ION MODE IN THE DNA LOW-FREQUENCY VIBRATION SPECTRA

S.M. PEREPELYTSYA, S.N. VOLKOV[1]

Taras Shevchenko Kyiv National University, Faculty of Physics
(64, Volodymyrska Str., Kyiv 01033, Ukraine; e-mail:perepelytsya@univ.kiev.ua),

[1]**Bogolyubov Institute for Theoretical Physics, Nat. Acad. Sci. of Ukraine**
(14b, Metrolohichna Str., Kyiv 03143, Ukraine)

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The vibrational dynamics of a DNA molecule with counterions neutralizing the charged phosphate groups has been studied. With the help of the elaborated model, the conformational vibrations of a DNA double helix with alkaline metal ions have been described both qualitatively and quantitatively. For the complexes of DNA with counterions Li^+, Na^+, K^+, Rb^+, and Cs^+, the normal modes have been found, and a mode characterized by the most notable ion displacements with respect to the DNA backbone has been determined. The vibration frequency of counterions has been established to decrease as the ion mass increases. The results of theoretical calculations are shown to be in good agreement with the experimental data of Raman spectroscopy.

Introduction

Starting with the early research by Watson and Crick [1], it is well known that a DNA macromolecule in the natural form is a salt, a complex of nucleic acid and metal cations. The ion environment of the double helix plays the dominant role in the helical structure formation. The concentration of the counterions in a DNA solution determines the macromolecule helix twisting, bending, and the recognition of the DNA sites by proteins and drugs [2—5]. Therefore, metal cations are of paramount importance in the DNA functioning in living systems.

Metal ions interacting with DNA can be divided into two groups [4, 5]. The first group represents the ions belonging to the diffusion atmosphere of the macromolecule. These ions keep their hydrate envelopes as it is typical of their state in solutions. Another group is the ions that are directly bound with different structural elements of the double helix. The interaction of ions of this group is very specific and depends on their type. Transition and alkaline-earth metal ions are bound principally with nucleic base atoms, the cations of alkaline metals being bound with phosphate groups of the helix backbone [5].

Under ordinary conditions, thermal fluctuations cause vibrations of DNA structural elements and counterions around their equilibrium positions. The vibrations of alkaline metal ions with respect to the DNA backbone phosphates (ion-phosphate modes) are likely to be visual and vastly intense in vibrational spectra because of the homogeneity of backbone phosphate groups and interacting cations. The determination of the character of these vibrations is of great interest for understanding the counterion role in the DNA helix mobility and conformational transformations.

The vibrations of the double helix structure elements can be observed in the low-frequency region because of the massiveness of DNA atomic groups and a relatively weak interaction between them. In fact, the DNA vibration spectra show the set of modes in the region lower than 250 cm^{-1} [6—17]. The low-frequency spectra of DNA can be conditionally divided into three ranges. The lowest range (10—30 cm^{-1}) characterizes vibrations of the double helix backbone [16, 19]. The DNA frequencies in this range depend on the counterion type [13,15,16], and humidity [9,16]. The middle range (60—120 cm^{-1}) is generated by vibrations of the hydrogen bonds and depends on the internucleoside mobility [16,19]. A mode strongly depending on the counterion type has been observed in the range 120—250 cm^{-1} [17]. In this frequency range, an internal vibrational mode of nucleic bases can be also observed [14, 18]. Therefore, it is important to estimate a possible range of the DNA ion-phosphate modes and their dependence on the ion type.

To describe the low-frequency vibrational spectra of a DNA macromolecule, a theoretical approach has been developed in [19,20]. However, in this approach, the counterion vibrations have not been taken into consideration. The problem of the ion effect on the DNA low-frequency modes has been studied in [12,21,22]. The results showed that the DNA low-frequency vibrational spectra depend on counterions, but the specific ion mode was not found.

