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Molecular relaxation processes in calf-thymus DNA, in the presence of Mn^{2+} and Na^{+} 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 Mn^{2+} ion concentration (0–600 mM), in the presence of two concentrations of Na^{+} cations, respectively. The dependencies of the half bandwidths and of the global relaxation times on DNA molecular subgroup structure, on Mn^{2+} and Na^{+} ions concentrations, respectively, are reported. It is shown that changes in the (sub)picosecond dynamics of molecular subgroups in calf-thymus DNA can be monitored with Raman spectroscopy.

In this study the Raman band parameters for the vibrations at 729 cm^{-1} (dA), 787 cm^{-1} (dC), 1094 cm^{-1} (PO_2^-), 1376 cm^{-1} (dA, dG, dT, dC), 1489 cm^{-1} (dG, dA) and 1578 cm^{-1} (dG, dA) of calf thymus DNA are presented. The full-widths at half-height (FWHH) of the bands in calf-thymus DNA are typically in the wavenumber range from 9 to 33.5 cm^{-1}. It can be observed that the molecular relaxation processes studied in this work, have a global relaxation time smaller than 1.179 ps and larger than 0.317 ps.

Mn^{2+}-induced DNA structural changes result for the vibrations at 729 cm^{-1} and 787 cm^{-1} in smaller global relaxation times, and larger half bandwidths, respectively, as compared to the starting value of 0 mM Mn^{2+}. The vibrational energy transfer processes of these two subgroups (dA, dC), respectively, are slower in the case of DNA samples at 10 mM NaCl, as compared to the corresponding DNA samples at 150 mM NaCl. However, the behaviour of the global relaxation times characteristic to the bands at 729 and 787 cm^{-1} is similar with respect to manganese(II) ions concentration, in the case of the two values of Na^{+} ions content, respectively.

On the contrary, the molecular dynamics is slower for the base vibrations at 1376, 1489 and 1578 cm^{-1}, in the case of DNA samples at 150 mM NaCl, as compared to the corresponding samples at lower Na^{+} concentration, in almost all Mn^{2+} ions concentration range. The molecular relaxation processes in these three cases, respectively, are quite different for the corresponding samples with different Na^{+} ions content, upon increasing divalent manganese ions concentration.

The molecular dynamics characterizing the band near 1094 cm^{-1} of the DNA backbone PO_2^- symmetric stretching vibration is faster upon increasing the Mn^{2+} ions concentration between 0–600 mM and seems not to be influenced by the Na^{+} ions content, specific to our experimental conditions.

Keywords: (Sub)picosecond dynamics, calf-thymus DNA, Mn^{2+} concentration, Na^{+} ions, Raman spectroscopy

1. Introduction

Vibrational relaxation plays a crucial role in many aspects of chemistry, physics and biology. The dynamics and vibrational relaxation processes of biomolecules in aqueous solutions have motivated

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several researches [1]. Studies of molecular relaxations in liquids are valuable in providing information about the intermolecular interaction processes in condenced matter [2]. The most significant information concerning the behaviour of a condensed system in the picosecond timescale is offered by vibrational spectroscopies (infrared and Raman) ([3] and references therein).

Among the techniques available for the study of molecular dynamics, Raman scattering has the distinct advantage, that it enables simultaneous analyses of both reorientational and vibrational processes ([2,3] and references therein). The bandwidths in the Raman spectra are sensitive to a dynamics active on a time scale from 0.1 to 10 ps [4]. The macromolecular motion in fluids is generally too slow to be observed in the Raman time window that is accessible in the frequency domain. In principle motion of the molecular subgroups can be fast enough [5].

Time-dependent forces broaden the vibrational bands [4]. Dynamic parameters of atomic and molecular motions determine the vibrational band shapes. A number of dynamical processes have been identified to broaden the vibrational bands of nucleic acids in the frequency domain, e.g. vibrational energy exchange, vibrational resonance coupling, vibrational dephasing and rotational broadening ([4] and references therein). Different vibrations may be sensitive to different relaxation mechanisms, and this kind of information is available from spontaneous Raman measurements ([4] and references therein).

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 [6,7].

It was shown that the Raman bandwidths in polynucleotides are in the wavenumber range between 8–35 cm^{-1}, and the corresponding time scale of the perturbing forces ranges from fractions of a picosecond to several picoseconds [4].

A study into the vibrational bandwidths of adenine in the polynucleotide poly(rA) has been done [8]. The bandwidths obtained for poly(rA) were compared with those of the mononucleotide rAMP, in the temperature range where poly(rA) gradually changes from a base stacked structure to an unstacked structure [8]. The influence of macromolecular dynamics and solvent dynamics on the bandwidths of base vibrations in the single stranded polynucleotide poly(rA) have been elucidated [8].

Besides, 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 [7].

In the study of nucleic acids, phosphate groups are particularly very important in the structure, dynamics and interactions of mono- and polynucleotides [9,10]. 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 [10]. The υ_s ($PO_3{}^{2-}$) FTIR band shape of cytidine 5′-monophosphate (5′-CMP) in H_2O at low concentration has been analysed in relation to the dynamics of the phosphate group of the nucleotide. It has been found that the relaxation of this symmetric stretching mode in aqueous solution seems to be predominantly vibrational [10]. Besides, FTIR measurements on the υ_s ($PO_3{}^{2-}$) band shape of 5′-CMP in ^2H_2O solution at different concentrations and temperatures, have been interpreted in terms of the dynamics of the $PO_3{}^{2-}$ group and the self-association processes of this mononucleotide. A possible aggregation process of 5′-CMP has been detected from the second derivative and the integrated intensity of the band [11].

