Molecular Relaxation Processes in Nucleic Acids Components as Probed with Raman Spectroscopy

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In this work the Raman total half bandwidths of five free nucleic acids components (cytidine - 5' - monophosphate, 2' - deoxycytidine 5' - monophosphate, 2' - deoxyguanosine - 5' - monophosphate, thymidine - 5' - monophosphate disodium salt hydrate and uridine - 5' - monophosphate disodium salt) have been measured, respectively. Raman scattering can be used to study the fast molecular relaxation processes of free nucleic acids components in solid phase. The dependencies of the total half bandwidths and of the corresponding global relaxation times, on functional groups and on the type of DNA and RNA constituents, are reported. In our study, the full widths at half-maximum (FWHMs) for the Raman bands of these nucleic acids components, are typically in the wavenumber range from 9 to 28 cm^{-1}. Besides, it can be observed that the (sub)picosecond dynamics studied in this work, has a global relaxation time value smaller than 1.18 ps and larger than 0.38 ps. We have found that the band centered at 1264 cm^{-1} for cytidine - 5' - monophosphate, the profile near 1373 cm^{-1} attributed to thymidine - 5' - monophosphate disodium salt hydrate and the band around 1233 cm^{-1} attributed to uridine - 5' - monophosphate disodium salt, respectively, are suitable for studying the dynamical behavior of molecular fragments in nucleic acids components. For the case of solid phase samples of nucleic acids components, we can suppose that the dominant relaxation mechanism is of the vibrational type one.

Keywords: nucleic acids components, Raman spectroscopy, full width at half-maximum (FWHM), (sub)picosecond global relaxation time

Vibrational relaxation processes play a crucial role in many aspects of physics, chemistry and biology ([1, 2] and references therein). Biological world is one of perpetual movement. The dynamics of biomolecules is thus a fundamental component of their behavior. Particularly, DNA polymer has a complex dynamics, being the key molecule in the genetic material of the living cell. The static structures of nucleic acids must function in dynamic processes in the living cell, through participation in specific interactions with other molecules.

Among the techniques available for the study of molecular motions in condensed phases, Raman scattering has the distinct advantage, that it enables simultaneous analyses of both reorientational and vibrational dynamics ([3-6] and references therein).

The vibrational excitation energy will be used for intermolecular and in a lesser extent for intramolecular energy transfer through different vibrational relaxation channels and reorientational motions. The magnitude of the global relaxation time reflects a faster or a slower energy transfer through the relaxation mechanisms ([7] and references therein).

The Raman bands of some nucleic acid components have been analyzed in order to obtain information about their dynamics and vibrational relaxation processes in solution [7-9]. Study of dynamics of the functional groups in purinic and pyrimidinic compounds can give information on their mobility and interactions. Particularly, the charged phosphate group in nucleotides and nucleic acids is responsible for interactions with counterions and important features of the reactivity of these molecules [1]. For this reason, the analysis of the IR $\nu_s(PO_3^{2-})$ band shape of disodium deoxycytidine 5'-monophosphate, 5'-dCMP, in H_2O and ^2H_2O solutions at different concentrations and temperatures, providing information on the relaxation and dynamics of the phosphate group was completed. The second derivative spectra revealed the presence of 5'-dCMP aggregates at certain concentrations. A similar self-association process was observed for mononucleotide 5'-CMP [1].

In this paper Raman total half bandwidths of five free nucleic acids components (cytidine - 5' - monophosphate, 2' - deoxycytidine 5' - monophosphate, 2' - deoxyguanosine - 5' - monophosphate, thymidine - 5' - monophosphate disodium salt hydrate and uridine - 5' - monophosphate disodium salt) in solid phase, respectively, have been measured. The dependencies of the total half bandwidths and of the corresponding global relaxation times on molecular fragments and on the type of nucleic acid compound are reported. Molecular relaxations corresponding to different vibrational modes of nucleic acids components have been investigated. It was shown, that (sub)picosecond dynamics of functional groups in nucleic acids components, can be monitored with Raman spectroscopy.