The purpose of this paper is to describe the low-frequency vibrations of DNA with counterions, as well as to determine a place of the ion-phosphate mode and its dependence on the counterion type.

1. Model of DNA with Counterions

In frame of the approach [19, 20], the improved model of the DNA vibrations is elaborated [23]. The model presents DNA as a double chain of the backbone masses m_0 ($PO_2 + 2O{+}C_5$) with connected pendulum-nucleosides m (sugar+base) (Fig. 1). The counterions are modelled as masses (m_a) bound to the backbone. The nucleoside bases of different chains are connected by hydrogen bonds (Fig. 1). The heterogeneity of the DNA bases is important for vibrations in H-bond base pairs and the mode of intranucleoside mobility [19, 20]. The heterogeneity of the system makes a contribution in the wildness of the vibrational bands of the low-frequency spectra. In present paper, we intend to find the place of the ion mode in the haul DNA low-frequency spectra. On this stage, the heterogeneity of the masses of nucleic bases and the internucleoside mobility are not considered.

Let us write the energy of the system as

$$E = \sum_n \sum_{i=1}^{2} (K_{ni} + U_{ni}) + \sum_{n,n-1} U_{n,n-1}, \tag{1}$$

where K_{ni} and U_{ni} are the kinetic and the potential energy of the n-th monomer link of the system, and $U_{n,n-1}$ is the interaction along the chain.

The kinetic energy of the n-th monomer can be written as

$$K_{ni} = \frac{1}{2} M \dot{Y}_{ni}^2 + \frac{1}{2} I \dot{\theta}_{ni}^2 + m l_s \dot{\theta}_{ni} \dot{Y}_{ni} +$$

$$+ \frac{1}{2} m_a (2\dot{Y}_{ni} \dot{\xi}_{ni} + \dot{\xi}_{ni}^2), \tag{2}$$

where $M = m_0 + m + m_a$; Y_n is the displacement of the n-th nucleoside and phosphate group mass; $I = ml^2 + m_a r_0^2$ is the inertia moment of the nucleotide with a counterion; l is the reduced length of the pendulum-nucleoside, r_0 is the equilibrium distance between an ion and a phosphate group; θ_n is the angle of a displacement of the n-th nucleoside from the equilibrium state θ_{eq}; $l_s = l \sin\theta_{\text{eq}}$; ξ_n is a displacement of the n-th ion from the equilibrium state.

For small displacements, the potential energy of the monomer link can be presented as a sum of three terms describing the energy of H-bond stretching in the pair, the energy of torsion motions of a nucleoside around the backbone chains, and the energy of the ion-phosphate bond. The potential energy of a monomer link of the chain may be written as follows:

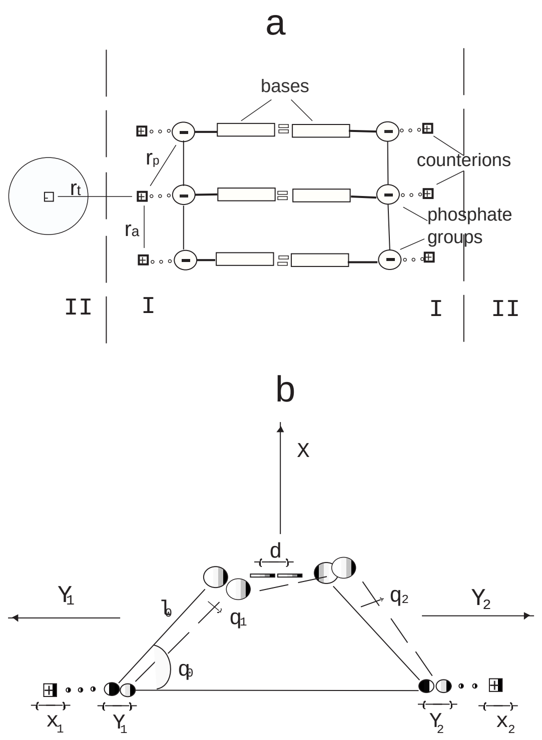

Fig. 1. The four mass model with counterion. *a* — the monomer links of the DNA. *I* — the counterions that directly bind to the DNA structure elements, *II* — the diffusion atmosphere of the macromolecule. *b* — the displacements of the atomic groups and ions in a monomer link