The analysis of the IR υ_s ($PO_3{}^{2-}$) band shape of disodium deoxycytidine 5′-monophosphate, 5′-dCMP, in ^2H_2O and H_2O solutions at different concentrations and temperatures provides information on the relaxation and dynamics of the phosphate group. Self-association of this mononucleotide is detected at concentrations higher than $\sim$0.28 mol dm^{-3} [1].

In this paper, the complex system of calf thymus DNA, in an aqueous buffer solution, is studied by Raman spectroscopy, at different concentrations of Mn^{2+} ions, in the presence of two Na^{+} ions concentrations, respectively. Monitoring the changes in the full-widths at half-height (FWHH) and, correspondingly, in the global relaxation time of the molecular subgroups in DNA, upon changing the concentration of divalent and monovalent metal ions, is of interest.

2. Experimental procedure

The experimental details were given in Muntean et al. [12] for MnDNA complexes, in the presence of 10 mM NaCl, 10 mM Na-cacodylate and in Muntean et al. [13] for MnDNA complexes, in the presence of 150 mM NaCl, 10 mM Na-cacodylate. Raman spectra were measured at 0, 5, 100, 200, 300, 400, 500 and 600 mM $MnCl_2$, respectively, for each spectra set. The pH values were around 6.2 and were controlled in the dialysis buffers and in the DNA samples, respectively. A critical concentration has been found at 100 mM Mn^{2+}, in the case of the sample containing 10 mM NaCl, where condensation of DNA occurred and no Raman spectrum was obtained. The Raman spectra were recorded with a Raman spectrometer T64000 (Jobin Yvon, France) equipped with a liquid nitrogen-cooled charge-coupled-device (CCD) detector, at the Max-Delbrück-Centrum für Molekulare Medizin Berlin-Buch, Germany and are presented elsewhere [12,13].

Raman data were analyzed with the software packages LabSpec (Jobin Yvon, France) and GRAMS (Thermo Galactic, USA). Solution spectra were corrected by subtraction of the averaged buffer spectrum and fluorescence background that was approximated by a polynomial curve [12,13].

Peak positions and FWHH of the bands were determined using SpectraCalc software. The FWHHs were evaluated from the half maximum Raman bands.

3. Results and discussions

The earlier studies of the molecular relaxation processes developed by Rakov [7,14] were centered on the relaxation times and the activation energies.

In this approximation, the total half bandwidth of the depolarized Raman lines contain two contributions:

- 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:

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

The potential barrier against reorientation can be obtained as:

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

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.

The Rakov relationship can be written as:

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

One can obtain U_{or} as the slope of this linear dependence of $(\Delta_{1/2} - \delta_0)$ *vs* $\frac{10^3}{T}$.

It was demonstrated that the temperature "independent" part, due to the vibrational relaxation, δ_{v}, presents small temperature dependence, opposite as the one due to the reorientational relaxation. For large molecules, in aqueous solutions the vibrational contribution becomes important. Using polarized light, it is possible to do the selection of these two contributions from Raman measurements. Into a first approximation, one can assume the existence of a global relaxation time, τ, obtained from the total Raman half bandwidth. This parameter can be related with the intrinsic parameters of the analyzed system through the relationship:

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

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.

The dominant contribution of one or another molecular relaxation process can be controlled through:

(a) the selection of the molecular system; in the case of large molecules, solved in polar media (e.g. water), one can assume that the vibrational relaxation dominates (is the most efficient relaxation mechanism); one can neglect the reorientational contribution, being a very slow molecular motion;
(b) temperature dependence; with the temperature increase, the half bandwidth increases, see Eq. (1); if one observe a weak temperature dependence or even a decrease of the half bandwidth with the temperature increase, the dominant contribution is the vibrational relaxation;
(c) a proper selection of the solvents, e.g. in strong polar media, the vibrational contribution is dominant; in the case of inert, non-polar solvent media, on the contrary, the rotational relaxation must be taken into account.

Molecular dynamics studies for mononucleotides [11] or deoxymononucleotides [10] in aqueous solutions were done by using these approximations.

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 are considered.

A study into the Raman vibrational bandwidths of molecular subgroups in calf-thymus DNA, upon changing the Mn^{2+} ions concentration, in the presence of Na^{+} ions, is of interest (see Tables 1, 2 and 4, 5). It is shown that changes in (sub)picosecond dynamics of molecular subgroups in calf-thymus DNA can be monitored with Raman spectroscopy.

