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Normal coordinate analysis of 5′-dGMP and its deuterated derivatives

A calculated approach to designate the guanine-residue vibration modes in B and Z forms of DNA

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Abstract. By calculations based on the Wilson GF-method and using a valence force field, the vibration modes of 5′-dGMP have been assigned. Good agreement was obtained between the calculated and experimental results corresponding to the Raman and infrared spectra of 5′-dGMP. The calculations can also predict the displacement of infrared bands observed upon selective deuteration on C 8 and simultaneously on the C 8, N 1 and N 2 atoms of the guanine ring. In order to preserve the harmonic approximation of the potential field, the redundancy between the internal coordinates is entirely removed using a $B \cdot \tilde{B}$ matrix-product diagonalization procedure. In this treatment the local symmetry of different constituents of the molecule is taken into consideration, thus avoiding extensive linear combinations of internal coordinates.

The extension of these calculations to the guanosine-moiety involved in the double helix structures of DNAs allowed us to reproduce a certain number of the characteristic guanine vibration modes altered by the $B \rightarrow Z$ transitions of poly(dG-dC) · poly(dG-dC) and $d(CG)_3 \cdot d(CG)_3$.

Key words: Normal coordinate analysis, 5′-dGMP, DNA, guanosine, poly(dG-dC) · poly(dG-dC) and $d(CG)_3 \cdot d(CG)_3$

Introduction

In recent years, the vibrational spectra of the nucleic acids, expecially those of DNA, have been extensively studied. Because of the conformational flexibility of DNA most of these studies have concentrated on the changes in Raman and infrared spectra as a function of the DNA structure (Pohl et al. 1973; Thamann et al. 1981; Taillandier et al. 1981; Pilet and Leng 1982; Nishimura et al. 1983; Benevides and Thomas 1983; Chinsky et al. 1984; Taboury et al. 1984). The interpretation of these spectra obviously requires a good knowledge of the base and phosphate-backbone vibration modes. From a theoretical point of view, finding a force field which faithfully reproduces all of the characteristic infrared and Raman bands needs a substantial investigation, because the number of force constants is always several times larger then the number of available experimental frequencies. Thus, the problem should be resolvable by studying the vibration modes of the different components appearing in the overall DNA macromolecular structure. The calculation of the vibrational spectra corresponding to the mononucleosides or mononucleotides can be considered as a first step in attaining this goal.

Our purpose in this paper is to study the vibration modes of 2′-deoxyguanosine 5′-monophosphate (5′-dGMP). The present work was possible because of the recent calculations on guanine and guanine-residue vibration modes (Majoube 1984; Majoube 1985) and those corresponding to tetrahydrofuran (Eyster and Prohofsky 1974a).

To test the validity of the force field obtained for 5′-dGMP, we have tried to use it in the case of the guanosine-moiety found in right handed (*B* form) and left-handed (*Z* form) poly(dG-dC) · poly(dG-dC). It was found that the geometry change corresponding to the $B \rightarrow Z$ transition can be considered to be responsible for the appearance of some characteristic Raman lines and infrared bands involving the guanine moiety vibrations.

Theory

The vibration mode calculations are based on the Wilson GF-method (Wilson et al. 1955). This matrix procedure, which is developed within the framework of the harmonic approximation of the potential field, gives rise to a secular equation for the

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molecular movement of the following form:

$$GFL = L\Lambda\,, \tag{1}$$

where G is the kinetic matrix and F reflects the interatomic interaction matrix involving the harmonic force constants. L represents the eigenvector matrix including the atomic displacements and Λ the diagonal matrix of which the element λ_i is proportional to the square of the i-th mode wavenumber, ν_i ($\lambda_i = 4\pi^2 C^2 \nu_i^2$).

The B matrix relates the column matrix, R (internal coordinates) to the column matrix, X (cartesian displacements) according to the equation:

$$R = BX\,. \tag{2}$$

The G matrix can be expressed as:

$$G = BM^{-1}\tilde{B}\,, \tag{3}$$

where M is the atomic mass diagonal matrix.

