Subpicosecond dynamics in calf-thymus DNA, in the presence of Zn^{2+} ions: A Raman spectroscopic study

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Abstract. In this paper the Raman total half bandwidths of calf-thymus DNA vibrations have been measured as a function of Zn^{2+} ions concentration, in the presence of a constant concentration of Na^+ ions, respectively. The dependencies of the total half bandwidths and of the global relaxation times, on DNA molecular subgroup structure and on Zn^{2+} ions concentration, are reported. It is shown that changes in the subpicosecond dynamics of molecular subgroups in ZnDNA complexes can be monitored with Raman spectroscopy.

Particularly, the Raman band parameters for the vibrations at 729 cm^{-1} (dA), 792 cm^{-1} (dC, dT and $5'\text{-C-O-P-O-C-3'}$ network), 1094 cm^{-1} (DNA backbone PO_2^- symmetric stretching), 1377 cm^{-1} (dA, dT, dC), 1489 cm^{-1} (the guanine N-7 and adenine rings) and 1581 cm^{-1} (dG, dA) of ZnDNA complexes, in the presence of Zn^{2+} ions concentrations that varied between 0 and 250 mM, are presented. In our study, the full widths at half-maximum (FWHM) of the bands in calf-thymus DNA complexes are typically in the wavenumber range from 10 to 50 cm^{-1} . It can be observed that the molecular relaxation processes studied in this work, have a global relaxation time smaller than 0.94 ps and larger than 0.21 ps. The limit values are characterizing the dA and dG residues, respectively (vibrations at 729 cm^{-1} and 1489 cm^{-1}).

Binding of Zn^{2+} ions to double helical calf-thymus DNA results for some vibrations in smaller global relaxation times and larger bandwidths, respectively, possible as a consequence of the increased interaction of the base moieties with the solvent molecules in unstacked structures.

The fastest and the slowest dynamics for different DNA structural subgroups and different Zn^{2+} ions concentrations, respectively, have been analyzed.

A comparison between different time scales of the vibrational energy transfer processes, characterizing the ZnDNA structural subgroups has been given.

We have found that metal ion's type and concentration are modulators for the (sub)picosecond dynamics of calf thymus DNA molecular subgroups.

Keywords: Subpicosecond dynamics, calf-thymus DNA, Zn^{2+} ions, Raman spectroscopy

1. Introduction

Among the techniques available for the study of molecular motions in liquids, Raman scattering has the distinct advantage, that it enables simultaneous analyses of both reorientational and vibrational

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processes ([1–3] and references therein). Studies of molecular relaxations in liquids are valuable in providing information about the intermolecular interaction processes in condensed matter [1].

Time-dependent forces broaden the vibrational bands [4]. Vibrational frequencies depend on static molecular parameters as force constants, bond distances and angles, atomic masses, and electric charges.

Dynamic parameters of atomic and molecular motions determine the vibrational band shapes [3–5]. Vibrational energy exchange, vibrational resonance coupling, vibrational dephasing and rotational broadening are a number of dynamical processes which have been considered to broaden the vibrational bands of nucleic acids in the frequency domain ([4,5] and references therein). Different relaxation mechanisms may characterize different vibrations, and this kind of information is available from spontaneous Raman measurements ([3–5] and references therein).

Vibrational relaxation plays a crucial role in many aspects of chemistry, physics and biology, e.g. photochemistry, electron transfer, reaction dynamics, thermal chemistry, photobiological processes such as vision and photosynthesis and excimer formation ([6] and references therein).

The dynamics and vibrational relaxation processes of biomolecules in aqueous solutions have motivated several researches [6].

The macromolecular motion in fluids is generally too slow to be observed in the Raman time window that is accessible in the frequency domain. On contrary, the motion of molecular subgroups can be fast enough [7].

It was demonstrated that Raman bandwidths in polynucleotides range from 8 to 35 wavenumbers, and the corresponding time scale of the perturbing forces ranges from fractions of a picosecond to several picoseconds [3,4].