For the case of aqueous solutions of DNA molecules we can suppose that mainly, 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. Particularly, the absence of reorientational broadening

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

Mn^{2+} ions concentration (mM)	Vibrational modes, ν (cm^{-1})					
	729 (A)	787 (C)	1094 (PO_2^-)	1376 (A, G, T, C)	1489 (G, A)	1578 (G, A)
	FWHH, $\Delta\nu_{1/2}$ (cm^{-1})					
0	10	24	19	25.5	18.5	17
5	10.5	25.5	18.7	23	18.5	16
200	11.2	29.5	22.5	24.5	19	17.3
300	11	27.3	23.3	25	20.3	17.5
400	10	27.8	23.8	25	19	17
500	10.5	27	25.5	23	19	16.8
600	11.5	33.5	25	24.5	19.5	17

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

Mn^{2+} ions concentration (mM)	Vibrational modes, ν (cm^{-1})					
	729 (A)	787 (C)	1094 (PO_2^-)	1376 (A, G, T, C)	1489 (G, A)	1578 (G, A)
	Relaxation time, τ ($s \times 10^{-12}$)					
0	1.061	0.442	0.559	0.416	0.574	0.624
5	1.010	0.416	0.568	0.462	0.574	0.663
200	0.948	0.360	0.472	0.433	0.559	0.614
300	0.965	0.389	0.456	0.425	0.523	0.607
400	1.061	0.382	0.446	0.425	0.559	0.624
500	1.010	0.393	0.410	0.462	0.559	0.632
600	0.923	0.317	0.424	0.433	0.544	0.624

in polynucleotides indicates that the bases in polynucleotides reorient through an angle of 41° in times slower than 21 ps ([4] and references therein).

The Raman band parameters obtained for the adenine vibration at 729 cm^{-1} [13,15–17], the cytosine ring breathing mode at 787 cm^{-1} [7,16,18–20], the DNA backbone PO_2^- symmetric stretching vibration at 1094 cm^{-1} [12,16,19], the purines (dA, dG) and pyrimidines (dT, dC) residues band at 1376 cm^{-1} [17–19], the guanine (N-7) and adenine rings vibration at 1489 cm^{-1} [16,17] and the purines (dG, dA) 1578 cm^{-1} vibration ([21] and references therein) of calf-thymus DNA, at different Mn^{2+} ions concentrations, in the presence of Na^+ ions, are summarized in Tables 1, 2 and 4, 5, respectively.

The full-widths at half-height (FWHH) of the bands in calf-thymus DNA are presented at 7 different Mn^{2+} ions concentrations, in the presence of 10 mM NaCl and are typically in the wavenumber range from 10 to 33.5 cm^{-1} (see Table 1). Besides, the half bandwidths of calf-thymus DNA are presented at 8 different Mn^{2+} ions concentrations, in the presence of 150 mM NaCl and are typically in the wavenumber range from 9 to 31.5 cm^{-1} (see Table 4).

Also, the global relaxation times were evaluated on the basis of Eq. (4). From the vibrations at 729, 787, 1094, 1376, 1489 and 1578 cm^{-1} it can be observed that the global relaxation times, for molecular subgroups in dissolved calf-thymus DNA, in the presence of different Mn^{2+} ion concentrations are slower than 0.317 and faster than 1.061 ps for samples at 10 mM NaCl (see Table 2) and are in the range

Table 3
Wavenumbers (cm^{-1}) of the different vibrations in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of 10 mM NaCl

Mn^{2+} ions concentration (mM)	Vibrational modes, ν (cm^{-1})					
	729 (A)	787 (C)	1094 (PO_2^-)	1376 (A, G, T, C)	1489 (G, A)	1578 (G, A)
	Wavenumber, ν (cm^{-1})					
0	728.5	787	1093.5	1376	1489	1577.5
5	729	787	1094	1376	1489	1578
200	729	787	1093.5	1375.5	1489	1578
300	729	786.5	1093.5	1376	1489	1578
400	729.5	788	1094	1376.5	1489.5	1578.5
500	728.5	786	1093.5	1375.5	1489	1578
600	729.5	787.5	1094	1376.5	1489	1579

Table 4
Dependence of the Raman half bandwidths (cm^{-1}) of different vibrations in calf-thymus DNA, on Mn^{2+} ions concentration, in the presence of 150 mM NaCl

Mn^{2+} ions concentration (mM)	Vibrational modes, ν (cm^{-1})					
	729 (A)	787 (C)	1094 (PO_2^-)	1376 (A, G, T, C)	1489 (G, A)	1578 (G, A)
	FWHH, $\Delta\nu_{1/2}$ (cm^{-1})					
0	9	24.4	17	20.8	17.7	16.3
5	10.3	26	17.8	20	17	15.2
100	13.5	29	20.8	21.8	18	15.3
200	13.5	31.5	21.5	16	16.5	14.5
300	12.5	30	24.5	22.5	17.8	16.5
400	11.5	30	25.5	23.5	18.5	17.5
500	13	29.5	25.5	22.5	18.5	16.2
600	12	30.3	29	24.5	19.5	18

of 0.337–1.179 ps for samples at 150 mM NaCl (see Table 5). 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].

Tables 3 and 6 present the dependence of the wavenumbers (cm^{-1}) characterizing the band maximum for different vibrations in calf-thymus DNA, on Mn^{2+} ions concentration, in the presence of two concentrations of Na^+ ions, respectively.

Figures 1–6 present the half bandwidths (FWHH) characteristic to molecular subgroups vibrations in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^+ ions, respectively, for the modes at 729 cm^{-1} (dA), 787 cm^{-1} (dC), 1094 cm^{-1} (PO_2^-), 1376 cm^{-1} (dA, dG, dT, dC), 1489 cm^{-1} (dG, dA) and 1578 cm^{-1} (dG, dA).

