Vibrations of ordered counterions around left- and right-handed DNA double helixes

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Abstract. The vibrations of ordered counterions around right- and left-handed DNA double helix are studied. To determine the modes of DNA conformational vibrations the structure of the double helix with counterions is considered as ionic lattice (ion-phosphate lattice). Using the developed approach the frequencies and Raman intensities for right-handed B-form and left-handed Z-form of the double helix with Na\(^+\), K\(^+\), Rb\(^+\), Cs\(^+\), and Mg\(^{2+}\) counterions are calculated. The obtained frequencies of vibrations of internal structure elements of the double helix (<100 cm\(^{-1}\)) weakly depend on counterion type. In contrast, the vibrations of the ion-phosphate lattice are determined by counterion mass and charge. The frequencies of ion-phosphate vibrations of alkali metal counterions decrease from 180 to 100 cm\(^{-1}\), while their Raman intensities increase as the counterion mass increases for both B- and Z-DNA. In case of Z-DNA new mode of ion-phosphate vibrations near 150 cm\(^{-1}\) is found. This mode is characterized by vibrations of Mg\(^{2+}\) counterions with respect to the phosphates of different strands of the double helix. Our results explain the experimental Raman spectra of Z-DNA.

1. Introduction
Under the natural conditions DNA forms the double helix consisted of negatively charged phosphate groups outside and nucleic bases inside the macromolecule. For the stability of the double helix the DNA phosphate groups must be neutralized by some positively charged ions of the solution (counterions) [1]. In water solution with monovalent metal counterions DNA double helix is usually in the right-handed B-form [2, 3], but increasing the concentration of counterions it may take the left-handed Z-form [1]. Z-DNA has a significant importance for many processes of DNA biological functioning [4]. The counterion concentration and type determine the structure and dynamics of the double helix in many respects [5, 6, 7, 8], but in the same time the role of counterions in conformational transformations of the double helix is not completely understood.

In solid samples of DNA the counterions occupy defined positions with respect to macromolecule atomic groups [9, 10, 11]. The monovalent counterions are usually localized near the oxygen atoms of phosphate groups from outside of the macromolecule [9, 10], while the counterions of higher charge may be also localized between phosphate groups of different DNA strands or bind to the nucleic bases [9, 11]. In solution the counterions are mobile, and together with water molecules they form the dynamical ion-hydrate shell around DNA macromolecule [1, 2, 8]. In the experiments for DNA solutions the counterions of the ion-hydrate shell are observed as a cloud around the double helix [12, 13, 14, 15]. The existence of counterion
cloud around DNA has been predicted within the framework of counterion condensation theory and numerical calculations of Poisson-Boltzmann equation [16, 17, 18, 19]. Increasing the concentration of counterions this cloud shrinks and counterions become closer to the surface of the double helix [12, 13, 14, 15]. Under such conditions the phosphate groups of DNA with counterions should form the regular structure along the double helix that may be considered as the lattice of ionic type (ion-phosphate lattice).

The molecular dynamics simulations of DNA with counterions show that the lifetime of counterion-phosphate complex is about 1 ns [20, 21, 22, 23, 24]. This time is rather long comparing to the period of molecular vibrations, therefore the dynamics of DNA ion-phosphate lattice should be characterized by counterion vibrations with respect to the phosphate groups (ion-phosphate vibrations). In the same time, the dynamics of the ion-phosphate lattice should be the part of conformational dynamics of DNA double helix, and its vibrations should be coupled with the internal dynamics of the double helix. Thus the determination of vibrational modes of the ion-phosphate lattice is of paramount importance for the understanding of counterion role for DNA structure and dynamics.

The modes of DNA ion-phosphate vibrations should be localized in the low-frequency spectra range (<200 cm$^{-1}$) the same as modes of ion vibrations in case of ionic crystals and electrolyte solutions [25, 26]. This spectra range is known to be characterized by the modes of DNA conformational vibrations describing the vibrations of atomic groups of the double helix (phosphates, nucleosides and nucleic bases) [27, 28, 29, 30, 31, 32, 33]. In our previous works [34, 35, 36, 37, 38, 39] the model of conformational vibrations of the right-handed DNA double helix with counterions has been developed basing on the approach [40, 41, 42, 43]. As the result the frequencies of ion-phosphate vibrations for DNA with Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ counterions are determined. The obtained frequency values of DNA ion-phosphate vibrations decrease from 180 to 100 cm$^{-1}$ as counterion mass increases that agree with the experimental data [28, 32]. The vibrations of heavy counterions (Cs$^+$) influence the internal dynamics of the double helix, while light counterions (Na$^+$) play the role of counteractive charges for the phosphate groups and do not disturb the motions in nucleotide pairs. In contrast, the Raman intensities of the ion-phosphate modes increase as the counterion mass increases [36, 37] that agree with the experimental data [44].