$$U_{ni} = \frac{1}{2} \left(\alpha \delta_n^2 + \beta \theta_{ni}^2 + \gamma \xi_{ni}^2 \right), \tag{3}$$

where α is the force constant of the hydrogen bond stretching in pairs, δ_n is the base pair stretching, β is the force constant of a nucleoside vibration relative to a phosphate group, γ is the constant of ion-phosphate vibrations. From the geometric configuration of the model (Fig. 1), the stretching of base pairs is described as

$$\delta_n = [(\delta_0 + \delta_c + \delta_y)^2 + \delta_s^2]^{\frac{1}{2}} - \delta_0. \tag{4}$$

Here, δ_0 is the equilibrium distance; $\delta_c = 2l\cos\theta_0 - l\cos(\theta_0 + \theta_{1n}) - l\cos(\theta_0 + \theta_{2n})$; $\delta_y = Y_{1n} + Y_{2n}$; $\delta_s = l\sin(\theta_0 + \theta_{1n}) + l\sin(\theta_0 + \theta_{2n})$. For small displacements, expression (4) takes the form:

$$\delta_n \approx l_s(\theta_{1n} + \theta_{2n}) + Y_{1n} + Y_{2n}. \tag{5}$$

In this work, we are interested in the modes of the limited long-range vibrations of the optic type that are observed in spectroscopic experiments. Thus, the interaction of the monomers along the chain ($U_{n,n-1}$) can be waved.

Using the expressions for the energy (1), (2), (3), and (5), we can write the Lagrange equations of motion for this system. For the convenience of the subsequent consideration, we introduce the variables:

$$Y = Y_1 + Y_2, \quad y = Y_1 - Y_2,$$

$$\theta = \theta_1 + \theta_2, \quad \eta = \theta_1 - \theta_2,$$

$$\xi = \xi_1 + \xi_2, \quad \rho = \xi_1 - \xi_2. \tag{6}$$

In variables (6), the equations of motion for the whole system are separated into two systems of connected vibrations:

$$\ddot{Y} + \frac{ml_s}{M}\ddot{\theta} + \frac{m_a}{M}\ddot{\xi} = -\alpha_0(l_s\theta + Y),$$

$$\ddot{\theta} + \frac{ml_s}{I}\ddot{Y} = -\beta_0\theta - \alpha_0\frac{Ml_s}{I}(l_s\theta + Y),$$

$$\ddot{Y} + \ddot{\xi} = -\gamma_0\xi; \tag{7}$$

$$\ddot{y} + \frac{ml_s}{M}\ddot{\eta} + \frac{m_a}{M}\ddot{\rho} = 0,$$

$$\ddot{\eta} + \frac{ml_s}{I}\ddot{y} = -\beta_0\eta,$$

$$\ddot{y} + \ddot{\rho} = -\gamma_0\rho. \tag{8}$$

Here, $\alpha_0 = 2\alpha/M$, $\beta_0 = \beta/I$, and $\gamma_0 = \gamma/m_a$.

We seek for the normal modes of system (7) and (8) in the form $q = q_0e^{-i\omega t}$. The system of equations (7) yields the equation for frequencies:

$$(\gamma_0 - \omega^2)\left[(\alpha_0 - \omega^2)(p_0 - \omega^2) - \frac{Ml_s^2}{I}\times \right.$$

$$\left. \times(\alpha_0 - \omega^2 m/M)^2\right] - \frac{m_a}{M}\omega^4(p_0 - \omega^2) = 0. \tag{9}$$

Here, $p_0 = \alpha_0 Ml_s^2/I + \beta_0$. The solutions of Eq. (9) are the modes ω_1, ω_2, and ω_3.