Isotropic and anisotropic spontaneous Raman spectra were obtained from solutions of poly(rA) and rAMP in buffer [8]. To elucidate the influence of macromolecular dynamics and solvent dynamics on the bandwidths of base vibrations in the single stranded polynucleotide poly(rA) [8], the temperature dependence of these spectra was measured. It has been found that the full widths at half-maximum (FWHM) of the bands in poly(rA) are typically in the wavenumber range from 12 to 20 cm^{-1} [3,8].

Upon changing the structure of the nucleic acid by the presence of proteins, ionic salts, pH, metal ions and intercalators, different vibrational modes of the molecule can behave quite different [5,9,10].

A confocal Raman microspectroscopic study into the vibrational half bandwidths of molecular subgroups in calf-thymus DNA, upon lowering the pH, and in the presence of Na^+ , Ca^{2+} and Mg^{2+} ions, respectively, was previously reported by us [10]. In this study the half bandwidths of the vibrations in calf-thymus DNA were typically in the wavenumber range from 7.4 to 31 cm^{-1} . The bandwidths in the Raman spectra were sensitive to a dynamics active on a time scale from 0.34 to 1.44 ps [3,10].

Also, the dependencies of the full widths at half-maximum (FWHM) and of the global relaxation times on DNA molecular subgroup structure, and on Mn^{2+} and Na^+ ions concentrations, respectively, have been reported [5].

The complex system of calf thymus DNA, in an aqueous buffer solution, was studied by Raman spectroscopy, at reduced and low pH values, in the presence of Mn^{2+} ions, respectively. The molecular relaxation processes of DNA subgroups were presented. The full widths at half-maximum (FWHM) of the bands in calf-thymus DNA were typically in the wavenumber range from 11 to 27 cm^{-1} and the molecular relaxation processes studied in that work, had a global relaxation time smaller than 0.965 ps and larger than 0.393 ps [3].

In the study of nucleic acids, phosphate groups are particularly very important in the structure, dynamics and interactions of mono- and polynucleotides [5,11,12]. A study of the dynamics of the PO_3^{2-}

group in aqueous solution can give information on the mononucleotide mobility and interactions in its natural solvent [3,12] .

The IR $\nu_s(\text{PO}_3^{2-})$ band shape of cytidine 5'-monophosphate (5'-CMP) in H_2O solution at different concentrations, 0.009–0.300 mol dm $^{-3}$, has been analysed in relation to the dynamics of the phosphate group of the nucleotide. The relaxation of this mode in aqueous solution seems to be predominantly vibrational [3,12]. Besides, FTIR measurements on the $\nu_s(\text{PO}_3^{2-})$ band shape of 5'-CMP in $^2\text{H}_2\text{O}$ solution at different concentrations, 0.002–0.58 mol dm $^{-3}$, and temperatures, 10–55°C have been interpreted in terms of the dynamics of the PO_3^{2-} group and the self-association processes of this mononucleotide [13]. Second derivative spectra and integrated intensities reveal a possible aggregation of 5'-CMP in $^2\text{H}_2\text{O}$ at concentrations higher than 0.3 mol dm $^{-3}$ [3,5,13].

In relation to the relaxation processes of the IR $\nu_s(\text{PO}_3^{2-})$ band of disodium deoxycytidine 5'-monophosphate, 5'-dCMP, in $^2\text{H}_2\text{O}$ and H_2O , a band-shape analysis of this vibrational mode has been performed [6]. The second derivative spectra reveal the presence of 5'-dCMP aggregates when concentration reaches ~ 0.28 mol dm $^{-3}$. A similar self-association process was detected for the mononucleotide 5'-CMP [6].

In this paper, the complex system of calf thymus DNA, in an aqueous buffer solution, is studied by Raman spectroscopy, as a function of Zn^{2+} ions concentration, and in the presence of a constant concentration of Na^+ ions, respectively. The molecular relaxation processes of DNA subgroups are presented. Monitoring the changes in the Raman vibrational full widths at half-maximum (FWHM) and, correspondingly, in the global relaxation times of the molecular subgroups in DNA, upon varying the Zn^{2+} concentration and in the presence of a constant concentration of Na^+ ions, is of interest.