The experimental data for the left-handed DNA double helix show that in the low-frequency spectrum new mode near 150 cm$^{-1}$ is observed [33]. This mode may characterize the specific vibrations of counterions and atomic groups of DNA. To determine the origin of this mode the approach [34, 35, 36, 37, 38, 39] should be extended for the case of the ion-phosphate lattice of DNA in the left-handed form of the double helix.

The goal of the present work is to find the modes of ion-phosphate vibrations of Z-DNA and compare them with the ion-phosphate modes of right-handed DNA double helix. To solve this problem in section 2 the model of conformational vibrations of Z-DNA with counterions is introduced. In section 3 frequencies of Z-DNA are calculated and the Raman spectra are for the right- and left-handed DNA with counterions are analyzed. As the result the specific modes of Z-DNA ion-phosphate vibrations are determined. The calculated Raman spectrum of Z-DNA agree with the experimental data.

2. Models of conformational vibrations of DNA ion-phosphate lattices

The structure of DNA ion-phosphate lattice depends on the double helix form and counterion type. According to the experimental data [9] and molecular dynamics simulations [21, 22, 20, 23] in case of the right-handed double helix the monovalent metal ions usually neutralize the negatively charged phosphate groups, localizing from the outside of the double helix (single-stranded position of counterion). The left-handed double helix has significantly different structure and for its stabilization the both monovalent and bivalent counterions are necessary.
The structure of Z-DNA is favorable for the localization of counterions outside of the double helix and inside of its minor groove. The counterions inside the minor groove of Z-DNA neutralize the phosphate groups of different strands along the line orthogonal to the helical axis (cross-stranded neutralization). The models of DNA ion-phosphate lattice in case of the right- and left-handed DNA double helix are shown in the figure 1a.

The dynamics of DNA ion-phosphate lattice we describe in framework of phenomenological approach for conformational vibrations of the double helix [40, 41, 42], which in the previous works has been extended for consideration of counterion vibrations in the right-handed DNA double helix [34, 35, 38, 39]. In the present work the developed model of the ion-phosphate lattice dynamics is improved for the description of the left-handed double helix.

The model of the ion-phosphate lattice dynamics presents the DNA macromolecule as the chain of monomer links. In case of the right-handed double helix the monomer link consists of nucleotide pairs, while in case of the left-handed double helix it consists of two nucleotide pairs (Figure 1b). The nucleotides are modelled as masses of phosphate groups $m_0$ (PO$_4$+C$_5'$) and masses of nucleosides $m$. The nucleosides rotate as the physical pendulums with respect to the phosphate groups in plane of nucleotide pair. The physical pendulums are characterized by reduced length $l$. The nucleosides of different chains are paired by H-bonds (Figure 2). The counterions are modelled as charges tethered to the phosphate groups. In case of single-strand neutralization one counterion with the mass $m_a$ is tethered to one phosphate group from the

Figure 1. DNA with counterions. (a) Ion-phosphate lattices of the right- and left-handed DNA double helix. (b) Chain of monomer links in case of right- and left-handed double helix. The rectangles symbolize the nucleotide pairs.
Figure 2. Monomer links of the right-handed (a) and left-handed (b) double helixes. $l$ is reduced length of pendulum-nucleoside; $\theta_0$ is equilibrium angle; $m$, $m_0$, and $m_a$ are masses of nucleosides, phosphate groups, and counterions, respectively; $X$, $Y$, $\theta$, $\rho$, and $\xi$ are vibrational coordinates of the model (see text). The arrows indicate positive directions of displacements; $XYZ$ and $xyz$ are the reference frames connected with the monomer link and nucleoside, respectively.

Outside of macromolecule. The counterions in cross-stranded positions with the mass $M_a$ are localized between phosphate groups in the minor groove of the double helix (Figure 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 [40, 41, 42] and are beyond the scope of this work.

The displacements of nucleosides and phosphate groups in DNA monomer link are described by coordinates $X$ and $Y$. The coordinates $\theta$ describe the deviations of pendulum-nucleosides from their equilibrium position in the plane of complementary DNA pair (angle $\theta_0$). The vibrations of deoxyribose and base with respect to each other, inside the nucleoside (intraneucleoside vibrations), are described by changes of pendulum lengths $\rho$. The vibrations of counterions in single-stranded positions are described by coordinates $\xi$. For description of vibrations of a counterion between phosphate groups the coordinate $Y_a$ is used. The vibrational coordinates of the model and the positive directions of displacements are showed on Figure 2.

Within the framework of introduced model of the dynamics of DNA ion-phosphate lattice the energy of vibrations of double helix structural elements may be written as follows:

$$E = \sum_n \left( K_n + U_n + U_{n,n-1} \right),$$  

where $K_n$ and $U_n$ are the kinetic and potential energies of the monomer link, $U_{n,n-1}$ is the potential energy of interaction along the chain.