Experimental part

Chemicals

Cytidine - 5' - monophosphate (C-1131 Sigma), 2' - Deoxycytidine 5' - monophosphate (D-7750 Sigma), 2' - Deoxyguanosine - 5' - monophosphate (D-9625 Sigma), Thymidine - 5' - monophosphate disodium salt hydrate (89290 Fluka) and Uridine - 5' - monophosphate disodium

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salt (94352 Fluka) have been used without further purification.

Raman spectroscopy

Powders of nucleic acids components were put on coverslips, respectively. A drop of distilled water has been used in each case to glue the sample on the glass. Raman spectra of nucleic acids components were measured after water evaporation.

The experimental part of this work was carried out at Department of Proteomics, Institute for Analytical Sciences, Dortmund, Germany.

Standard Raman measurements have been done at room temperature, using a KAISER Raman HoloSpec f/1.8i spectrometer, with an approximately 3 cm^{-1} spectral resolution. 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 was about 15.4 mW [10].

The Raman band parameters (full widths at half-maximum FWHMs and global relaxation times) were determined for the five mentioned molecules.

For each experimental band profile, an individual baseline was taken into account. FWHMs of the bands were obtained using SpectraCalc software. The FWHMs were evaluated from the half maximum experimental Raman bands.

For the cases of overlapped Raman profiles, only half of the total half bandwidth (FWHM), in the side where the bands were not superposed, was taken into account and later on it was multiplied by two.

Results and discussions

Raman spectral profiles of five nucleic acids components are given in figures 1-5, in the region 500-1800 cm^{-1}. Labels indicate wavenumber values for prominent bands in each spectrum (cm^{-1} units). Molecular structures of nucleic acids components, including atom numbering are also presented, respectively [11-15].

In this work cytidine - 5' - monophosphate, 2' - deoxycytidine 5' - monophosphate, 2' - deoxyguanosine - 5' - monophosphate, thymidine - 5' - monophosphate disodium salt hydrate and uridine - 5' - monophosphate disodium salt, respectively, have been studied from the (sub)picosecond relaxation processes point of view.

Relating to molecular relaxation processes, Rakov developed one of the well-known procedures of obtaining the relaxation times and the activation energy ([5-6, 16] and references therein). As a first approximation, one can assume, the existence of a global relaxation time,τ, obtained from the total Raman half band width. This band parameter can be related with the intrinsic parameters of the analyzed system through the relationship:

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

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. $\Delta \nu_{1/2}^{1R,2R}$ are obtained from IR and Raman bands, respectively.

For the case of solid phase samples of nucleic acids components, 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 reflects mostly the quasi equilibrium positions of the functional groups under study [17].

In this paper we will concentrate on the vibrational band widths. Only the relatively isolated nucleic acids components vibrations will be considered ([5] and references therein). A study into the Raman vibrational bandwidths and into the corresponding global relaxation times of molecular fragments in nucleic acids components, respectively, is of interest.

The Raman band parameters for the vibrations near 582 cm^{-1}, 627 cm^{-1}, 716 cm^{-1}, 1264 cm^{-1}, 1350 cm^{-1}, 1432 cm^{-1} and 1543 cm^{-1}, characteristic to cytidine - 5' - monophosphate are summarized in table 1. Also, the Raman band parameters attributed to the vibrational modes of 2'-deoxycytidine 5'-monophosphate, 2' - deoxyguanosine - 5' - monophosphate, thymidine -5'-monophosphate disodium salt hydrate and uridine -5'-monophosphate disodium salt are presented in tables 2-5, respectively.

The full widths at half-maximum (FWHM) of the Raman bands in nucleic acids components are typically in the wavenumber range from 9 to 24 cm^{-1} for data presented in table 1 (cytidine - 5' - monophosphate) and from 10.5 to 19 cm^{-1} for data in table 2 (2' - deoxycytidine 5' - monophosphate). Besides, they vary between 18-25 cm^{-1} for 2' - deoxyguanosine - 5' - monophosphate (table 3), in the wavenumber range 24.5-28 cm^{-1} for thymidine - 5' - monophosphate disodium salt hydrate (table 4) and between 12-16.5 cm^{-1} for uridine - 5' - monophosphate disodium salt (table 5), respectively.