From (8), the following equation is obtained:

$$\omega^4\mu + \omega^2(\beta_0' + \gamma_0') + \gamma_0\beta_0 = 0. \tag{10}$$

Here, $\beta_0' = \beta_0(m_a/M - 1)$, $\gamma_0' = \gamma_0(m^2l_s^2/MI - 1)$, and $\mu = 1 - m_a/M - m^2l_s^2/MI$. The solutions of (10) are the modes ω_4 and ω_5:

$$\omega_{4,5}^2 = \frac{-(\beta_0' + \gamma_0') \pm \sqrt{(\beta_0' + \gamma_0')^2 - 4\mu\beta_0\gamma_0}}{2\mu}. \tag{11}$$

Let us analyze the modes $\omega_{4,5}$. Taking into account that, for all the counterion types, m_a/M and $m^2l_s^2/MI$ are rather small (about 0.1), formula (11) may be transformed as

$$\omega_4^2 \approx \gamma_0, \tag{12}$$

$$\omega_5^2 \approx \beta_0. \tag{13}$$

Expressions (12) and (13) show that the modes ω_4 and ω_5 depend, respectively, only on the constant of ion vibrations and the constant of backbone vibrations. Analyzing the ratios of the amplitudes obtained from (8)

$$\frac{y_0}{\eta_0} = \frac{(\beta_0 - \omega^2)I}{\omega^2 ml_s}, \tag{14}$$

$$\frac{\rho_0}{\eta_0} = \frac{(\beta_0 - \omega^2)I}{(\gamma_0 - \omega^2)ml_s}, \tag{15}$$

it is clear that the amplitude of ion vibrations (ρ_0) is much larger in the mode ω_4 in comparison with the amplitudes of the phosphate (y_0) and nucleoside (η_0) motions. So, the mode ω_4 is characterized mostly by ion displacements. That is why, we consider that this mode is the mode of ion vibrations.

Let us analyze Eq. (9). As seen, the form of Eq. (9) depends on the counterion mass (m_a). Taking into account that the ratio m_a/M is very small (about 0.05) for light ions (Li^+ and Na^+), the last term in Eq. (9) can be waved as

$$(\gamma_0 - \omega^2)\left[(\alpha_0 - \omega^2)\times \right.$$

$$\left. \times(p_0 - \omega^2) - \frac{Ml_s^2}{I}(\alpha_0 - \omega^2 m/M)^2\right] \approx 0. \tag{16}$$

One of the solutions of (16) is $\omega_1 \approx \sqrt{\gamma_0}$. The amplitude of ion vibrations in the mode ω_1 is the largest in comparison with the amplitudes of the phosphate (Y_0) and nucleoside (θ_0) motions. So, we have found that, for light counterions, the mode ω_1 can be also considered as a mode of ion vibrations. This means that, for light counterions in the DNA low-frequency spectra, there is a twice degenerated mode of ion vibrations ($\omega_1 = \omega_4 \approx \sqrt{\gamma_0}$).

The analysis for heavy ions (Rb^+ and Cs^+) shows that, in the mode ω_1, the H-bond stretching amplitude is the largest one. This means that the mode ω_1 becomes the H-bond stretching mode. So, the structure of the DNA low-frequency spectra is qualitatively different for light and heavy counterions.