It will be shown that changes in the subpicosecond dynamics of molecular subgroups in ZnDNA complexes, can be monitored with Raman spectroscopy.

2. Experimental procedure

The experimental details were given in [14] for ZnDNA complexes, at different concentrations of Zn^{2+} cations. Calf-thymus DNA samples were obtained in the presence of 10 mM Bis-Tris, 10 mM NaCl, pH = 6.2 ± 0.1 , and 0, 10, 50, 100, 150, 200 and 250 mM Zinc acetate dihydrate $(\text{CH}_3\text{COO})_2\text{Zn} \times 2\text{H}_2\text{O}$, respectively [14].

Standard Raman measurements have been carried out at room temperature, using a KAISER Raman HoloSpec f/1.8i spectrometer, at the Institute for Analytical Sciences (ISAS), Dortmund, Germany and are presented elsewhere [14]. Raman spectra were excited with a 785 nm laser line. HOLOGRAMS software for KAISER spectrometer was used for data acquisition. The laser power at the sample space was about 60 mW. Software package GRAMS (Thermo Galactic, USA) was used to perform Raman spectra analysis. DNA sample solution spectra were corrected by subtraction of the buffer spectrum [14].

Full widths at half-maximum (FWHM) of the bands were determined using SpectraCalc software. The FWHM was evaluated from the half maximum Raman bands.

3. Results and discussions

In the study of the molecular relaxation processes, Rakov developed one of the well-known procedures of obtaining the relaxation times and the activation energy [3,5,10,15].

The total half bandwidth of the depolarized Raman lines contains in this approximation, two contributions [3,5,10]:

- an intrinsic bandwidth, δ_0 , considered temperature independent in that time;
- another contribution $\Delta(T)$ which is temperature dependent.

The total half bandwidth can be written as:

$$\Delta\nu_{1/2} = \delta_0 + \Delta(T) = \delta_0 + \frac{1}{\pi c \tau_r}. \quad (1)$$

The potential barrier against reorientation can be obtained as:

$$\tau_r = \tau_0 \exp\left(\frac{U_{\text{or}}}{kT}\right), \quad (2)$$

where τ_0 is the period of the molecule oscillation around the equilibrium position, and U_{or} is the energy barrier or the activation energy [5,10].

The Rakov relationship can be written as:

$$\Delta\nu_{1/2} = \delta_0 + \frac{1}{\pi c \tau_0} \exp\left(\frac{-U_{\text{or}}}{kT}\right). \quad (3)$$

From the $(\Delta\nu_{1/2} - \delta_0)$ vs. $\frac{10^3}{T}$ dependencies one can obtain U_{or} as the slope of this linear dependence [3,5,10].

The temperature “independent” part, due to the vibrational relaxation, δ_v , presents small temperature dependence, opposite to the one due to the reorientational relaxation.

The vibrational contribution becomes important for large molecules, in aqueous solutions. From Raman measurements, using polarized light, it is possible to do the selection of these two contributions [5,10]. One can assume, as a first approximation, the existence of a global relaxation time, τ , obtained from the total Raman half bandwidth. This band parameter can be related with the intrinsic parameters of the analyzed system through the relationship:

$$\tau_{v,1R,2R} = \frac{1}{\pi c \Delta\nu_{1/2}^{v,1R,2R}}, \quad (4)$$

where the half bandwidth includes the vibrational ($\Delta\nu_{1/2}^v$) and rotational ($\Delta\nu_{1/2}^{1R,2R}$) contributions and c is the velocity of light. $\Delta\nu_{1/2}^{1R,2R}$ is obtained from IR and Raman bands, respectively [3,5,10].

One can control the dominant contribution of one or another molecular relaxation process through [3,5,10]:

- (a) the selection of the molecular system;
- (b) temperature dependence;
- (c) a proper selection of the solvents.

Molecular dynamics studies for mononucleotides [13] or deoxymononucleotides [12] in aqueous solutions were done by using these approximations [5,10].