The global relaxation times were evaluated on the basis of eq. 1.

It can be observed that the global relaxation times of functional groups in the investigated DNA and RNA components are slower than 0.38 ps and faster than 1.18 ps for different vibrational modes. The fastest vibrational energy transfer process was obtained for the thymidine - 5' - monophosphate disodium salt hydrate band at 1373 cm^{-1} (global relaxation time 0.38 ps) and the slowest dynamics was found for the cytidine - 5' - monophosphate band near 1350 cm^{-1} (global relaxation time 1.18 ps).

We will analyze in the following, data presented in tables 1-2.

The cytidine - 5' - monophosphate Raman bands are characterized by global relaxation times in the subpicosecond range between 0.44-1.18 ps (see Table 1). The fastest dynamics was found for the stretching mode of the ring (N1-C2-N3) near 1264 cm^{-1} and the slowest energy transfer was detected in the case of the C=C-H bending mode at 1350 cm^{-1}. Global relaxation times of 0.56 ps have been found by us for the vibrational bands of cytidine - 5' - monophosphate at 582 cm^{-1} and near 627 cm^{-1}, both being attributed to the deformation mode of ring (C2-N3-C4). Also, in the case of this compound's profiles around 716 cm^{-1} (cytosine + ribose) and 1432 cm^{-1} [deformation mode OH (ribose)], the corresponding global relaxation times calculated on the basis of the FWHMs were found to be 0.76 ps.

Besides, vibrational energy transfer processes, characterized by global relaxation times between 0.56-1.01 ps have been found by us for functional groups in 2' - deoxycytidine 5' - monophosphate (table 2). The low limit value of this range corresponds to the band near 623 cm^{-1}, attributed to the deformation mode of ring (C2-N3-C4). For this compound we have also observed the maximum value of 1.01 ps for the stretching mode near 966 cm^{-1} [ν(C4-C5)].

In the following we will compare the Raman band parameters corresponding to similar functional groups in the cytosine-based compounds (cytidine- 5'- monophosphate, 2' - deoxycytidine 5' - monophosphate).

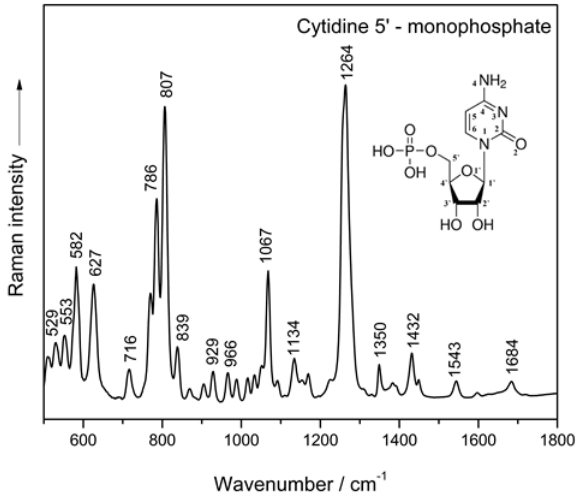

Fig. 1. Raman spectrum of cytidine - 5' - monophosphate compound. Exposure time: 50 s; 5 accumulations; laser power at the sample: 15.4 mW. The molecular structure of the investigated compound, including atom numbering, is also illustrated

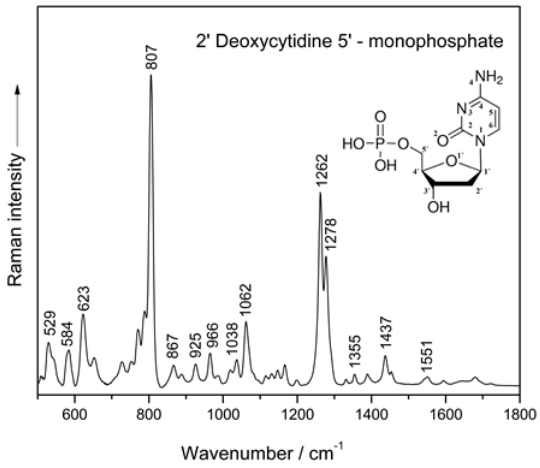

Fig. 2. Raman spectrum of 2 - deoxycytidine 5'- monophosphate compound. Exposure time: 40 s; 5 accumulations; laser power at the sample: 15.4 mW. The molecular structure of the investigated compound, including atom numbering, is also illustrated