Let us consider the kinetic and potential energies of the monomer link as a sum of vibrational energy of DNA atomic groups and energy of counterion vibrations: $K_n + U_n = K_{0n} + U_{0n} + K_{an} + U_{an}$. In such a way the energy of vibrations of structural elements in monomer link $n$ of right-handed double helix may be written as follows:

$$K_{0n}^R = \frac{1}{2} \sum_j [M_j \dot{Y}_{nj}^2 + m_j (\dot{\theta}_{nj}^2 + \dot{\theta}_{nj} l_j^2 \dot{\theta}_{nj} + 2l_j \dot{\theta}_{nj} \dot{Y}_{nj} + 2b_j \dot{\theta}_{nj} \dot{Y}_{nj})],$$

$$U_{0n}^R = \frac{1}{2} \alpha \delta_n^2 + \frac{1}{2} \sum_j [\sigma \dot{\rho}_{nj}^2 + \beta \dot{\theta}_{nj}^2],$$
where \( l_j^s = l_j a_j; \) \( a_j = \sin \theta_{0j}; \) \( b_j = \cos \theta_{0j}; \) the index \( j = 1, 2 \) enumerates the chain of the double helix; the force constants \( \alpha, \sigma, \) and \( \beta \) describe H-bond stretching in base pairs, intranucleoside mobility, and rotation of nucleosides with respect to the backbone chain in base-pair plane, respectively. The variable \( \delta_n \) describes stretching of H-bonds in the base pairs (Fig. 1b): 

\[
\delta_n \approx l_1^s \theta_{n1} + l_2^s \theta_{n2} + Y_{n1} + Y_{n2} + b_1 \rho_{n1} + b_2 \rho_{n2}.
\]

Analogically, for the left-handed double helix:

\[
K_{0n}^L = \frac{1}{2} \sum_i^2 \sum_j^2 [M_{ij} \dot{Y}_{nij}^2 + m_{ij} (\dot{\rho}_{nij}^2 + l_1^j \dot{\theta}_{nij} + 2l_{sij} \dot{\theta}_{nij} \dot{Y}_{nij} + 2b_{ij} \dot{\rho}_{nij} \dot{Y}_{nij})],
\]

\[
U_{0n}^L = \frac{1}{2} \sum_i^2 \sum_j^2 [\alpha \dot{\theta}_{nij}^2 + \sum_j^2 (\sigma_{ij} \rho_{nij}^2 + \beta_{ij} \dot{\theta}_{nij})^2] + \sum_j^2 \gamma_1 \left[(\dot{\theta}_{n1j} - \dot{\theta}_{n2j})^2 + (\dot{\rho}_{n1j} - \dot{\rho}_{n2j})^2 \right] + g_2 (Y_{n1j} - Y_{n2j})^2.
\]

In the formulae (4) and (5) the index \( n \) enumerates dimers of macromolecule and the index \( i \) enumerates the nucleotide pairs in the dimers. The force constants \( g_1 \) and \( g_2 \) describe the interaction of nucleic bases and the interaction between phosphate groups in dimers.

The energy of counterion vibrations in case of the ion-phosphate lattice of the right-handed double helix may be written as:

\[
K_{an}^R = \frac{m_a}{2} \sum_j (\dot{\xi}_{nij}^2 + \dot{Y}_{nij}^2),
\]

\[
U_{an}^R = \frac{\gamma_1}{2} \sum_j \xi_{nij}^2.
\]

Analogically, for the left-handed double helix:

\[
K_{an}^L = \frac{M_a}{2} \dot{Y}_{an}^2 + \frac{m_a}{2} [(\dot{Y}_{n11} + \dot{\xi}_{n11})^2 + (\dot{Y}_{n22} + \dot{\xi}_{n22})^2],
\]

\[
U_{an}^L = \frac{\gamma_1}{2} (\xi_{n11}^2 + \xi_{n22}^2) + \frac{\gamma_2}{2} \left[(Y_{an} - Y_{n22})^2 + (Y_{an} + Y_{n11})^2 \right].
\]

In the formulae (7) and (9) the parameters \( \gamma_1 \) and \( \gamma_2 \) are the force constants for the counterions in single-stranded and cross-stranded positions, respectively. Note, the energy of vibrations for the ion-phosphate lattice of DNA in the right-handed form of the double helix may be obtained from (8) and (9) by putting parameters \( \gamma_2, g_1, \) and \( g_2 \) to zero and omitting the index of summation \( i \).