Figures 7–12 present the global relaxation times of molecular subgroups vibrations in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^+ ions, respectively, for the modes at 729 cm^{-1} (dA), 787 cm^{-1} (dC), 1094 cm^{-1} (PO_2^-), 1376 cm^{-1} (dA, dG, dT, dC), 1489 cm^{-1} (dG, dA) and 1578 cm^{-1} (dG, dA).

Metal ion-induced DNA structural changes are responsible for their behaviour.

Mn^{2+}-induced structural changes of calf-thymus DNA double helix result for the vibrations at 729 and 787 cm^{-1} in smaller global relaxation times, and larger half bandwidths (Figs 1, 2, 7, 8), respectively, as

Table 5
Global relaxation times for different molecular subgroups in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of 150 mM NaCl

Mn^{2+} ions concentration (mM)	Vibrational modes, ν (cm^{-1})					
	729 (A)	787 (C)	1094 (PO_2^-)	1376 (A, G, T, C)	1489 (G, A)	1578 (G, A)
	Relaxation time, τ ($s \times 10^{-12}$)					
0	1.179	0.435	0.687	0.510	0.660	0.716
5	1.030	0.408	0.596	0.531	0.624	0.698
100	0.786	0.366	0.510	0.487	0.590	0.694
200	0.786	0.337	0.493	0.663	0.643	0.732
300	0.849	0.354	0.433	0.472	0.596	0.643
400	0.923	0.354	0.416	0.452	0.574	0.606
500	0.816	0.360	0.416	0.472	0.573	0.655
600	0.884	0.350	0.366	0.433	0.544	0.590

Table 6
Wavenumbers (cm^{-1}) of the different vibrations in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of 150 mM NaCl

Mn^{2+} ions concentration (mM)	Vibrational modes, ν (cm^{-1})					
	729 (A)	787 (C)	1094 (PO_2^-)	1376 (A, G, T, C)	1489 (G, A)	1578 (G, A)
	Wavenumber, ν (cm^{-1})					
0	728.5	788	1093.5	1376.2	1490	1578
5	729.5	787.5	1094	1376.5	1489.5	1578.5
100	729	787.5	1093.5	1376.5	1489.5	1578.5
200	729	788	1094	1376	1489.5	1578.5
300	729.5	787.5	1093.5	1376	1489.5	1578.5
400	729	787.5	1094	1376	1489	1579
500	729	787.5	1094	1376.5	1489	1578.5
600	729.5	788	1094.5	1376.5	1489	1579

compared to the starting value of 0 mM Mn^{2+}, as a consequence of the interaction of dA and dC residues with divalent metal cations. This observation is valid for both Na^+ ions concentrations, but above 5 mM Mn^{2+}, the molecular dynamics of these two subgroups is slower in the case of the DNA samples at 10 mM NaCl, as compared with the corresponding samples at 150 mM NaCl. The vibrational energy transfer processes are the most rapid for the adenine 729 cm^{-1} vibration around 100–200 mM Mn^{2+}, in the case of DNA samples at 150 mM NaCl (global relaxation time 0.786 ps). The fastest dynamics characterizing the same band, in the case of DNA samples at 10 mM NaCl, is around 600 mM Mn^{2+} (global relaxation time 0.923 ps), comparable with the value at 200 mM Mn^{2+} (global relaxation time 0.948 ps). For the band at 729 cm^{-1}, in the case of both samples sets, the global relaxation times increase slightly in the manganese(II) concentration range of 200–400 mM, before starting to decrease (Fig. 7).

The vibrational energy transfer processes are the most rapid, for the 787 cm^{-1} cytosine band, around 200 mM Mn^{2+}, in the case of DNA samples at 150 mM NaCl (global relaxation time 0.337 ps). The fastest dynamics characterizing the same vibration, in the case of DNA samples at 10 mM NaCl is around 600 mM Mn^{2+} (global relaxation time 0.317 ps), however a local minimum exists also around 200 mM Mn^{2+} (global relaxation time 0.360 ps). For the vibration at 787 cm^{-1} the global relaxation

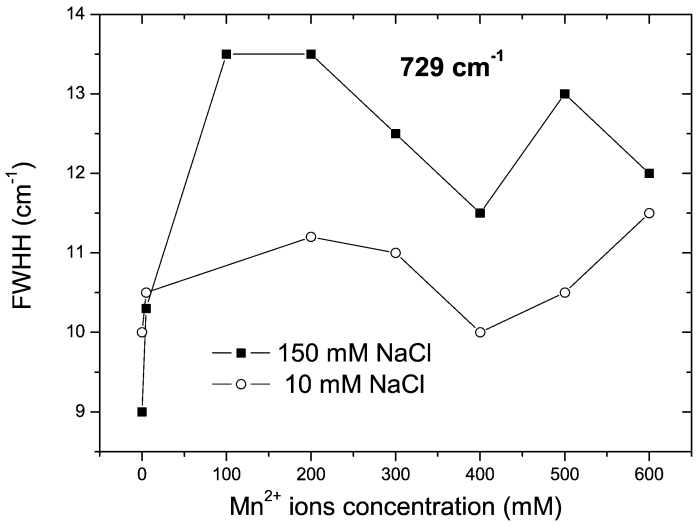

Fig. 1. Half bandwidth (FWHH) of the adenine vibration at 729 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^{+} ions, respectively.