It is known (Mills 1969) that the harmonic approximation is valid if the vibration modes are calculated on a non-redundant basis of 3N-6 coordinates (N: number of atoms). Otherwise the first-order terms of the potential energy do not all vanish and the force constants are consequently not harmonic. The existence of redundant coordinates leads to the G matrix singularity. It can be shown (Gusoni and Zerbi 1968) that G matrix diagonalization gives as many null-eigenvectors as the number of redundant internal coordinates. In the case of low-symmetry molecules, such as 5′-dGMP, the geometry dependent part of the G matrix, i.e. $B \cdot \tilde{B}$ matrix product, reflects the same singularity. Thus, by diagonalizing $B \cdot \tilde{B}$ and eliminating the eigenvectors relative to the null-eigenvectors, one obtains a set of 3N-6 non-redundant coordinates, S, related to the redundant internal coordinates, R, by the intermediate of the orthogonal U matrix (Gusoni and Zerbi 1968):

$$S = UR\,. \tag{4}$$

Using Eq. (4), the secular equation (Eq. (1)) may be written as:

$$G_S F_S L_S = L_S \Lambda_S\,. \tag{5}$$

This equation is based on the S coordinates and gives 3N-6 vibration mode frequencies. Each mode is characterized by a normal coordinate Q_i ($i = 1, \ldots, 3N\text{-}6$) which is expressed as a linear combination of the S coordinates:

$$Q = L_S^{-1} S\,, \tag{6}$$

where L_S^{-1} is the inverse of the L_S matrix.

Obviously, the potential energy distribution (PED) calculated from Eq. (5) is expressed in terms of the independent S coordinates.

As there are 35 atoms in 5′-dGMP, one expects $3 \times 35 - 6 = 99$ vibration modes. Neglecting the 13 out-of-plane modes corresponding to the guanine-residue which are not considered in this work and will be explained in a forthcoming publication, our calculations have been performed on a set of $99 - 13 = 86$ independent S coordinates. 112 internal coordinates are numbered in 5′-dGMP (37 stretchings, 65 angular bendings and 10 torsion coordinates). So $112 - 86 = 26$ superfluous coordinates may be removed. To perform this, we have written a computer program which treats the redundancies in polyatomic molecules. The input includes the atomic cartesian coordinates and the definition of redundant internal coordinates for constructing the $B \cdot \tilde{B}$ matrix product. The output contains the non-redundant S coordinates which are the linear combinations of the internal coordinates (Eq. (4)). In order to calculate the B and $\tilde{B}$ matrices, the geometrical data for 5′-dGMP, found from X-ray patterns of disodium deoxyguanosine-5′-phosphate tetrahydrate, were used (Young et al. 1974). In order to avoid numerous, non-useful expressions for the S coordinates the redundant coordinates have been treated separately in the guanine-residue, the sugar and in the tetrahedral sites. The 86 coordinates thus obtained ($S_1, \ldots, S_{86}$) are listed in Tables 1 a, b, c.

To evaluate the F-matrix, a series of calculations based on the planar vibration modes of the nucleic acids bases involving the guanine-residue have been reported by Tsuboi et al. (1973) using a Urey-Bradley force field (UBFF). Recently, Majoube (1984) has performed a normal coordinate analysis of in-plane guanine modes using both UBFF and the simplified valence force field (SVFF). The calculated results which show the advantage of SVFF in comparison with UBFF (SVFF takes into account the π-electron delocalization in the molecular ring) are supported by some valuable Raman and infrared data on polycrystalline guanine and its deuterated and ^{15}N-substituted analogs. Majoube then extended his calculations to 9-methylguanine in which the methyl-group is considered as a rigid unit whose mass is concentrated on carbon (Majoube 1985). In this work we have employed Majoube's SVFF force constants.

As far as the sugar is concerned, we assume that the valence force field obtained for tetrahydrofuran and its deuterated analogs (Eyster and Prohofsky 1974a) is also valid for the 2′-deoxyribose found in 5′-dGMP. It should be mentioned that tetrahydrofuran presents a planar ring and belongs to the C_{2v} point group (Eyster and Prohofsky 1974a), while the 5′-dGMP sugar has an O1′-endo, C4′-exo conformation with overall C_1-symmetry (Young et al. 1974).

