pair (cross-strand neutralization), and in the case of overtwisted double helix (Fig. 1c) the counterion may be coordinated by the phosphates of the neighboring nucleotide pairs (longitudinal neutralization).

The number of phosphate groups that are neutralized by counterions increases as the concentration of counterions in the solution grows. Thus, under a certain concentration the regular structure of counterions and phosphate groups should be formed. In the present work such a structure is considered as an ion-phosphate lattice. According to possible cases of counterion localization with respect to the phosphate groups three types of DNA ion-phosphate lattices may be considered. The first is a lattice with counterions in single-stranded position (Fig. 1a), the second is a lattice with cross-stranded counterions (Fig. 1b), and the third is a lattice with longitudinal counterions (Fig. 1c). Herein, the conformational dynamics of these lattices is studied.

To determine the frequencies and amplitudes of conformational vibrations for DNA with counterions we extend our model [31,32] developed on the basis of an approach to conformational vibrations of the double helix [23–26]. Within the framework of this approach the DNA macromolecule is represented as a double chain of phosphate group masses m_0 ($PO_4+C_{5'}$) and masses of nucleosides m. The nucleosides rotate as physical pendulums with respect to the phosphate groups in the plane of the nucleotide pair. The physical pendulums are characterized by reduced length l. The nucleosides of different chains are paired by H-bonds (Fig. 2). The motions of structural elements of the monomer link are considered in the plane orthogonal to the helical axis (transverse vibrations). The longitudinal vibrations of the macromolecule atomic groups have much higher frequencies [23–26] and are beyond the scope of this work.

The counterions are model as masses m_a tethered to the phosphate groups. In the case of single-strand neutralization one counterion neutralizes one phosphate group from the outside of the macromolecule (Fig. 2a). The counterions in cross-stranded (Fig. 2b) and longitudinal (Fig. 2c) positions are localized between phosphate groups in the minor groove of the double helix. In the case of cross-strand neutralization the counterion is tethered to the phosphate groups of the same monomer link, and in the case of longitudinal neutralization it is tethered to the phosphate groups of neighboring monomer links.

The displacements of nucleosides and phosphate groups in the DNA monomer link are described by coordinates X_{n1}, X_{n2}, Y_{n1}, and Y_{n2}. The coordinates θ_{n1} and θ_2 describe the deviations of pendulum-nucleosides from their equilibrium position in the plane of complementary DNA pair (angle θ_0). The vibrations of deoxyribose and base with respect to each other, inside the nucleoside (intranucleoside vibrations), are described

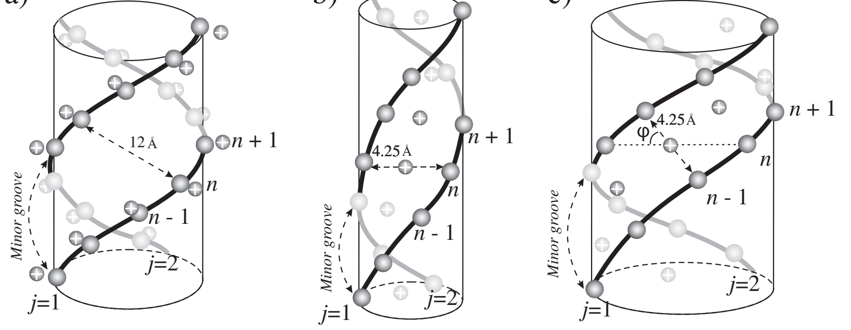

Fig. 1. Schemes of counterion localization with respect to the phosphate groups in DNA ion-phosphate lattice. (a) Single-stranded position of counterions. Width of the minor grove is shown. (b) Cross-stranded position of counterions. Ion-phosphate distance is shown. (c) Longitudinal position of counterions. Ion-phosphate distance is shown. φ is angle determining direction of ion-phosphate bond in the minor groove.