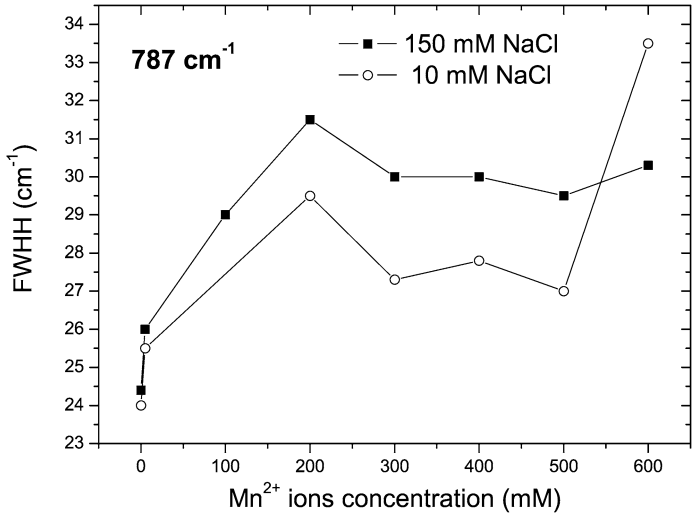

Fig. 2. Half bandwidth (FWHH) of the cytosine vibration at 787 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^{+} ions, respectively.

times increase slightly in the manganese(II) concentration range of 200–500 mM, before starting to decrease (Fig. 8). However, the local maximum of this Raman band parameter, corresponding to both Na^{+} ions concentrations, has a lower value as compared to the global relaxation time characterizing the initial concentration of 0 mM Mn^{2+}, respectively.

On the basis of our experimental results, the molecular relaxation processes are slower for the dA residues (characteristic band around 729 cm^{-1}), as compared to those of the dC residues (characteristic vibration at 787 cm^{-1}).

Previously, it was established, that all the studied adenine, thymine, and uracil vibrations have

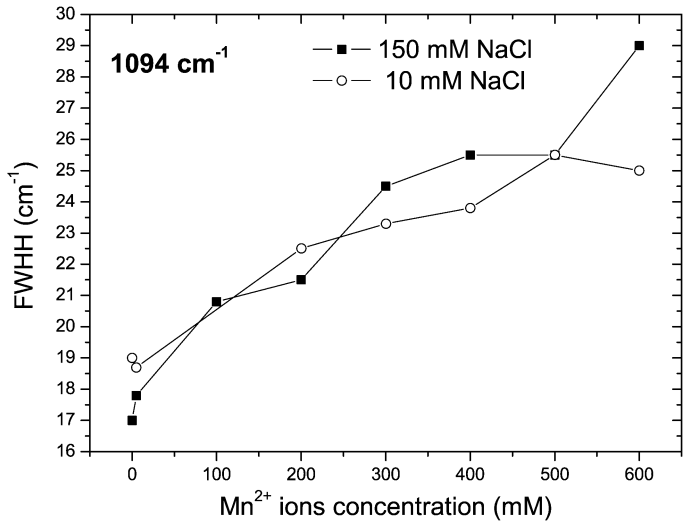

Fig. 3. Half bandwidth (FWHH) of the DNA backbone PO_2^- symmetric stretching vibration at 1094 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^+ ions, respectively.

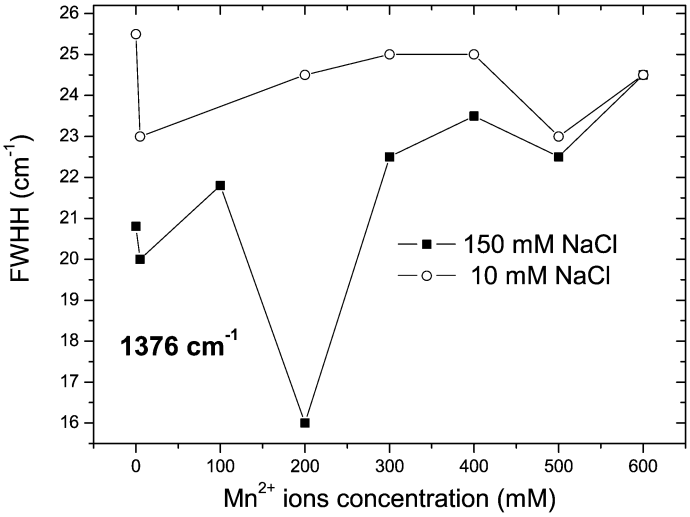

Fig. 4. Half bandwidth (FWHH) characteristic to the purines (dA, dG) and pyrimidines (dT, dC) residues vibration at 1376 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^+ ions, respectively.

a smaller bandwidth in stacked structures than in unstacked structures and mononucleotides [4].