For the further analysis of the ion mode, let us determine the constant of ion vibrations. Since counterions form a regular structure around the sugar-phosphate backbone of the DNA, such a system can be considered as an ion crystal. According to the classical study, the ion interaction energy in a crystal can be presented by the potential [24]

$$V(r) = -\frac{M_\alpha e^2}{4\pi\varepsilon\varepsilon_0 r} + B\exp\left(-\frac{r}{b}\right), \tag{17}$$

where M_α is the Madelung constant, e is the ion charge, ε is the dielectric constant, r is the distance between charges, and b characterizes the repulsion between ions. The first and second terms describe, respectively, the electrostatic attraction and the Born—Mayer repulsion. Expanding energy (17) in a series in small displacements from their equilibrium positions $\xi = r - r_0$, $V \approx \gamma\xi^2/2$, and the constant of ion vibrations is

$$\gamma = \frac{M_\alpha e^2}{4\pi\varepsilon\varepsilon_0 r_0^3}\left(\frac{r_0}{b} - 2\right). \tag{18}$$

Using the expression for the constant of ion vibrations (18) and (12), we get the approximate formula for the mode of ion vibration as

$$\omega_{ion} \approx \sqrt{\frac{M_\alpha e^2}{4\pi\varepsilon\varepsilon_0 m_a r_0^3}\left(\frac{r_0}{b} - 2\right)}. \tag{19}$$

Analyzing (19), we see that the ion mode depends strongly on the equilibrium distance r_0 and the ion mass m_a. Thus, we can conclude that the ion mode has to decrease with increase in the ion mass:

$$\omega_{\mathrm{Li}} > \omega_{\mathrm{Na}} > \omega_{\mathrm{K}} > \omega_{\mathrm{Rb}} > \omega_{\mathrm{Cs}}. \tag{20}$$

The ion mode also depends on the Madelung constant M_α. This constant is lowest for a dipole ($M_\alpha = 1$) and is big enough for a NaCl ion crystal ($M_\alpha = 1.748$). In DNA, the value of the Madelung constant is not known, but we can say that the Madelung constant depends on the ion concentration, and it will be different in a dilute solution and in a saturated one. This means that the ion mode has to depend on the ion force of a solution.

The constant of ion vibrations also depends on the other parameters (M_α, b, ε), which will be considered in the following section.

2. Constant of Ion Vibrations

Here, we study the conformational vibrations of DNA with alkaline metals. So, the equilibrium distance r_0 is estimated as a sum of Pauling radii of the ion and the oxygen atom of a phosphate group (Table 1). The parameter b is taken to be equal to values that are known for the ion crystals LiF, NaF, KF, RbF, and CsF [25] (Table 1).

Let us estimate the dielectric constant. The value of this constant depends on the distance between the ions and the nature of the environment. The dielectric constant determination for the DNA presents some difficulties [27—32]. The vacuum dielectric constant ($\varepsilon = 1$) is not suitable for the description of the electrostatic interaction in DNA, because, in this case, the potential near DNA is too high [29]. While solving the Poisson–Boltzman equation, the dielectric constant of the DNA—solution system is considered very often between 2 and 4 [29]. Hingerty with coworkers developed the approach, where the dielectric constant is presented as a function of the distance r is the distance between charges in angstroms [27]:

$$\varepsilon(r) = 78 - 77(r/2.5)^2\exp(r/2.5)(\exp(r/2.5) - 1)^{-2}. \tag{21}$$

Lavery with coworkers improved the function of Hingerty [28]:

$$\varepsilon(r) = \varepsilon_\infty - \frac{\varepsilon_\infty - 1}{2}[(sr)^2 + 2sr + 2]e^{-sr}, \tag{22}$$

where $\varepsilon_\infty = 78$ and $s = 0.16$. There exist also other distance-dependent dielectric functions [29–31], but the functions of Hingerty (21) and Lavery (22) are most commonly used. The dielectric constants calculated by formulas (21) and (22) are shown in Table 1.