The development of fast and accurate curve fitting programs allows the analysis of the vibrational spectra of complicated biological molecules containing often more than 40 vibrational bands ([4] and references therein).

In this paper we will concentrate on the vibrational bandwidths. Only the relatively isolated nucleic acids vibrations will be considered [5,10]. A study into the Raman vibrational bandwidths and the corresponding global relaxation times of molecular subgroups in calf-thymus DNA, upon changing Zn^{2+} concentration, and in the presence of Na^+ ions, is of interest.

For the case of aqueous solutions of DNA molecules we can suppose 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 the DNA macromolecule in aqueous solution [5]. Particularly, the absence of reorientational broadening in polynucleotides indicates that the bases in polynucleotides reorient through an angle of 41° in times slower than 21 ps ([3,4] and references therein).

The Raman band parameters obtained for the adenine vibration at 729 cm^{-1} [16–19] the dC, dT and $5'\text{-C-O-P-O-C-3'}$ network mode near 792 cm^{-1} [10,14,18,20–22], the DNA backbone PO_2^- symmetric stretching vibration at 1094 cm^{-1} [18,21,23], the purines (dA) and pyrimidines (dT, dC) residues band near 1377 cm^{-1} [19–21] the guanine (N-7) and adenine rings vibration at 1489 cm^{-1} [18,19] and the purines (dG, dA) 1581 cm^{-1} vibration ([24] and references therein) of calf-thymus DNA, at different Zn^{2+} ions concentrations, and in the presence of Na^+ ions, are summarized in Tables 1 and 2, respectively.

The full widths at half-maximum (FWHM) of the Raman bands in calf-thymus DNA, are presented at 7 different concentrations of Zn^{2+} ions, and are typically in the wavenumber range from 10 to 50 cm^{-1} (see Table 1). Besides, the global relaxation times were evaluated on the basis of Eq. (4). From the vibrations around 729, 792, 1094, 1377, 1489 and 1581 cm^{-1} it can be observed that the global relaxation times, for molecular subgroups in dissolved calf-thymus ZnDNA complexes, are slower than 0.21 ps and faster than 0.94 ps (see Table 2). The limit values are characterizing the dA and dG residues, respectively (vibrations at 729 and 1489 cm^{-1}). As a general rule, the bandwidths in the Raman spectra are sensitive to a dynamics active on a time scale from 0.1 to 10 ps [4,5].

Table 1

Dependence of the Raman total half bandwidths (cm^{-1}) of different vibrations in calf-thymus DNA, on Zn^{2+} ions concentration, and in the presence of 10 mM NaCl, respectively

Zn^{2+} ions concentration (mM)	Vibrational modes, ν (cm^{-1})					
	729 (dA)	792 ($5'\text{-C-O-P-O-C-3'}$, dC, dT)	1094 (PO_2^-)	1377 (dA, dT, dC)	1489 (dG, dA)	1581 (dG, dA)
FWHM, $\Delta\nu_{1/2}$ (cm^{-1})						
0	10	27	25	26	16	27
10	12	28	23	13.5	15.5	18
50	10	40	22	23	14	16
100	12	30	24	28	24	18
150	16	28	23	30	24	17
200	12	24	24	23	21	15.5
250	13	33.5	28.5	—*	50	22

*Not possible to be read.

Table 2

Global relaxation times for different molecular subgroups in calf-thymus DNA, as a function of Zn^{2+} ions concentration, and in the presence of 10 mM NaCl, respectively

Zn^{2+} ions concentration (mM)	Vibrational modes, ν (cm^{-1})					
	729 (dA)	792 (5'-C-O-P-O-C-3', dC, dT)	1094 (PO_2^-)	1377 (dA, dT, dC)	1489 (dG, dA)	1581 (dG, dA)
Relaxation time, τ (ps)						
0	0.94	0.39	0.42	0.41	0.66	0.30
10	0.88	0.38	0.46	0.79	0.68	0.59
50	0.94	0.27	0.48	0.46	0.76	0.66
100	0.88	0.35	0.44	0.38	0.44	0.59
150	0.66	0.38	0.46	0.35	0.44	0.62
200	0.88	0.44	0.44	0.46	0.51	0.68
250	0.82	0.32	0.37	—**	0.21	0.48

**Not possible to be calculated.

Fig. 1. Raman total half bandwidth (FWHM) of the adenine vibration at 729 cm^{-1} in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^+ ions, respectively.