Accordingly to our approach \[34, 35\] we will consider the limited long-wave vibrational modes of the ion-phosphate lattice that are sufficient for interpretation of the experimental vibrational spectra. As known only long-range lattice vibrations interact with the electro-magnetic fields and manifest themselves in vibrational spectra \[25\]. In long-wave limit, when the wave vector leads to zero (\( \vec{k} \rightarrow 0 \)), the frequencies of optical types modes weakly depend on the \( \vec{k} \) value. From the point of the theory of the lattice vibrations such approximation is the same as the neglecting interaction along the chain. So, in the following consideration we will neglect by the interaction term: \( U_{n,n-1} \approx 0 \). Within the framework of this approximation the equations of motions may be written as follows:

\[
d \frac{\partial K_{0n}}{\partial \dot{q}_n} + d \frac{\partial K_{an}}{\partial \dot{q}_n} - \frac{\partial U_{0n}}{\partial q_n} - \frac{\partial U_{an}}{\partial q_n} = 0,
\]

where \( q_n \) denotes some vibrational coordinate in the monomer link of model (Figure 2). The equations of motions (10) may be solved using the substitution: \( q_n = \tilde{q}_n \exp(i \omega t) \), where \( \tilde{q}_n \) and
ω are amplitude and frequency for some coordinate of vibrations, respectively. The equations of motion (10) in explicit form are shown in Appendix for right- and left-handed double helix of DNA.

The Raman intensities for the modes of DNA conformational vibrations are calculated within the framework of phenomenological approach developed in our previous work [36, 37]. It is based on the valence-optic theory [45] and our model for the conformational vibrations of DNA with counterions [34, 35]. The analytical expression for some mode of DNA conformational vibrations is shown in Appendix.

To estimate the frequencies of conformational vibrations of B-DNA the force constants α = 85 kcal/mole Å^2, β = 40 kcal/mole, and σ = 43 kcal/mole Å^2 are taken from [40, 41, 42]. In case of Z-DNA the constant α is the same as in B-DNA, while the constants β and σ for guanosine (G) and cytosine (C) nucleosides are taken the same as in A- and B-forms, respectively. The difference of these constants for G and C appear due to the dimeric structure of the left-handed double helix. In case of A-DNA the constants β and σ have the following values 46 kcal/mole and 22 kcal/mole Å^2, respectively [40, 41, 42]. The constant of ion-phosphate vibrations γ^1 has been determined by us earlier for Na^+, K^+, Rb^+, and Cs^+ counterions, and it vary from 42 to 52 kcal/mole Å^2 depending on counterion type. The constant γ^2 = 62 kcal/mole Å^2 is taken for the case of Mg^{2+} counterions in cross-stranded position [39]. The magnesium counterion is considered with the hydration shell because the size of hydrated Mg^{2+} ion corresponds to the distances between phosphate groups of the left-handed double helix. The hydration shell of magnesium ion consists of 4 water molecules strongly bond to the ion [46]. The structure parameters of the model for Z-DNA is determined using the X-ray data (pdb code: 1dcg) [47]. Using such parameters the frequencies and amplitudes of Z-DNA conformational vibrations are estimated by the formulae (1) – (10).

3. Frequencies of DNA conformational vibrations

Using the developed approach the frequencies of right- and left-handed double helix with different alkali metal counterions are calculated. The right-handed double helix is considered in natural B-form of DNA with the alkali metal counterions in single-stranded position outside macromolecule. In case of left-handed double helix bivalent magnesium counterions are localized between phosphate groups of the DNA strands, and the monovalent alkali metal counterions are localized outside the double helix. The obtained frequency values for B- and Z-DNA conformational vibrations are shown in the Table 1. According to the character of motions of structural elements in DNA nucleotide pairs the obtained modes may be classified as the modes of ion-phosphate vibrations (Ion), H-bond stretching modes (H), modes of intranucleoside vibrations (S), and modes of backbone vibrations (B). The low-frequency spectra of B- and Z-DNA have different number of modes with different frequency values. Such difference appear because in Z-DNA the stacking interaction between nucleic bases differ from B-DNA, and the additional interaction between phosphate groups via cross-linked Mg^{2+} counterion makes the structure of nucleotide dimer more rigid.

The obtained results show that the low-frequency spectra of DNA may be parted on three ranges: the lowest range (from 10 to 30 cm^−1), the middle range (from 30 to 110 cm^−1), and the high range (from 110 to 180 cm^−1). At the lowest frequency range the modes of backbone vibrations are observed. In case of B-DNA there are two B modes with close frequency values (ω_{B1} ≈ ω_{B2}). In case of Z-DNA the number of B modes is twice higher and the frequencies ω_{B1} and ω_{B2} are different, while the frequencies ω_{B3} ≈ ω_{B4}. The additional modes in the spectra of Z-DNA appear due to the dimeric structure of the left-handed double helix. Increasing the counterion mass the frequency values ω_{B1} and ω_{B2} decrease, while ω_{B3} ≈ ω_{B4} remain practically the same.

The middle frequency range is characterized by the modes of intranucleoside vibrations and
H-bond stretching. In case of $B$-DNA there are two H and one S modes, while in case of $Z$-DNA there are four H and three S modes. The S modes of $Z$-DNA have close frequency values that are essentially lower than in $B$-DNA. The modes of H-bond stretching have two characteristic frequency values near 110 cm$^{-1}$ and 60 cm$^{-1}$. The modes of the middle frequency range gradually decrease as counterion mass increases.