υ_{max} (cm^{-1}) [a]	$\Delta\upsilon_{1/2}$ (cm^{-1})	τ (ps)	Tentative assignment [a]
582 m	19	0.56	δ ring (C2-N3-C4)
627 m	19	0.56	δ ring (C2-N3-C4)
716 w	14	0.76	cytosine + ribose
1264 vs	24	0.44	ν ring (N1-C2-N3)
1350 w	9	1.18	δ (C=C-H)
1432 w	14	0.76	δ OH (ribose)
1543 w	15	0.71	ν ring

[a] *Abbreviations: vs, very strong; m, medium; w, weak; δ, deformation mode; ν, stretching mode; δ bending mode.*

Table 1
TOTAL HALF BAND WIDTHS (cm^{-1}) OF RAMAN VIBRATIONAL MARKERS, GLOBAL RELAXATION TIMES OF FUNCTIONAL GROUPS (ps) AND OBSERVED WAVENUMBERS (cm^{-1}) FOR CYTIDINE - 5' - MONOPHOSPHATE COMPOUND. SEE FIGURE 1 FOR ATOM NUMBERING IN CYTIDINE - 5' - MONOPHOSPHATE COMPOUND [7, 11, 14, 18, 19]

υ_{max} (cm^{-1}) [a]	$\Delta\upsilon_{1/2}$ (cm^{-1})	τ (ps)	Tentative assignment [a]
584 w	17	0.62	δ ring (C2-N3-C4)
623 m	19	0.56	δ ring (C2-N3-C4)
807 vs	12.5	0.85	Ring breathing
966 w	10.5	1.01	ν (C4-C5)
1062 m	12.7	0.84	ν N1-C_{ribose}
1262 s	11[lf]	0.97	ν ring (N1-C2-N3)
1278 m	14[hf]	0.76	ν ring (N3-C4)
1437 w	13.3	0.80	δ OH (ribose)

[a] *Abbreviations: vs, very strong; s, strong; m, medium; w, weak; δ, deformation mode; ν, stretching mode.*
[lf] *- Low frequency side of the band was read; later on the respective profile was symmetrized.*
[hf] *- High frequency side of the band was read; later on the respective profile was symmetrized.*

Table 2
TOTAL HALF BAND WIDTHS (cm^{-1}) OF RAMAN VIBRATIONAL MARKERS, GLOBAL RELAXATION TIMES OF FUNCTIONAL GROUPS (ps) AND OBSERVED WAVENUMBERS (cm^{-1}) FOR 2' - DEOXYCYTIDINE 5' - MONOPHOSPHATE COMPOUND. SEE FIGURE 2 FOR ATOM NUMBERING IN 2' - DEOXYCYTIDINE 5' - MONOPHOSPHATE COMPOUND [7, 11, 14, 18, 19]

The global relaxation time of the cytidine-5'-monophosphate band near 582 cm^{-1} [deformation mode of ring (C2-N3-C4)] has the value of 0.56 ps. Comparatively, in the case of 2' - deoxycytidine 5' - monophosphate mode at 584 cm^{-1} [δ ring (C2-N3-C4)], the vibrational energy transfer process is characterized by a global relaxation time of 0.62 ps, reflecting changes in the atomic neighborhood of the molecular fragment under study. Identical values of the Raman global relaxation times have been found for the bands at 627 cm^{-1} [δ ring (C2-N3-C4)] and 623 cm^{-1} [δ ring (C2-N3-C4)], respectively, in the case of solid phase cytosine-based compounds, respectively (0.56 ps).

Besides, we have observed a global relaxation time of 0.44 ps for the cytidine - 5' - monophosphate profile near 1264 cm^{-1} [ν ring (N1-C2-N3)]. A slower dynamics was

found by us for the 2' - deoxycytidine 5' - monophosphate corresponding band at 1262 cm^{-1} attributed to the stretching mode of ring (N1-C2-N3) (0.97 ps).