Based on our data, the global relaxation time of the band near 1094 cm^{-1} of the DNA backbone PO_2^- symmetric stretching vibration [22,23], has a tendency to decrease upon increasing the Mn^{2+} ions concentration between 0–600 mM (Fig. 9). Mn^{2+}-induced calf-thymus DNA structural changes result for the vibration at 1094 cm^{-1} in larger half bandwidths, upon increasing the concentration of divalent metal cations (Fig. 3). The fastest dynamics was observed for this band at 600 mM Mn^{2+} in the case of DNA samples at 150 mM NaCl (global relaxation time 0.366 ps) and at 500 mM Mn^{2+} in the case of DNA samples at 10 mM NaCl (global relaxation time 0.410 ps). However, the molecular

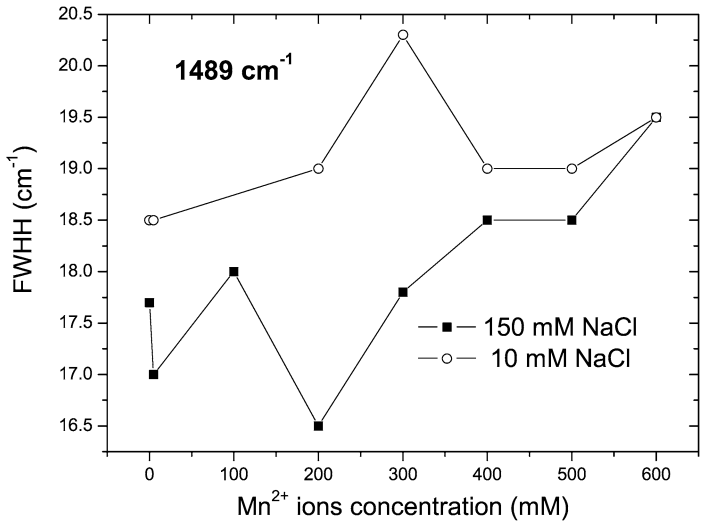

Fig. 5. Half bandwidth (FWHH) of the guanine (N-7) and adenine rings vibration at 1489 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^{+} ions, respectively.

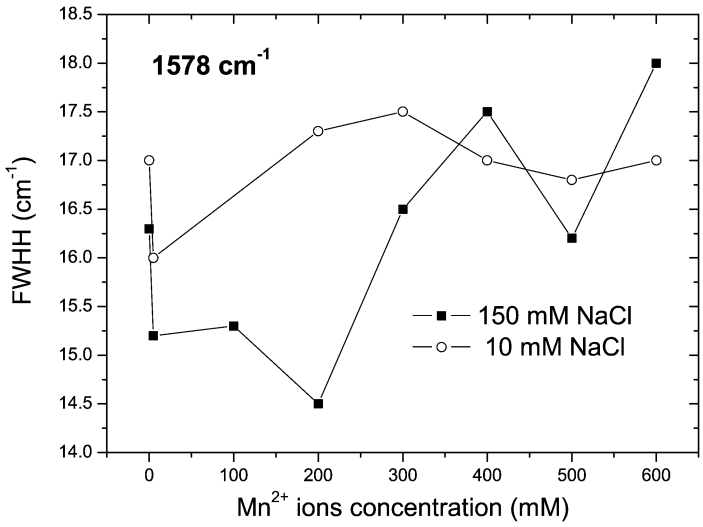

Fig. 6. Half bandwidth (FWHH) of the purines (dG, dA) 1578 cm^{-1} vibration in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^{+} ions, respectively.

relaxation processes of the 1094 cm^{-1} vibration, in MnDNA complexes, seem not to be influenced by the concentration of Na^{+} ions, in the limits of our experimental conditions.

Upon increasing Mn^{2+} ions concentration, the global relaxation times characterizing the bands at 1376, 1489 and 1578 cm^{-1}, exhibit a nonlinear behaviour, indicating slower relaxation processes in the case of higher Na^{+} concentration, as compared to the lower one, in almost all Mn^{2+} ions concentration range (Figs 10–12). This last observation is in contradiction with the dynamics characterizing the vibrations at 729, 787 and 1094 cm^{-1}.

The behaviour of the Raman band parameters of the purines (dA, dG) and pyrimidines (dT, dC)

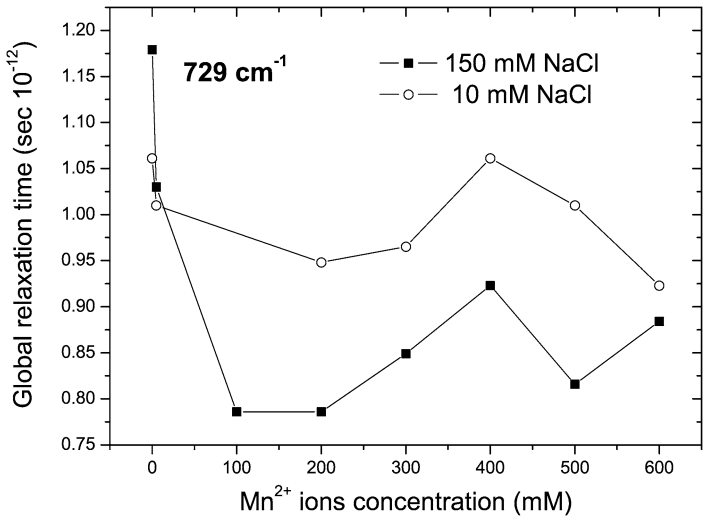

Fig. 7. Global relaxation time of the adenine vibration at 729 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^{+} ions, respectively.