At the high frequency range the modes of ion-phosphate vibrations are observed. The frequencies of ion-phosphate vibrations depend on counterion position. In case of counterions in single-stranded position there are two degenerated modes ($\omega_{\text{Ion}1}$ and $\omega_{\text{Ion}2}$) with close frequencies. These modes are characteristic for the both right- and left-handed double helix forms. The vibrations of hydrated Mg$^{2+}$ ions in cross-stranded position are characterized by one mode ($\omega_{\text{Ion}3}$). The vibrations of Mg$^{2+}$ counterion in cross-stranded position are not sensitive to the vibrations of counterions outside of the double helix. Increasing the counterion mass the frequencies of ion-phosphate vibrations $\omega_{\text{Ion}1}$ and $\omega_{\text{Ion}2}$ decrease from 180 to 110 cm$^{-1}$. The same frequency dependence on counterion type has been observe in infrared spectra of DNA dry films with alkali metal counterions [32].

**Table 1.** Frequencies of $B$- and $Z$-DNA conformational vibrations with different alkali metal counterions (cm$^{-1}$). The monomer links of $Z$-DNA contain Mg$^{2+}$ counterion between phosphate groups of different strands.

|        | Na$^+$ | K$^+$ | Rb$^+$ | Cs$^+$ |
|--------|--------|-------|--------|--------|
|        | B-form | Z-form | B-form | Z-form | B-form | Z-form |
| Ion $\omega_{\text{Ion}1}$ | 182 | 181 | 151 | 146 | 120 | 110 | 118 | 110 |
| $\omega_{\text{Ion}2}$ | 182 | 181 | 151 | 146 | 113 | 107 | 108 | 107 |
| $\omega_{\text{Ion}3}$ | –  | 153 | 152 | 152 | 152 | 152 | 152 | 152 |
| H $\omega_{\text{H}1}$ | 111 | 112 | 110 | 110 | 99 | 105 | 94 | 100 |
| $\omega_{\text{H}2}$ | –  | 107 | 106 | 106 | 103 | 103 | 103 | 96 |
| $\omega_{\text{H}3}$ | 99 | 96 | –  | 96 | 95 | –  | 92 | –  |
| $\omega_{\text{H}4}$ | 57 | 63 | 54 | 54 | 59 | 59 | 47 | 59 |
| S $\omega_{\text{S}1}$ | 79 | 51 | 75 | 44 | 64 | 40 | 58 | 37 |
| $\omega_{\text{S}2}$ | –  | 46 | –  | 43 | –  | 42 | –  | 42 |
| $\omega_{\text{S}3}$ | –  | 42 | –  | 39 | –  | 36 | –  | 35 |
| B $\omega_{\text{B}1}$ | 16 | 29 | 14 | 25 | 13 | 25 | 13 | 24 |
| $\omega_{\text{B}2}$ | 15 | 29 | 15 | 20 | 14 | 18 | 12 | 17 |
| $\omega_{\text{B}3}$ | –  | 13 | –  | 11 | –  | 11 | –  | 11 |
| $\omega_{\text{B}4}$ | –  | 12 | –  | 11 | –  | 11 | –  | 10 |

To determine the manifestations of counterion effects in the experimental spectra the Raman intensities for the modes of $B$- and $Z$-DNA are calculated using the approach developed in [38, 39]. As the result the low-frequency Raman spectra are built for the frequency range from 90 to 200 cm$^{-1}$, which is characterized by the ion-depended modes (Figure 3). The spectra intensity is normalized per intensity of the mode $\omega_{\text{H}1}$. The halfwidth of spectra lines is 5 cm$^{-1}$.

It is seen that in case of $B$-DNA the intensities of ion-phosphate modes increase as their frequency decrease (Figure 3a). Thus in case of light counterions (Na$^+$ and K$^+$) the intensities of these modes are low, while in case of heavy counterions (Rb$^+$ and Cs$^+$) they are high due to the coupling with the modes of H-bond stretching. Our calculations for $B$-DNA agree with
Figure 3. The low-frequency Raman spectra of B-DNA and Z-DNA. (a) B-DNA with Na\(^+\), K\(^+\), Rb\(^+\), and Cs\(^+\) counterions in single-stranded position. (b) Z-DNA with Mg\(^{2+}\) counterions in cross-stranded position and Na\(^+\), K\(^+\), Rb\(^+\), and Cs\(^+\) counterions in single-stranded position. The halfwidth of spectra lines is 5 cm\(^{-1}\).