The global relaxation time of the cytidine - 5' - monophosphate band near 1432 cm^{-1}, assigned to δ OH (ribose) vibration was established to be 0.76 ps, as compared with the corresponding global relaxation time of the 2' - deoxycytidine 5' - monophosphate band near 1437 cm^{-1}, attributed to the same mode (0.80 ps).

We will also discuss data in tables 3-5, in the next paragraphs.

Vibrational energy transfer processes, characterized by global relaxation times between 0.42-0.59 ps have been found in this study for molecular fragments in 2' - deoxyguanosine - 5' - monophosphate (table 3). The fastest relaxation process was found for the deformation modes of ring (6) and ring (5) (685 cm^{-1}) and the slowest one was detected in the case of the vibration near 860 cm^{-1} (out-of-plane bending mode N9-H). Also, we have found a fast dynamics for the δ_{ip} N1-H and ν ring (6) modes near 1365 cm^{-1} in this compound (global relaxation time 0.53 ps).

Referring to thymidine - 5' - monophosphate disodium salt hydrate bands (table 4), the vibrational energy transfer processes are characterized by global relaxation times ranging between 0.38-0.43 ps. The smallest global relaxation time was found for the ring stretching mode and CH_3 bending mode near 1373 cm^{-1} and the slowest dynamics, was observed for the ring stretching mode around 1238 cm^{-1} .

The uridine - 5' - monophosphate disodium salt Raman bands are characterized by global relaxation times in the subpicosecond range between 0.64-0.88 ps (table 5). The fastest dynamics was found for the deformation mode of OH (ribose) and in plane deformation mode of N3-H near 1398 cm^{-1}. Also the slowest dynamics was detected in the case of δ ring and í ring modes at 1014 cm^{-1}. Besides, global relaxation times of 0.76 ps each have been found by us for the Raman profiles of uridine - 5' - monophosphate disodium salt at 781 cm^{-1} (ring breathing) and near 899 cm^{-1}, respectively. A faster dynamics of the ring stretching mode in thymidine - 5' - monophosphate disodium salt hydrate at 1238 cm^{-1} was detected (global relaxation time 0.43 ps), as compared with the ring stretching mode (N1-C2-N3) in uridine - 5' - monophosphate disodium salt found near 1233 cm^{-1} (global relaxation time 0.66 ps).

Based on our present data, a comparison between different ranges of the Raman band parameters, in the case of solid phase dynamics of functional groups in nucleic acids components, is given in table 6.

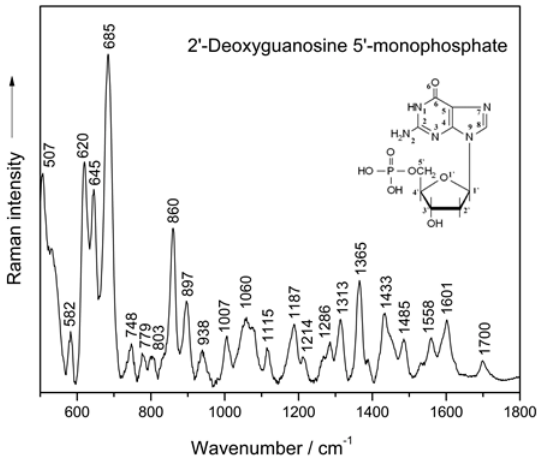

Fig. 3. Raman spectrum of 2' - deoxyguanosine - 5' - monophosphate compound. Exposure time: 25 s; 5 accumulations; laser power at the sample: 60 mW. The molecular structure of the investigated compound, including atom numbering, is also illustrated.