In the cases for which the Raman profiles were overlapped, only the half of the total half bandwidths (FWHM), in the side where the bands were not superposed, was taken into account and then it was multiplied by two.

Figures 1–6 present the Raman total half bandwidths (FWHM) characteristic to molecular subgroups vibrations in calf-thymus DNA complexes, as a function of Zn^{2+} concentration, for the modes at 729 cm^{-1} (dA), 792 cm^{-1} (dC, dT and 5'-C-O-P-O-C-3' network), 1094 cm^{-1} (PO_2^-), 1377 cm^{-1} (dA, dT, dC), 1489 cm^{-1} (dG, dA) and 1581 cm^{-1} (dG, dA), respectively.

Figures 7–12 present the global relaxation times of molecular subgroups in calf-thymus DNA complexes, as a function of Zn^{2+} concentration, for the modes near 729 cm^{-1} (dA), 792 cm^{-1} (dC, dT and 5'-C-O-P-O-C-3' network), 1094 cm^{-1} (PO_2^-), 1377 cm^{-1} (dA, dT, dC), 1489 cm^{-1} (dG, dA) and 1581 cm^{-1} (dG, dA), respectively.

Fig. 2. Raman total half bandwidth (FWHM) of the vibration at 792 cm^{-1} (dC, dT and $5'\text{-C-O-P-O-C-3}'$ network) in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^+ ions, respectively.

Fig. 3. Raman total half bandwidth (FWHM) of the DNA backbone PO_2^- symmetric stretching vibration at 1094 cm^{-1} in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^+ ions, respectively.

Zn^{2+} dependent DNA structural changes are responsible for the dynamical behaviour of ZnDNA complexes molecular subgroups.

Binding of Zn^{2+} ions to double helical calf-thymus DNA results for some vibrations in smaller global relaxation times and larger half bandwidths, respectively, possible as a consequence of the increased interaction of the base moieties with the solvent molecules, in unstacked structures [4,10,25]. This behaviour is most evident for the bands at 1377 cm^{-1} in the concentration range 10–150 mM Zn^{2+} ions, at 1489 cm^{-1} in the concentration ranges of divalent ions concentrations 50–150 mM, 200–250 mM, and is partially confirmed for the DNA backbone PO_2^- symmetric stretching vibration near 1094 cm^{-1} . We

Fig. 4. Raman total half bandwidth (FWHM) characteristic to the purines (dA) and pyrimidines (dT, dC) residues vibration at 1377 cm^{-1} in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^+ ions, respectively.

Fig. 5. Raman total half bandwidth (FWHM) of the guanine (N-7) and adenine rings vibration at 1489 cm^{-1} in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^+ ions, respectively.

can also observe a decrease of the global relaxation time corresponding to the vibration near 729 cm^{-1} , in the concentration range 50–150 mM Zn^{2+} ions.

Previously, it was established [4,10] that the bandwidths of the 1336 , 1480 and 1575 cm^{-1} adenine vibrations increase toward the value for the mononucleotides upon thermal melting of poly(rA). This temperature behavior of the bandwidths of poly(rA) were assigned to an increasing exposure of the bases to the solvent upon melting of the secondary structure. Moreover, all the studied adenine, thymine, and uracil vibrations have a smaller bandwidth in stacked structures than in unstacked structures and mononucleotides [3,4,10].

Fig. 6. Raman total half bandwidth (FWHM) of the purines (dG, dA) 1581 cm^{-1} vibration in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^{+} ions, respectively.

Fig. 7. Global relaxation time of the adenine vibration at 729 cm^{-1} in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^{+} ions, respectively.