Let us estimate the Madelung constant M_α. This constant characterizes the interaction of one ion with the other ions of the system. In our model, we consider the charges of phosphate groups and counterions that neutralize them and take into account that the

Table 1. Parameters for the ion vibration constant

Parameter	Li^+	Na^+	K^+	Rb^+	Cs^+
r_0(Å)	2.00	2.35	2.73	2.88	3.01
b (Å)	0.329	0.316	0.327	0.329	0.313
ε [27]	5.0	6.4	8.2	9.0	10.1
ε [28]	1.3	1.5	1.8	1.9	2.1
M_α (ε = const)	1.307	1.360	1.417	1.439	1.470
M_α (ε by [27])	1.045	1.067	1.099	1.114	1.136
M_α (ε by [28])	1.050	1.066	1.089	1.099	1.116

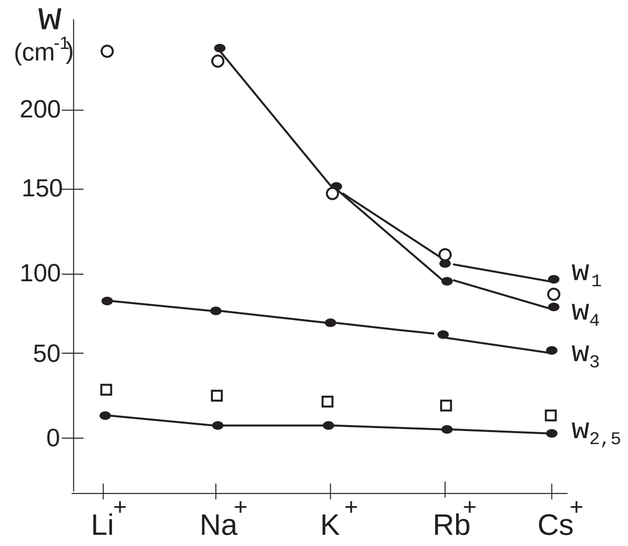

Fig. 2. The dependence of the low-frequency modes on counteriontype. ● — our results, o — [17], □ — [13]

negatively charged ions of Cl$^-$ are present in a solution. These anions are situated at the distance about 7 Å [4]. As usual, long-range electrostatic interactions in such systems as DNA are cut off at the distance of about 10 Å [26] that is approximately equal to the distance between two neighbor phosphate groups of one polymer chain. That is why, only the charges of neighbor ion-phosphate pairs and Cl$^-$ anions are considered in the calculations of the Madelung constant. The following formula for the Madelung constant is obtained:

$$M_\alpha = 1 + \frac{\epsilon(r_0)r_0}{\epsilon(r_t)r_t} + 2\left[\frac{\epsilon(r_0)r_0}{\epsilon(r_p)r_p} - \frac{\epsilon(r_0)r_0}{\epsilon(r_a)r_a}\right]. \qquad (23)$$

Here, $\epsilon(r)$ is the dielectric constant, r_t is the distance between an ion and a Cl$^-$ anion of the solution, r_p is the distance between an ion and a neighbor phosphate group of the same polymer chain, and r_a is the distance between neighbor ions of the same polymer chain (Fig. 1). The first term in (23) that is equal to 1 characterizes the interaction in the phosphate-counterion dipole, the second term describes the energy of interaction between the phosphate counterion and a Cl$^-$ anion of the solution, and the terms in brackets describe the interaction of the phosphate counterion with neighbor phosphate-counterion pairs. The values of the Madelung constant calculated by formula (23) are shown in Table 1. From the results of Table 1, we see that the Madelung constant strongly depends on the permittivity, but, nevertheless, the long-range electrostatic interactions make a big contribution to the constant of ion vibrations.

3. Ion Mode

Using the parameters shown in Table 1 and formula (18), we estimated the constant of ion vibrations (γ). The frequencies of ion vibrations (ω_4) calculated by expressions (11) are shown in Table 2.

Analyzing the results shown in Table 2, we can say that the best agreement with the experimental data is reached with the value of $\varepsilon = 2$ and the Lavery dielectric function [28]. We note that the mode near 170 cm^{-1} was found in works [12, 17] for a solution of DNA + NaCl, but the authors consider this mode as the mode of internal vibrations of NaCl crystals.