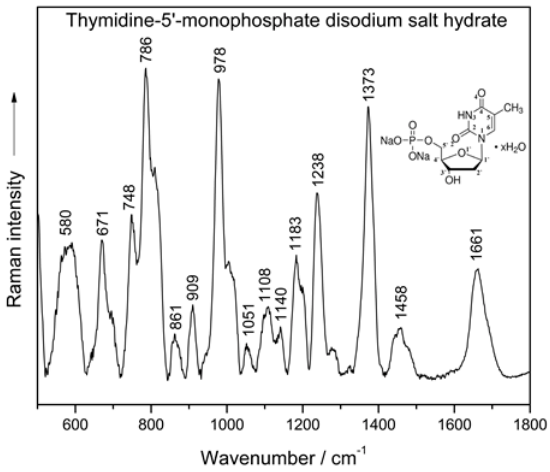

Fig. 4. Raman spectrum of thymidine - 5' - monophosphate disodium salt hydrate compound. Exposure time: 60 s; 5 accumulations; laser power at the sample: 15.4 mW. The molecular structure of the investigated compound, including atom numbering, is also illustrated

υ_{max} (cm^{-1}) [a]	$\Delta\upsilon_{1/2}$ (cm^{-1})	τ (ps)	Tentative assignment [a]
685 vs	25	0.42	δ ring (6) + δ ring (5)
860 m	18	0.59	δ (N9-H) out-of-plane
1365 m	20	0.53	δ_{ip} N1-H; ν ring (6)

[a] *Abbreviations: vs, very strong; m, medium; δ, deformation mode; δ, bending mode; ν, stretching mode; ip, in plane. Number in brackets (5) and (6) indicates five-membered and six-membered ring, respectively.*

Table 3

TOTAL HALF BANDWIDTHS (cm^{-1}) OF RAMAN VIBRATIONAL MARKERS, GLOBAL RELAXATION TIMES OF FUNCTIONAL GROUPS (ps) AND OBSERVED WAVENUMBERS (cm^{-1}) FOR 2' - DEOXYGUANOSINE - 5' - MONOPHOSPHATE COMPOUND. SEE FIGURE 3 FOR ATOM NUMBERING IN 2' - DEOXYGUANOSINE - 5' - MONOPHOSPHATE COMPOUND [7, 11, 18, 19]

υ_{max} (cm^{-1}) [a]	$\Delta\upsilon_{1/2}$ (cm^{-1})	τ (ps)	Tentative assignment [a]
1238 s	24.5	0.43	ν ring
1373 vs	28	0.38	ν ring, δ CH_3

[a] *Abbreviations: s, strong; vs, very strong;* ν *- stretching mode;* δ *- bending mode.*

Table 4

TOTAL HALF BANDWIDTHS (cm^{-1}) OF RAMAN VIBRATIONAL MARKERS, GLOBAL RELAXATION TIMES OF FUNCTIONAL GROUPS (ps) AND OBSERVED WAVENUMBERS (cm^{-1}) FOR THYMIDINE - 5' - MONOPHOSPHATE DISODIUM SALT HYDRATE COMPOUND. SEE FIGURE 4 FOR ATOM NUMBERING IN THYMIDINE - 5' - MONOPHOSPHATE DISODIUM SALT HYDRATE COMPOUND [7, 11, 20]

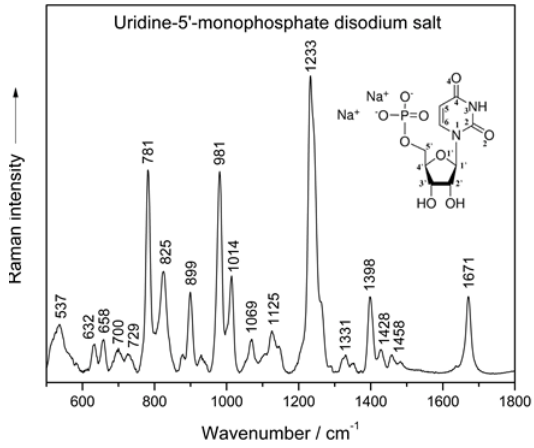

Fig. 5. Raman spectrum of uridine - 5' - monophosphate disodium salt compound. Exposure time: 8 sec; 5 accumulations; laser power at the sample: 60 mW. The molecular structure of the investigated compound, including atom numbering, is also illustrated