In our study, the best vibrational energy transfer processes were obtained for the adenine band at 729 cm^{-1} at a concentration of 150 mM Zn^{2+} (global relaxation time 0.66 ps), for the dC, dT and $5'\text{-C-O-P-O-C-3'}$ network mode near 792 cm^{-1} around 50 mM Zn^{2+} (global relaxation time 0.27 ps), for the band at 1094 cm^{-1} at a concentration of 250 mM Zn^{2+} (global relaxation time 0.37 ps), for the vibration near 1377 cm^{-1} at 150 mM Zn^{2+} (global relaxation time 0.35 ps), for the mode at 1489 cm^{-1} around 250 mM Zn^{2+} (global relaxation time 0.21 ps), and for the vibration near 1581 cm^{-1} at a concentration of 0 mM Zn^{2+} (global relaxation time 0.30 ps).

We have found that a minimum of the global relaxation time corresponds to the bands near 729 cm^{-1}

Fig. 8. Global relaxation time of the vibration at 792 cm^{-1} (dC, dT and 5'-C-O-P-O-C-3' network) in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^+ ions, respectively.

Fig. 9. Global relaxation time of the DNA backbone PO_2^- symmetric stretching vibration at 1094 cm^{-1} in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^+ ions, respectively.

and 1377 cm^{-1} , at 150 mM Zn^{2+} ions, respectively. Besides, the fastest dynamics was detected around 250 mM Zn^{2+} ions for the vibrations near 1094 and 1489 cm^{-1} .

The highest value of the global relaxation time was observed for the band near 729 cm^{-1} at 0 and 50 mM Zn^{2+} ions concentrations, respectively (global relaxation time 0.94 ps), for the mode near 792 cm^{-1} at 200 mM Zn^{2+} (global relaxation time 0.44 ps), for the vibration around 1094 cm^{-1} at 50 mM Zn^{2+} (global relaxation time 0.48 ps), for the band near 1377 cm^{-1} at 10 mM Zn^{2+} (global relaxation time 0.79 ps), for the mode near 1489 cm^{-1} at 50 mM Zn^{2+} (global relaxation time 0.76 ps) and for the vibration near 1581 cm^{-1} at a concentration of 200 mM Zn^{2+} ions (global relaxation time 0.68 ps).

Fig. 10. Global relaxation time characteristic to the purines (dA) and pyrimidines (dT, dC) residues band at 1377 cm^{-1} in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^{+} ions, respectively.

Fig. 11. Global relaxation time of the guanine (N-7) and adenine rings vibration at 1489 cm^{-1} in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^{+} ions, respectively.

It can be observed, that the global relaxation times of the bands near 729 , 1094 and 1489 cm^{-1} have a maximum at 50 mM Zn^{2+} ions. A similar slow molecular relaxation process at 50 mM divalent cations concentration, was observed in this study for the guanine and adenine rings band near 1581 cm^{-1} . A maximum of the global relaxation time was also observed at 200 mM Zn^{2+} ions for the bands near 792 and 1581 cm^{-1} , respectively.

On the basis of our experimental results, the molecular relaxation processes are the slowest for the dA residues (characteristic band around 729 cm^{-1}), as compared to those of all the other bands (Table 2, Fig. 13). This result is similar with the observations made previously by us [5].

Fig. 12. Global relaxation time of the purines (dG, dA) 1581 cm^{-1} vibration in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration, and in the presence of Na^+ ions, respectively.

Fig. 13. A comparison between different time scales of the molecular relaxation processes of molecular subgroups in calf-thymus DNA complexes, as a function of Zn^{2+} ions concentration.

A comparison between different time scales of the molecular dynamics, characterizing several DNA complexes subgroups is given in Fig. 13. It is shown that the Raman band parameters obtained for the dC, dT and $5'\text{-C-O-P-O-C-3}'$ network mode near 792 cm^{-1} , the DNA backbone PO_2^- symmetric stretching vibration at 1094 cm^{-1} , the dA, dT, dC residues band near 1377 cm^{-1} , and of the purines (dG, dA) vibration at 1489 cm^{-1} of calf-thymus DNA have a similar behaviour in the Zn^{2+} concentration range 100–200 mM. Besides, the vibrational energy transfer processes of the bands around 792, 1094 and 1377 cm^{-1} are almost the same at 200 mM Zn^{2+} .