The experimental spectra for Cs-DNA water solution [44] where the intensity increase near 100 cm\(^{-1}\) has been observed. In the spectra of Z-DNA the modes of ion-phosphate vibrations \(\omega_{\text{Ion}1}\) and \(\omega_{\text{Ion}2}\) have about the same intensity ratio as in case of B-DNA (Figure 3b). The mode \(\omega_{\text{Ion}3}\) is rather intensive, and in experiment it is observed near 150 cm\(^{-1}\) [33]. In case of K\(^+\) counterions the modes \(\omega_{\text{Ion}1}\) and \(\omega_{\text{Ion}2}\) have about the same frequencies as the mode \(\omega_{\text{Ion}3}\) (Table 1), and they form a common band with increased intensity. In case of Rb\(^+\) and Cs\(^+\) counterions the intensities of the ion-phosphate modes are essentially higher than in B-DNA. Thus the calculations of the modes of DNA conformational vibrations show that the counterions essentially influence the dynamics of both right- and left-handed double helix. The manifestations of counterion influence are prominent in DNA low-frequency Raman spectra.

4. Conclusions

The vibrations of counterions neutralizing the negatively charged phosphate groups of right- and left-handed double helix of DNA are studied. To find vibrational modes of the double helix the phenomenological approach is used considering the structure of DNA with counterions as the lattice of ionic type (ion-phosphate lattice). In case of right-handed double helix the counterions are localized outside of the double helix near the phosphate groups, while in case of the left-handed DNA bivalent counterions localized between phosphate groups of different strands are also presented. Using the developed model the frequencies and the Raman intensities of vibrational modes are calculated for B- and Z-DNA with Na\(^+\), K\(^+\), Rb\(^+\), and Cs\(^+\) counterions. In case of Z-DNA the Mg\(^{2+}\) counterions are also considered. The results show that the modes of internal vibrations of the left-handed double helix (H-bond stretching in nucleotide pairs, intranucleoside vibrations, and backbone vibrations) change the frequency values comparing to the right-handed DNA double helix that is due to the dimeric structure of Z-DNA. The frequencies of these modes gradually decrease as counterion mass increases. The modes of ion-phosphate vibrations are at frequency range from 100 to 180 cm\(^{-1}\). The Raman intensities in case of heavy counterions (Rb\(^+\) and Cs\(^+\)) are higher than in case of light counterions (Na\(^+\) and K\(^+\)). New mode of ion-phosphate vibrations about the frequency 150 cm\(^{-1}\) is determined, which characterizes the vibrations of Mg\(^{2+}\) counterions with respect to the phosphate groups of different strands of Z-DNA. The intensity of this mode is rather large, therefore it is observed in the
experimental Raman spectra of Z-DNA. The frequency of vibration of magnesium counterions does not depend on the vibrations of counterions outside the double helix. According to our calculation the modes of ion-phosphate vibrations of Mg$^{2+}$ and K$^+$ counterions have close frequencies therefore in the low-frequency spectra of Z-DNA these modes form a common band with high intensity. The intensity increase of the band 150 cm$^{-1}$ due to the modes of ion-phosphate vibrations should be observed in the experimental spectra of Z-DNA with K$^+$ and Mg$^{2+}$ counterions.

Acknowledgments
The present work was partially supported by the Project of the NAS of Ukraine (0110U007540).

Appendix
For a more convenient form of the equations of motion the following variables are used in case of the right-handed double helix: $Y_n = Y_{n1} + Y_{n2}$, $y_n = Y_{n1} - Y_{n2}$, $\theta_n = \theta_{n1} + \theta_{n2}$. $\eta_n = \theta_{n1} - \theta_{n2}$, $\rho_n = \rho_{n1} + \rho_{n2}$, $r_n = \rho_{n1} - \rho_{n2}$. $\xi_n = \xi_{n1} + \xi_{n2}$, $\varsigma_n = \xi_{n1} - \xi_{n2}$. In these variables the system of equations of motion splits into two subsystems of coupling equations for $Y_n$, $\xi_n$, $\rho_n$, $\varsigma_n$, and $y_n$, $\eta_n$, $r_n$, $\varsigma_n$ coordinates. In a long-limit approximation the equations of motion (10) for B-DNA may be written as follows:

\[
\begin{align*}
\ddot{Y}_n + \frac{m_Y}{M} \ddot{\theta}_n + \frac{m_b}{M} \ddot{\rho}_n + \frac{m_c}{M} \ddot{\varsigma}_n &= -\alpha_0 (l_s \dot{\theta}_n + \dot{Y}_n + b \dot{\rho}_n); \\
\dot{\theta}_n + \frac{m_l}{M} \ddot{Y}_n &= -\alpha_0 b \frac{m_Y}{M} (l_s \dot{\theta}_n + \dot{Y}_n + b \dot{\rho}_n) - \sigma_0 \dot{\rho}_n; \\
\ddot{\varsigma}_n + \eta_n &= 0; \\
\ddot{\varsigma}_n + \frac{m_c}{M} \ddot{\varsigma}_n &= 0; \\
\ddot{\varsigma}_n + \theta_n &= 0.
\end{align*}
\]

where $\alpha_0 = 2\alpha / M$; $\sigma_0 = \sigma / m$; $\beta_0 = \beta / m^2$; $\gamma_0 = \gamma \rho_n$. Note, the same as in our previous works [34, 35] for B-DNA we consider the average values of the reduced lengths of pendulum-nucleosides ($l_j \equiv l$), equilibrium angles ($\theta_0 \equiv \theta_0$), and masses ($m_j \equiv m$).