From the data of Table 2, we can see that, in the case of ion Li$^+$, the calculated frequency of vibrations differs significantly from the experimental data. The reason for this situation can be connected with the effects of ion hydratability. An ion Li$^+$ has a very small weight (7 a.u.m.) and a radius (0.6 Å) as compared to molecules of water. Therefore, the influence of water on the lithium vibrations can be very large. Our estimations of the Li$^+$ vibration frequency in the case where it is in the complex with one ($\omega_4^{\mathrm{Li}} = 267$ cm^{-1}), two (209 cm^{-1}), and three (180 cm^{-1}) molecules of water show that the frequency becomes significantly lower. If we take into account that a lithium ion moves together with water molecules in the solution, the frequency becomes very close to the experimental value.

For the understanding of the dependence of low-frequency spectra on the counterion type, the frequencies of all five branches of vibrations ω_1, ω_2, ω_3, ω_4, and ω_5 are calculated. The obtained results are shown in Fig. 2.

As we can see, all the low-frequency modes obtained with the help of the proposed approach decrease with increase in the counterion mass. The ion mode (ω_1, ω_4) is most sensitive to the counterion type. Our calculations show the splitting of the ion mode for heavy ions that

Table 2. Frequencies of ion vibrations for *B*-DNA (cm^{-1})

Method	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
$\varepsilon = 2$	444	233	162	112	93
$\varepsilon = 4$	314	165	114	79	66
ε [28]	488	237	151	100	80
ε [27]	252	115	70	46	37
[17]	237* > (150)	230* > (150)	150	110	95
[14]		235			

Note: The asterisk * marks the values determined by us from the spectra of work [17].

was qualitatively obtained above. The theoretical results for the lowest mode ($\omega_{2,5}$) and for the ion mode (ω_4) correlate with the experimental data (Fig. 2). The counterion dependence of the H-bond stretching mode (ω_3) is not studied experimentally.

In conclusion, we emphasize that a specific mode of ion-phosphate vibrations is found. It lies in the frequency range 90 — 250 cm^{-1} and decreases with increase in the counterion mass. This mode is very sensitive to the counterion type and to the ion force of a solution. Moreover, the results presented in Fig. 2 show that all the low-frequency modes of a DNA macromolecule depend of the counterion type.