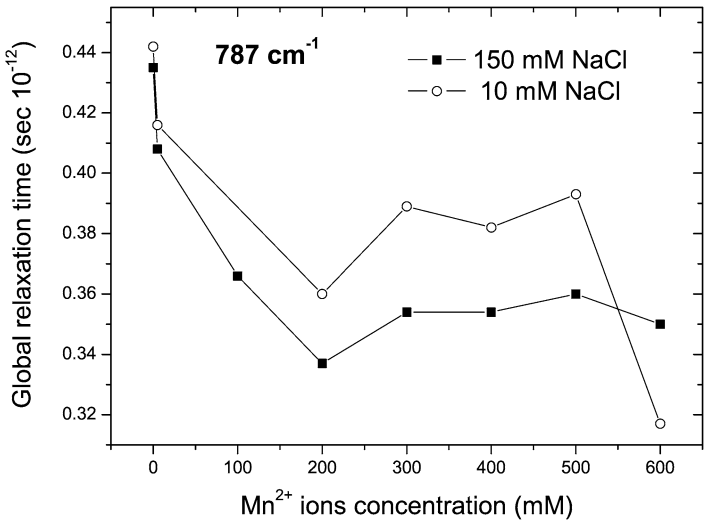

Fig. 8. Global relaxation time of the cytosine vibration at 787 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^{+} ions, respectively.

residues band at 1376 cm^{-1} [17–19], the guanine (N-7) and adenine rings vibration at 1489 cm^{-1} [16, 17] and the purines (dG, dA) 1578 cm^{-1} vibration ([21] and references therein) of calf-thymus DNA are not identical in the case of the samples at high Na^{+} concentration as compared to the corresponding samples at low Na^{+} ions content, upon changing the Mn^{2+} ions concentration.

The vibrational energy transfer processes are slowest for the vibrations at 1376, 1578 cm^{-1}, in the case of DNA samples at 150 mM NaCl, around 200 mM Mn^{2+} (global relaxation times 0.663 ps for the 1376 cm^{-1} band and 0.732 ps for the 1578 cm^{-1} band, respectively). The highest value of the global relaxation time is observed for the band at 1489 cm^{-1} around 0 mM Mn^{2+}, in the case of DNA samples

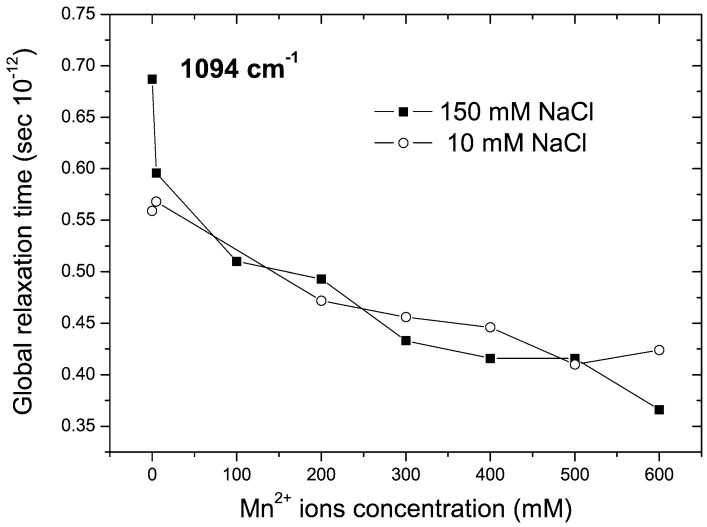

Fig. 9. Global relaxation time of the DNA backbone PO_2^- symmetric stretching vibration at 1094 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^+ ions, respectively.

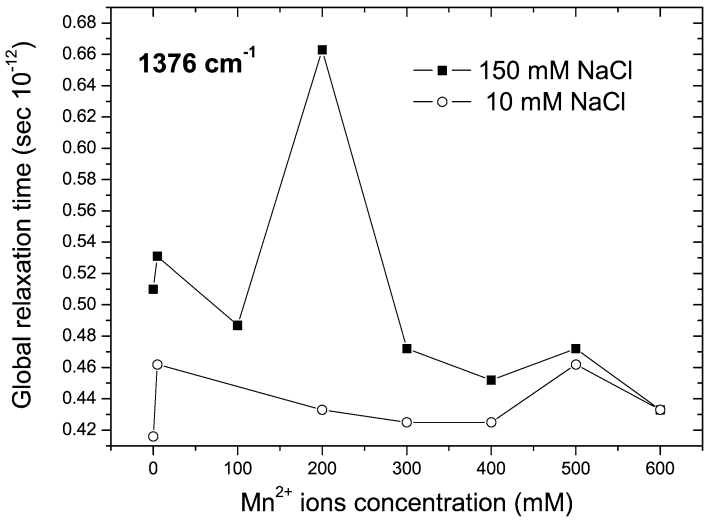

Fig. 10. Global relaxation time characteristic to the purines (dA, dG) and pyrimidines (dT, dC) residues band at 1376 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^+ ions, respectively.

at 150 mM NaCl (0.660 ps), being comparable with the value at 200 mM Mn^{2+} (0.643 ps). The fastest dynamics is observed for the vibrations at 1489, 1578 cm^{-1} around 300 mM Mn^{2+} in the case of DNA samples at 10 mM NaCl (global relaxation times 0.523 ps for the 1489 cm^{-1} band and 0.607 ps for the 1578 cm^{-1} band, respectively). The global relaxation time characteristic to the DNA bases vibration at 1376 cm^{-1} does not change too much upon varying the Mn^{2+} ions concentration, in the case of DNA samples at 10 mM NaCl (Fig. 10).