GUANINE-RESIDUE		
	COORDINATES	ASSIGNMENTS
S1	ν(C1'-N9)	glycosidic bond stretch
S2	ν(C8-H)	C8-H stretching
S3	ν(C6=O6)	C6=O stretching
S4	ν(N1-H)	N1-H stretching
S5	ν(C2-N2)	C2-N2 stretching
S6	0.707 [ν(N2-H)+ ν(N2-H')]	NH2-symmetric stretching
S7	0.707 [ν(N2-H)- ν(N2-H')]	NH2-antisymmetric stretching
S8	-0.475 δ(C2N2H) -0.338 δ(C2N2H')+0.813 δ(HN2H')	NH2-scissoring
S9	-0.664 δ(C2N2H) +0.743 δ(C2N2H')-0.079 δ(HN2H')	NH2-rocking
S10	0.599 ν(C5-N7) -0.412 ν(N3-C4) -0.290 δ(C1'N9C8)	
S11	-0.378 δ(C6N1H) +0.373 δ(C2N1H) +0.273 δ(C5C4C6)	
S12	0.383 ν(N3-C4) -0.335 ν(C5-C6) +0.281 δ(C2N1C6)	
S13	0.669 ν(N1-C6) +0.396 ν(N3-C4) +0.282 ν(C8-N9)	
S14	0.598 ν(N1-C2) +0.417 ν(C8-N9) +0.281 ν(C4=C5)	
S15	0.464 ν(C2=N3) +0.452 ν(C4=C5) -0.301 ν(C5-N7)	
S16	-0.578 ν(C5-C6) -0.327 ν(C5-N7) -0.313 ν(C4-N9)	
S17	-0.328 δ(C2N1C6)-0.320 δ(N1C6O6)-0.321 δ(C5C4N3)	
S18	-0.412 δ(C1'N9C8)+0.402 δ(N9C8H)-0.335 δ(N7C8N9)	
S19	0.451 δ(N7C8H) -0.406 δ(N9C8H)+0.261 δ(C5N7C8)	
S20	-0.428 ν(C4-N9) +0.417 ν(C2=N3) -0.386 ν(N7=C8)	
S21	-0.387 δ(N7C8H) +0.390 δ(N7C8N9)-0.357 δ(C5C6O6)	
S22	0.385 ν(C4-N9) +0.384 δ(N3C4N9)+0.338 ν(C2=N3)	
S23	0.535 δ(N3C2N2)-0.341 δ(N1C2N2)+0.282 δ(C1'N9C4)	
S24	0.320 δ(C5N7C8)-0.288 δ(N1C2N2)-0.281 δ(C1'N9C4)	
S25	0.444 ν(N1-C2) -0.400 ν(C8-N9) -0.286 δ(C1'N9C8)	
S26	-0.432 δ(C6N1H) +0.314 δ(C2N1H) +0.309 δ(N3C4N9)	
S27	0.365 δ(C2N1H) +0.314 δ(N1C2N3)-0.313 δ(C4C5C6)	
S28	0.338 δ(N1C2N3)+0.301 ν(C5-C6) -0.262 ν(C2=N3)	
S29	-0.498 ν(N7=C8) +0.301 δ(C5C6O6)-0.271 ν(C2=N3)	

Table 1a. Expressions for the non-redundant S coordinates relative to the guanine-residue. As $B \cdot \tilde{B}$ does not depend upon the atomic masses, the same coordinates are used in the calculations of the vibration modes of the 5′-dGMP deuterated analogs. In this table: ν designates a stretching coordinate and δ a bending one. Only the major contributions are reported

The complementary force constants are listed in Table 2. Their initial values are from Eyster and Prohofsky (1974a, b). As the phosphate-group in 5′-dGMP has C_{3v}-symmetry and is thus completely different from the same group included in nucleic acid chains (Eyster and Prohofsky 1974b), the corresponding force constants have been refined by a least-squares method in order to improve the agreement between the experimental and calculated results.

To resolve the secular equation (Eq. (5)) the NCTB program was used (Shimanouchi 1968). Frequencies of the 86 normal modes of 5′-dGMP have been calculated by introducing the atomic cartesian (Young et al. 1974) and the U-matrix of Eq. (4) (Table 1).

Results

A. 5′-dGMP and its deuterated derivatives

Raman spectra of 5′-dGMP at 30 °C have previously been published (Small and Peticolas 1971). The main peaks of these spectra are reported in Table 3. Infrared spectra of amorphous 5′-dGMP and its deuterated analogs have been discussed recently (Taboury et al. 1984) and are shown in Fig. 1 between 1800 and 600 cm^{-1}. The calculated frequencies and assignments of the vibration modes corresponding to 5′-dGMP, 5′-dGMP-d1 (C8-deuterated analog) and 5′-dGMP-d4 (C8, N1 and N2-deuterated analog) are listed in Tables 3 and 4 and compared to the experimental results. Due to the nature of the vibration modes, we present the calculated results for four distinct spectral regions:

1800–1200 cm^{-1} spectral region. Most of the observed Raman and infrared peaks are due to the guanine-residue in-plane vibration modes. The intense infrared band at 1697 cm^{-1} involves mainly the $\nu(C=0)$ stretching and NH2-scissoring modes. It is not affected by C8-deuteration but N1 and N2 deuteration leads to a displacement of about − 11 cm^{-1} of this band, as predicted by the calculations The 1660 cm^{-1} infrared band is not resolved in 5′-dGMP and 5′-dGMP-d4 spectra (Fig. 1) and has

SUGAR		
	COORDINATES	ASSIGNMENTS
S30	ν(C1'-H)	C1'-H stretching
S31	0.707 [ν(C2'-H)+ ν(C2'-H')]	CH2-symmetric stretching
S32	0.707 [ν(C2'-H)- ν(C2'-H')]	CH2 antisymmetric stretching
S33	ν(C3'-H)	C3'-H stretching
S34	ν(C3'-03')	C3'-03' stretching
S35	ν(C4'-H)	C4'-H stretching
S36	0.475 ν(C3'-C4') -0.428 ν(C2'-C3') +0.316 δ(01'C1'N9)	
S37	-0.456 δ(C2'C1'N9)+0.314 δ(C2'C1'H) -0.312 ν(C1'-C2')	
S38	0.500 δ(C2'C3'03')+0.347 δ(C4'C3'H)-0.338 δ(C2'C3'H)	
S39	0.438 δ(01'C4'C5')+0.423 ν(C1'-01')+0.362 ν(C4'-01')	
S40	0.464 δ(HC2'H) +0.346 ν(C1'-C2')-0.332 δ(C1'C2'C3')	
S41	0.446 δ(C3'C2'H) -0.349 ν(C2'-C3')-0.327 δ(HC2'H)	
S42	0.362 δ(C4'C3'H) -0.331 δ(C2'C3'03')+0.300 δ(C2'C1'N9)	
S43	0.453 δ(01'C4'H) -0.378 δ(C3'C4'C5')+0.302 ν(C4'-01')	
S44	-0.376 ν(C1'-01') +0.360 δ(N9C1'H) +0.323 ν(C4'-01'	
S45	0.368 δ(C2'C3'H) -0.362 δ(C3'C2'H) +0.350 δ(C1'C2'H)	
S46	-0.399 δ(C4'C3'H) -0.348 δ(01'C1'H) +0.296 ν(C4'-01')	
S47	-0.539 ν(C3'-C4') -0.330 δ(C3'C4'C5')+0.283 δ(C2'C3'03')	
S48	0.422 δ(HC2'H) -0.385 δ(C3'C4'H) +0.331 δ(C2'C1'H)	
S49	-0.365 δ(01'C4'H) -0.333 δ(C2'C3'C4')+0.282 δ(C2'C3'H)	
S50	-0.329 δ(C1'01'C4')-0.313 δ(01'C4'C5')-0.288 δ(C1'C2'H)	
S51	-0.496 δ(N9C1'H) +0.415 δ(03'C3'H) +0.408 δ(C3'C2'H)	
S52	-0.336 δ(C2'C1'H) -0.331 δ(C3'C4'C5')+0.307 δ(C5'C4'H)	
S53	0.396 δ(C1'C2'H) -0.336 ν(C2'-C3') -0.312 ν(C4'-01')	
S54	0.451 δ(C2'C3'H) -0.439 δ(C5'C4'H) +0.345 δ(HC2'H)	
S55	0.417 δ(C3'C4'H) -0.408 δ(C4'C3'03')-0.261 ν(C4'-01')	
S56	-0.439 δ(03'C3'H) +0.378 δ(01'C4'H) -0.377 δ(N9C1'H)	
S57	-0.367 δ(C3'C2'H) -0.360 δ(01'C4'C5')+0.311 δ(01'C1'H)	
S58	0.484 ν(C2'-C3') -0.392 ν(C1'-C2') +0.264 δ(C3'C4'C5')	
S59	0.493 ν(C1'-C2') +0.438 ν(C2'-C3') +0.263 δ(C2'C1'N9)	
S60	-0.335 ν(C3'-C4') -0.289 ν(C1'-C2') +0.284 ν(C2'-C3')	