1. *Watson J. D., Crick F. C. H.*// Nature.— 1953.— **171**.— P. 737 — 738.
2. *Williams L. D., Maher III L. J.*// Ann. Rev. Biophys. Biomol. Struct.— 2000.— **29**.— P. 497 — 521.
3. *Zigel H.* Ions of Metals in Biological Systems. — Moscow: Mir, 1982 (in Russian).
4. *Blagoi Yu. P., Galkin V. L., Gladchenko G. O. et al.* The Complexes of Nucleic Acids with Metal Cations in Solutions. — Kyiv: Naukova Dumka, 1991 (in Russian).
5. *Saenger W.* Principles of Nucleic Acid Structure.— New York: Springer-Verlag, 1984.
6. *Urabe H., Tominaga Y.*// J. Phys. Soc. Jpn.— 1981.— **50**.— P. 3543 — 3544.
7. *Lindsay S. M., Powell J. W., Rupprecht A.*// Phys. Rev. Lett.— 1984.— **53**.— P. 1853 — 1855.
8. *Tominaga Y., Shida M., Kubota K. et al.*// J. Chem. Phys.— 1985.— **83**.— P. 5972 — 5972.
9. *Demarco C., Lindsay S. M., Pokorny M. et al.*// Biopolymers.— 1985.— **24**.— P. 2035 — 2040.
10. *Wittlin A., Genzel L., Kremer F. et al.*// Phys. Rev. A.— 1986.— **34**.— P. 493 — 500.
11. *Urabe H., Sugawara Y., Tsukakoshi M. et al.*// Biopolymers.— 1987.— **26**.— P. 963 — 971.
12. *Powell J. W., Edwards G. S., Genzel L. et al.*// Phys. Rev. A.— 1987.— **35**.— P. 3929 — 3939.
13. *Weidlich T, Lindsay S. M., Ruprecht A.*// Phys. Rev. Lett.— 1988.— **61**.— P. 1674 — 1677.
14. *Lamba Om. P., Wang A. H.-J., Thomas G.J.jr.*// Biopolymers.— 1989.— **28**.— P. 667 — 678.
15. *Urabe H., Kato M., Tominaga Y. et al.*// J. Chem. Phys.— 1990.— **92**.— P. 768 — 774.
16. *Weidlich T., Lindsay S.M., Rui Qi. et al.*// J. Biomol. Struct. Dynam.— 1990.— **8**.— P. 139 — 171.
17. *Weidlich T., Powell J. W., Genzel L. et al.*// Biopolymers.— 1990.— **30**.— P. 477 — 480.
18. *Shishkin O. V., Gorb L., Hobza P., Leszczynski J.* // Intern. J. Quant. Chem.— 2000.— **80**.— P. 1116 — 1124.
19. *Volkov S. N., Kosevich A. M.*// Molecular Biology.— 1987.— **21**.— P. 797 — 806.
20. *Volkov S. N., Kosevich A. M.*// J. Biomol. Struct. Dynam.— 1991.— **8**.— P. 1069 — 1083.
21. *Young L., Prabhu V. V., Prohofsky E. W.*// Phys. Rev. A.— 1989.— **39**.— P. 3173 — 3180.
22. *Garcia A. E., Soumpasis D. M.*// Proc. Nat. Acad. Sci. USA.— 1989.— **86**.— P. 3160 — 3164.
23. *Volkov S. N., Perepelytsya S. M.*//Visnyk Kyiv Univ. Fiz. Mat.— 2002.— 1.— P. 388 — 396.
24. *Vaks V. G.*. Interatomic Interactions and Bonds in Solids. — Moscow: Izdat, 2002 (in Russian).
25. *Moelwyn-Hughes E. A.* Physical Chemistry.— London: Pergamon Press, 1961.
26. *Norberg J., Nilson L.*// Biophys. J.— 2000.— **79**.— P. 1537 — 1553.
27. *Hingerty B. E., Ritcheie R. H., Ferrell T. L. et al.*// Biopolymers.— 1985.— **24**.— P. 427 — 439.
28. *Ramstein J., Lavery R.*//Ibid.— 1988.— **85**.—P. 7231 — 7235.
29. *Mazur J., Jernigan R. L.*// Ibid.— 1991.— **31**.— P. 1615 — 1629.
30. *Wang L., Hingerty B. E., Srinivasan A. R. et al.*// Biophys. J.— 2002.— **83**.— P. 382 — 406.
31. *Srinivasan A. R., Olson W.*// J. Amer. Chem. Soc.— 1998.— **120**.— P. 484 — 491.
32. *Ramachandran G. N., Srinivasan R.*// Ind. J. Biochem.— 1970.— **7**.— P. 95 — 97.

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ІОННА МОДА У СПЕКТРІ НИЗЬКОЧАСТОТНИХ КОЛИВАНЬ МОЛЕКУЛИ ДНК

С. М. Перепелиця, С. Н. Волков

Резюме

Досліджено коливальну динаміку молекули ДНК з протиіонами, що нейтралізують заряди на фосфатних групах. За допомогою розвинутого підходу для описання конформаційних коливань макромолекули ДНК з іонами розглянуто коливальну динаміку подвійної спіралі з іонами лужних металів на якісному та кількісному рівнях. Знайдено нормальні моди комплексів Li-, Na-, K-, Rb- та Cs-ДНК і визначено моду, що характеризується сильними зміщеннями іонів по відношенню до остова ДНК. Показано, що частота іонних коливань зменшується зі збільшенням маси іона. Результати теоретичних розрахунків корелюють з експериментальними даними комбінаційного розсіяння світла.