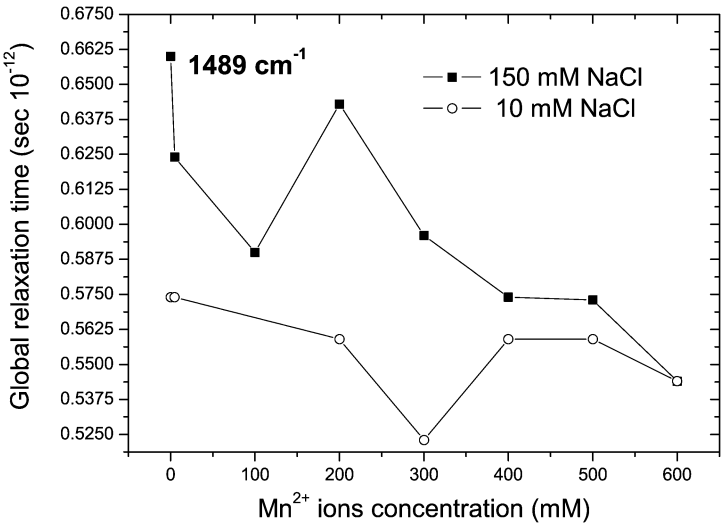

Fig. 11. Global relaxation time of the guanine (N-7) and adenine rings vibration at 1489 cm^{-1} in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^{+} ions, respectively.

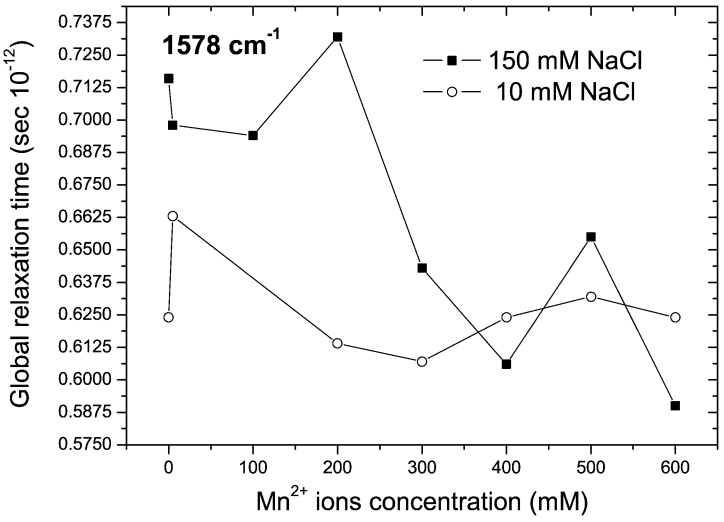

Fig. 12. Global relaxation time of the purines (dG, dA) 1578 cm^{-1} vibration in calf-thymus DNA, as a function of Mn^{2+} ions concentration, in the presence of Na^{+} ions, respectively.

4. Conclusions

Spontaneous Raman scattering can be used to study the fast (sub)picosecond dynamics of molecules [5]. This paper presents a Raman spectroscopic study into the vibrational total half bandwidths of molecular subgroups in calf-thymus DNA, upon changing the concentrations of Mn^{2+} ions, in the presence of two different concentrations 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), 787 cm^{-1} (dC), 1094 cm^{-1} (PO_2^-), 1376 cm^{-1} (dA, dG, dT, dC), 1489 cm^{-1} (dG, dA) and 1578 cm^{-1} (dG, dA) of calf-thymus DNA.

The study of vibrational half bandwidths of calf-thymus DNA revealed a sensitivity of these bandwidths to the concentration of divalent and monovalent cations, respectively. Moreover, this proved to be dependent on the vibration under study.

The Raman half bandwidths of calf-thymus DNA vibrations reveal a dynamic picture on a (sub)picosecond time scale. The full-widths at half-height (FWHH) of the bands in calf-thymus DNA are typically in the wavenumber range from 9 to 33.5 cm^{-1}. The bandwidths in the Raman spectra are sensitive to a dynamics active on a time scale from 0.317 to 1.179 ps.

Mn^{2+}-induced DNA structural changes result for the vibrations at 729 and 787 cm^{-1} in smaller global relaxation times, and larger half bandwidths, respectively, as compared to the starting value of 0 mM Mn^{2+}. The molecular dynamics of these two subgroups (dA, dC), respectively, is slower in the case of DNA samples at 10 mM NaCl, as compared with the corresponding samples at 150 mM NaCl, however the behaviour of the global relaxation times characteristic to these two values of Na^+ ions content, is similar with respect to manganese(II) ions concentration, in each case. On the contrary, the vibrational energy transfer processes are slower for the base vibrations at 1376, 1489 and 1578 cm^{-1}, in the case of DNA samples at 150 mM NaCl, as compared to the corresponding samples at lower Na^+ concentration, in almost all Mn^{2+} ions concentration range. In these three cases, respectively, the behaviour of the global relaxation time is quite different for the corresponding samples with different Na^+ content, upon increasing divalent metal ions concentration.

A decay of the global relaxation time, characterizing the vibration near 1094 cm^{-1} of calf thymus DNA, is observed upon increasing the Mn^{2+} ions concentration and seems not to be influenced by the concentration of Na^+ ions, in our experimental conditions.

We have found that the molecular dynamics is slower for the dA residues (characterizing band around 729 cm^{-1}), as compared to the relaxation processes of the dC residues (characterizing vibration at 787 cm^{-1}).

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