Table 1b. Expressions of the non-redundant *S* coordinates relative to the sugar. In this table: *ν* designates a stretching coordinate and *δ* a bending one. Only the major contributions are reported

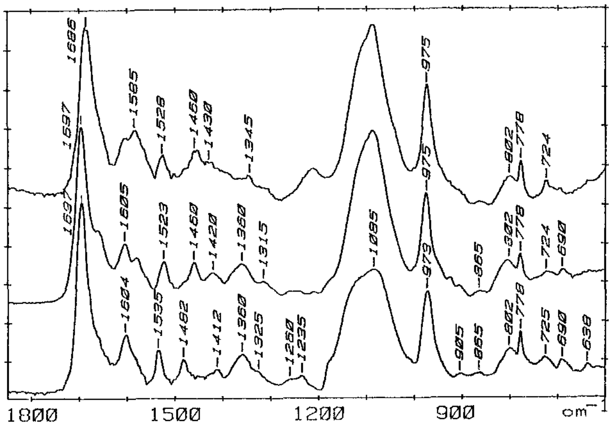

Fig. 1. Infrared spectra of 5′-dGMP and its deuterated derivatives. 5′-dGMP (bottom), 5′-dGMP-d1 (C8 deuterated) (middle) and 5′-dGMP-D4 (C8, N1 and N2 deuterated) (top)

a pyrimidic character. Its shift upon selective deuterations is negligible. The 1604 and 1580 cm^{-1} bands involve both pyrimidic and imidazolic modes of guanine. The localization of the modes responsible for the 1535 and 1482 cm^{-1} infrared bands, found in Raman spectra at 1542 and 1489 (Table 3), has been discussed in detail by several authors (Small and Peticolas 1971; Taboury et al. 1984). These calculations show that these bands include both the pyrimidic and imidazolic contributions. Their dependence on δ (C8-H) bending vibrations is proved by their relatively large shift upon C8-deuteration. The three bands at 1360, 1325 and 1260 cm^{-1} involve the puric vibrations. Finally, the infrared band at 1412 cm^{-1} (1421 Raman) is assigned to the δ(C-H) bendings and that at 1235 cm^{-1} to the skeletal vibration modes of the sugar ring.

Table 1c. Expressions of the non-redundant S coordinates relative to the C5′ and PO_3 tetrahedral sites in 5′-dGMP and the other coordinates involved in the calculations of the vibration modes. In this table: ν designates a stretching mode, δ a bending one and τ is relative to a torsion coordinate

	COORDINATES	ASSIGNMENTS
	C5'-TETRAHEDRON	
S61	ν(C4'-C5')	C4'-C5' stretching
S62	ν(C5'-O5')	C5'-O5' stretching
S63	0.707 [ν(C5'-H)+ ν(C5'-H')]	C5'H2 symmetric stretching
S64	0.707 [ν(C5'-H)- ν(C5'-H')]	C5'H2 antisymmetric stretching
S65	0.250 [δ(C4'C5'H)+ δ(C4'C5'H')- δ(O5'C5'H)- δ(O5'C5'H')]	C5'-wagging
S66	0.250 [δ(C4'C5'H)- δ(C4'C5'H')- δ(O5'C5'H)+ δ(O5'C5'H')]	C5'-twisting
S67	0.250 [δ(C4'C5'H)- δ(C4'C5'H')+ δ(O5'C5'H)- δ(O5'C5'H')]	C5'-rocking
S68	0.220 [- δ(C4'C5'H)- δ(C4'C5'H')- δ(O5'C5'H)- δ(O5'C5'H') +4.080 δ(HC5'H')]	C5'-scissoring
S69	0.189 [4.792 δ(C4'C5'O5')-1.018 δ(C4'C5'H)-1.019 δ(C4'C5'H') -1.019 δ(O5'C5'H) -1.019 δ(O5'C5'H')- δ(HC5'H')]	C5'-bending
	PO3-TETRAHEDRON	
S70	ν(P-O5')	P-O5' stretching
S71	0.577 [ν(P-O1)+ ν(P-O2)+ ν(P-O3)]	PO3-symmetric stretching
S72	0.408 [2 ν(P-O1)- ν(P-O2)- ν(P-O3)]	PO3-degenerate stretching
S73	0.707 [ν(P-O2)- ν(P-O3)]	PO3-degenerate stretching
S74	0.388 [-1.1 δ(O5'PO3)-1.1 δ(O5'PO1)-1.1 δ(O5'PO2)+ δ(O1PO3)- δ(O2PO3) + δ(O1PO2)]	PO3-symmetric deformation
S75	0.408 [2.0 δ(O1PO3) - δ(O2PO3) - δ(O1PO2)]	PO3-degenerate deformation
S76	0.707 [δ(O2PO3) - δ(O1PO2)]	
S77	0.408 [2.0 δ(O5'PO3)- δ(O5'PO1) - δ(O5'PO2)]	PO3-degenerate rotation
S78	0.707 [δ(O5'PO1)- δ(O5'PO2)]	
	OTHER COORDINATES	
S79	τ(C1'-N9)	glycosidic torsion
S80	ν(O3'-H)	O3'-H stretching
S81	δ(C3'O3'H)	C3'-O3'-H bending
S82	τ(C3'-O3')	C3'-O3' torsion
S83	τ(C4'-C5')	C4'-C5' torsion
S84	τ(C5'-O5')	C5'-O5' torsion
S85	τ(O5'-P)	O5'-P torsion
S86	δ(C5'O5'P)	C5'-O5'-P bending