Analogically for Z-DNA the following variables are used: $Y_c = Y_{11} + Y_{12}$, $y_c = Y_{11} - Y_{12}$, $\theta_c = \theta_{11} + \theta_{12}$, $\eta_c = \theta_{11} - \theta_{12}$, $\rho_c = \rho_{11} + \rho_{12}$, $r_c = \rho_{11} - \rho_{12}$, $Y_g = Y_{21} + Y_{12}$, $y_g = Y_{21} - Y_{12}$, $\theta_g = \theta_{21} + \theta_{12}$, $\eta_g = \theta_{21} - \theta_{12}$, $\rho_g = \rho_{21} + \rho_{12}$, $r_g = \rho_{21} - \rho_{12}$, $\xi_1 = \xi_{21} + \xi_{12}$, $\xi_2 = \xi_{21} - \xi_{12}$. As the result the equations of motion (10) for Z-DNA may be written as follows:

\[
\begin{align*}
\ddot{Y}_c + \frac{m_Y}{M} \ddot{\theta}_c + \frac{m_b}{M} \ddot{\rho}_c + \frac{m_c}{M} \ddot{\varsigma}_c &= -\alpha_0 Y_{2c} (Y_c - Y_g) + \alpha_c \left( Y_g + Y_c + l_s^2 \theta_c + l_s \dot{\theta}_c + b \phi \dot{\theta}_c + b \dot{\rho}_c \right) = 0; \\
\ddot{Y}_g + \frac{m_Y}{M} \ddot{\theta}_g + \frac{m_b}{M} \ddot{\rho}_g + \frac{m_c}{M} \ddot{\varsigma}_g &= -\alpha_0 Y_{2g} (Y_c - Y_g) + \alpha_g \left( Y_g + Y_c + l_s^2 \theta_g + l_s \dot{\theta}_g + b \phi \dot{\theta}_g + b \dot{\rho}_g + b \dot{\phi}_g \right) = 0; \\
\ddot{\theta}_g + \ddot{\theta}_c + \beta_g \dot{\theta}_g - g_1 \phi (\theta_c - \theta_g) + \alpha_G \frac{m_Y}{M} \dot{Y}_c (Y_c + l_s^2 \phi \dot{\theta}_c + l_s \phi \dot{\theta}_c + b \phi \dot{\phi}_g + b \dot{\phi}_c) &= 0; \\
\ddot{\theta}_c + \ddot{\theta}_g + \beta_c \dot{\theta}_c - g_1 \phi (\theta_g - \theta_c) + \alpha_G \frac{m_Y}{M} \dot{Y}_g (Y_c + l_s^2 \phi \dot{\theta}_c + l_s \phi \dot{\theta}_c + b \phi \dot{\phi}_c + b \dot{\phi}_g) &= 0; \\
\ddot{\rho}_g + b \ddot{Y}_g + \sigma_g \dot{\rho}_g - g_1 \phi (\rho_c - \rho_g) + \alpha_G \frac{m_Y}{M} \dot{Y}_g (Y_c + l_s^2 \phi \dot{\theta}_c + l_s \phi \dot{\theta}_c + b \phi \dot{\phi}_c + b \dot{\phi}_g) &= 0; \\
\ddot{\rho}_c + b \ddot{Y}_c + \sigma_c \dot{\rho}_c - g_1 \phi (\rho_g - \rho_c) + \alpha_G \frac{m_Y}{M} \dot{Y}_c (Y_c + l_s^2 \phi \dot{\theta}_c + l_s \phi \dot{\theta}_c + b \phi \dot{\phi}_c + b \dot{\phi}_g) &= 0; \\
\ddot{\varsigma}_c + \ddot{\varsigma}_g + \gamma_0 \phi \ddot{\varsigma}_c &= 0.
\end{align*}
\]
\[
\begin{align*}
\ddot{y}_c + \frac{m_{bc}}{M_c} \ddot{r}_c + \frac{m_{bc}}{M_c} \ddot{\eta}_c - \frac{M_c}{M_e} \gamma_{02} (2y_a - y_c) + g_{2c} (y_c + y_b) + \alpha_c \left(y_g + y_c + l_g^s \eta_g + l_c^s \eta_c + b_g r_g + b_c r_c\right) &= 0; \\
\ddot{y}_g + \frac{m_{bg}}{M_g} \ddot{r}_g + \frac{m_{bg}}{M_g} \ddot{\eta}_g - \frac{M_g}{M_e} \gamma_{02} (y_g + \xi_2) + g_{2g} (y_c + y_b) + \alpha_g \left(y_g + y_c + l_g^s \eta_g + l_c^s \eta_c + b_g r_g + b_c r_c\right) &= 0; \\
\ddot{\eta}_b + \ddot{\eta}_g + \beta_g \eta_g + g_{1g} (\eta_c + \eta_g) + \alpha_g \frac{M_{bg} \eta_g}{m_{bg} a} \left(y_g + y_c + l_g^s \eta_g + l_c^s \eta_c + b_g r_g + b_c r_c\right) &= 0; \\
\ddot{\eta}_c + \ddot{\eta}_g + \beta_c \eta_c + g_{1c} (\eta_c + \eta_g) + \alpha_c \frac{M_{bc} \eta_c}{m_{bc} a} \left(y_g + y_c + l_g^s \eta_g + l_c^s \eta_c + b_g r_g + b_c r_c\right) &= 0; \\
\ddot{r}_g + b_g \ddot{y}_g + \sigma_{gr} g_{1g} (r_c + r_g) + \alpha_g \frac{M_{bg} h_g}{m_{bg} a} \left(y_g + y_c + l_g^s \eta_g + l_c^s \eta_c + b_g r_g + b_c r_c\right) &= 0; \\
\ddot{r}_c + b_c \ddot{y}_c + \sigma_{cr} g_{1c} (r_c + r_g) + \alpha_c \frac{M_{bc} h_c}{m_{bc} a} \left(y_g + y_c + l_g^s \eta_g + l_c^s \eta_c + b_g r_g + b_c r_c\right) &= 0; \\
\ddot{y}_g + \ddot{\xi}_2 + \gamma_0_\xi_2 &= 0; \\
2\ddot{y}_a + 2\gamma_{02} (2Y_a - y_c) &= 0,
\end{align*}
\]