Also, the global relaxation time characteristic to the DNA bases vibration at 1377 cm^{-1} does not

change too much upon changing the Zn^{2+} ions concentration, except the value corresponding to 10 mM divalent metal ions (Figs 10 and 13). This behaviour is similar to that observed previously by us upon varying the Mn^{2+} ions concentration, in the case of DNA samples at 10 mM NaCl [5].

Some differences in the molecular relaxation processes of DNA subgroups are to be observed upon changing the Zn^{2+} ions concentration, as compared to the corresponding dynamics, found previously by us, for calf-thymus MnDNA complexes [5]. Hence, metal cation's type and concentration are modulators for the (sub)picosecond dynamics in calf-thymus DNA complexes [5,10].

4. Conclusions

Spontaneous Raman scattering can be used to study the fast (sub)picosecond dynamics of molecules [7].

This paper presents a Raman spectroscopic study into the vibrational total half bandwidths of molecular subgroups in calf-thymus DNA, upon changing the concentration of Zn^{2+} ions, and in the presence of a constant concentration of Na^+ cations, respectively. Besides, the corresponding global relaxation times have been derived. The Raman band parameters were obtained for the modes at 729 cm^{-1} (dA), 792 cm^{-1} (dC, dT and 5'-C-O-P-O-C-3' network), 1094 cm^{-1} (PO_2^-), 1377 cm^{-1} (dA, dT, dC), 1489 cm^{-1} (dG, dA) and 1581 cm^{-1} (dG, dA) of calf-thymus DNA complexes. It has been shown that changes in the subpicosecond dynamics of molecular subgroups in ZnDNA complexes, can be monitored with Raman spectroscopy.

The study of the vibrational total half bandwidths of calf-thymus ZnDNA complexes, revealed a sensitivity of FWHM to the concentration of Zn^{2+} cations. Moreover, this proved to be dependent on the vibration under study. The Raman total half bandwidths of calf-thymus ZnDNA vibrations revealed a dynamic picture on a subpicosecond time scale. Full widths at half-maximum (FWHM) of the bands in calf-thymus DNA complexes are typically in the wavenumber range from 10 to 50 cm^{-1} . The half bandwidths in the Raman spectra are sensitive to a dynamics active on a time scale from 0.21 to 0.94 ps.

Binding of Zn^{2+} ions to double helical calf-thymus DNA results for some vibrations in smaller global relaxation times and larger total half bandwidths, respectively, possible as a consequence of the increased interaction of the base moieties with the solvent molecules, in unstacked structures [4,10,25]. This behaviour is most evident for the bands at 1377 cm^{-1} in the concentration range 10–150 mM Zn^{2+} ions, at 1489 cm^{-1} in the concentration ranges of divalent ions concentrations 50–150 mM, 200–250 mM, and is partially confirmed for the DNA backbone PO_2^- symmetric stretching vibration near 1094 cm^{-1} . We can also observe a decrease of the global relaxation time corresponding to the vibration near 729 cm^{-1} , in the concentration range 50–150 mM Zn^{2+} ions.

The fastest and the slowest relaxation processes for different DNA structural subgroups, upon changing the Zn^{2+} ions concentration, respectively, have been analyzed. Particularly, the slowest dynamics corresponding to the vibrations near 729, 1094 and 1489 cm^{-1} takes place at 50 mM Zn^{2+} ions.

A comparison between different time scales of the molecular dynamics, characterizing several ZnDNA structural subgroups, has been given.

Some differences in the vibrational energy transfer processes of DNA subgroups have been observed upon changing the Zn^{2+} ions concentration, as compared to the corresponding dynamics, found previously by us, for calf-thymus MnDNA complexes [5]. Hence, metal cation's type and concentration are modulators for the (sub)picosecond dynamics in calf-thymus DNA complexes [5,10].

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