Table 5

TOTAL HALF BAND WIDTHS (cm^{-1}) OF RAMAN VIBRATIONAL MARKERS, GLOBAL RELAXATION TIMES OF FUNCTIONAL GROUPS (ps) AND OBSERVED WAVENUMBERS (cm^{-1}) FOR URIDINE - 5' - MONOPHOSPHATE DISODIUM SALT COMPOUND. SEE FIGURE 5 FOR ATOM NUMBERING IN URIDINE - 5' - MONOPHOSPHATE DISODIUM SALT COMPOUND [7, 11, 12, 18, 19]

υ_{max} (cm^{-1}) [a]	$\Delta\upsilon_{1/2}$ (cm^{-1})	τ (ps)	Tentative assignment [a]
781 s	14	0.76	ring breathing
899 m	14	0.76	
981 s	16.3	0.65	$\nu s\ PO_3^{2-}$
1014 m	12^{hf}	0.88	δ ring; ν ring
1233 vs	16^{lf}	0.66	ν ring (N1-C2-N3)
1398 m	16.5	0.64	δ_{ip} N3-H, δ OH (ribose)

[a] Abbreviations: s, strong; m, medium; vs, very strong; ν, stretching mode; S, symmetrical; δ, bending mode; δ, deformation mode; ip, in plane.

[hf] - High frequency side of the band was read; later on the respective profile was symmetrized.

[lf] - Low frequency side of the band was read; later on the respective profile was symmetrized.

Compound	FWHM range $\Delta\nu/cm^{-1}$	Global relaxation time range τ/ps
cytidine - 5' - monophosphate	9-24	0.44-1.18
2' - deoxycytidine 5' - monophosphate	10.5-19	0.56-1.01
2' - deoxyguanosine - 5' - monophosphate	18-25	0.42-0.59
thymidine - 5' - monophosphate disodium salt hydrate	24.5-28	0.38-0.43
uridine - 5' - monophosphate disodium salt	12-16.5	0.64-0.88

Table 6

COMPARISON BETWEEN RANGES OF THE RAMAN BAND PARAMETERS, IN THE CASE OF DIFFERENT NUCLEIC ACIDS COMPONENTS

Conclusions

The dynamics of nucleic acids and their components is crucial for biological function and plays a significant role in the molecular recognition of DNA-protein and DNA-ligand systems [21]. Relaxation processes of these biomolecules are thus a fundamental component of their behaviour.

This work presents a Raman spectroscopic study concerning the vibrational total half bandwidths of functional groups in five free DNA and RNA components (cytidine - 5' - monophosphate, 2' - deoxycytidine 5' - monophosphate, 2'- deoxyguanosine - 5' - monophosphate, thymidine - 5' - monophosphate disodium salt hydrate and uridine - 5' - monophosphate disodium salt), respectively. Besides, the corresponding global relaxation times have been derived.

We have shown that Raman scattering can be used to study the fast (sub)picosecond dynamics of molecular fragments in nucleic acids components.

The study of vibrational total half bandwidths of DNA and RNA components, revealed a sensitivity of FWHM to the type of free compound. Moreover, this proved to be dependent on the vibration under study. The Raman total half bandwidths of cytidine - 5' - monophosphate, 2' - deoxycytidine 5' - monophosphate, 2' - deoxyguanosine - 5' - monophosphate, thymidine - 5' - monophosphate disodium salt hydrate and uridine - 5' - monophosphate disodium salt vibrations, respectively, revealed a dynamic picture on a (sub)picosecond time scale.

In our study, the full widths at half-maximum (FWHMs) for the Raman bands of these nucleic acids constituents, are typically in the wavenumber range from 9 to 28 cm^{-1}. Besides, the bandwidths of the Raman vibrations of DNA and RNA components (tables 1-5) are sensitive to a dynamics active on a time scale from 0.38 to 1.18 ps.

A comparison between different ranges of the Raman band parameters, in the case of solid phase dynamics of functional groups in nucleic acids components, respectively, has also been given.

For the case of solid phase samples of nucleic acids components, 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 reflects mostly the quasi equilibrium positions of the functional groups under study.

In the future, a direct linkage between changes in the dynamics of DNA/RNA functional groups with physical-chemical parameters and some mechanisms which imply nucleic acids is possible to be established.

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