where \(\alpha_g = \alpha / M_g\), \(\alpha_c = \alpha / M_c\), \(\beta_g = \beta / m_g l_g^2\), \(\beta_c = \beta / m_c l_c^2\), \(\sigma_g = \sigma / m_g\), \(\sigma_c = \sigma / m_c\), \(\gamma_{01} = \gamma_1 / m_a\), \(\gamma_{02} = \gamma_2 / M_a\), \(g_{1g} = g_1 / m_g l_g^2\), \(g_{1c} = g_1 / m_c l_c^2\), \(g_{2g} = g_2 / m_a\), \(g_{2c} = g_2 / m_c\), \(a_c = \sin \theta_{0c}\), \(a_g = \sin \theta_{0g}\), \(b_c = \cos \theta_{0c}\), \(b_g = \cos \theta_{0g}\), \(l_g^c = l_c \sin \theta_{0c}\), \(l_g^s = l_g \sin \theta_{0g}\).

According to the developed approach [36, 37], the intensity of some mode of DNA conformational vibrations that is observed in the Stokes part of the Raman spectra at the right angle geometry is determined as follows:

\[
J_s \approx 3k_J \left(1 - e^{-\frac{\hbar \nu_s}{k_B T}}\right),
\]

where:

\[
A = \sum_{ij} A_{ij} \left(\ddot{\theta}_{ij} + \ddot{\rho}_{ij} \rho_{ij}\right), \quad B = \sum_{ij} B_{ij} \left(\ddot{\theta}_{ij} + \ddot{\rho}_{ij} \rho_{ij}\right).
\]

The parameters \(A_{ij}\) and \(B_{ij}\) are the combinations of the components of nucleoside polarizability tensors and structural parameters of the model:

\[
A_{ij} = [(b_{ij}^{xy} - b_{ij}^{xz}) \sin 2\theta_{0ij} + 2(-1)^j b_{ij}^{xy} \cos 2\theta_{0ij}],
\]

\[
B_{ij} = [(b_{ij}^{xy} - b_{ij}^{xz})(-1)^j \cos 2\theta_{0ij} - 2b_{ij}^{xy} \sin 2\theta_{0ij}],
\]

where \(\kappa = 13 \cdot 2^3 \pi^3 / (9c^4)\); \(J_0\) and \(\nu_0\) are intensity and frequency of incident light; \(\nu_s\) is frequency of a molecular normal vibration that has usual interdependence with cyclic frequency \(2\pi \nu_s = \omega\); index \(x\) enumerates the mode of normal vibrations; \(c\) is velocity of light; \(h\) is the Plank constant; \(k_B\) is the Boltzmann constant; \(b_{ij}^{zz}, b_{ij}^{xy}\) and \(b_{ij}^{yy}\) are components of nucleoside polarizability tensor determined in the nucleoside reference frame \(xyz\) (Figure 2). The components of nucleoside polarizability tensor are calculated as a sum of polarizability tensors of nucleoside chemical bonds analogically to our previous works [36, 37].

5. References

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