Table 2. Complementary force constants of 5′-dGMP. (a) The initial values corresponding to the calculations on poly(rA)·poly(rU) (Eyster and Prohofsky 1974b). (b) Present work. The guanine-residue force constants are from Majoube (1985) and those corresponding to the sugar are those adopted by Eyster and Prohofsky (1974a) for tetrahydrofuran

STRETCH F.C.	VALUE (mdyn/A) (a)	(b)	BEND. F.C.	VALUE (mdyn.A) (a)	(b)
K(C3'-O3')	4.745	4.745	H(C-C-N)	1.508	1.508
K(C5'-O5')	4.342	4.342	H(O-C-N)	1.163	1.363
K(C4'-C5')	4.652	4.652	H(C-O-P)	1.496	1.496
K(P-O5')	6.02(P O)	4.310	H(O5' P -O)	1.612(O-P=O)	1.612
K(P-O)	7.80(P=O)	6.50	H(O-P-O)	1.701(O-P-O)	1.459
K(O3'-H)		5.534	H(C3'-O3'-H)		0.530
ST.ST. F.C.	**VALUE (mdyn/A) (a)**	**(b)**	**ST.BEND. F.C.**	**VALUE (mdyn) (a)**	**(b)**
C-O,O-P	0.325	0.30	C-N,O-C-N	0.347	0.347
O5'-P,O-P		0.30	C-N,C-C-N		0.347
P-O,P-O		0.60	C-O,C-O-P	0.246	0.246
			O-P,C-O-P	0.255	0.255
BEND.BEND. F.C.	**VALUE (mdyn/A) (a)**	**(b)**	**TORSION F.C.**	**VALUE (mdyn.A) (a)**	**(b)**
N-C-O,C-C-O	-0.041	-0.041	Y(C1'-N)	0.52	0.100
			Y(C-C)	0.021	0.010
			Y(C-O)	0.010	0.010
			Y(P-O)	0.037	0.037

EXPERIMENTAL (cm^{-1})		CALCULATED (cm^{-1})	ASSIGNMENTS (POTENTIAL ENERGIE DISTIBUTION %)
INFRARED	RAMAN		
		1700	S3(44)+S11(31)
1697(vs)			
		1698	S8(63)+S5(12)
1660(sh)		1666	S8(23)+S17(15)+S26(14)+S23(11)+S18(11)
1604(s)		1619	S11(23)+S19(17)+S17(12)
1580(sh)	1579	1586	S27(34)+S5(12)+S18(10)
1535(s)	1542	1528	S18(27)+S19(19)+S17(12)+S27(12)
1482(m)	1489	1480	S26(47)+S19(30)
1412(w)	1421	1428	S51(10)+S42(10)
1385(sh)		1386	S28(16)+S1(14)+S11(13)
1360(m)	1369	1371	S26(13)+S20(12)+S11(10)
		1326	S66(90)
1325(sh)	1327		
		1318	S19(17)+S21(12)+S48(12)
1260(w)		1266	S18(10)+S12(10)+S19(10)
1235(w)		1230	S49(21)+S44(16)
1175(sh)	1177	1170	S44(31)+S51(10)
		1141	S9(38)+S11(11)
1135(s)			
		1120	S72(20)+S62(10)+S34(10)
1085(s)	1086	1083	S73 (75)
	1061	1055	S54(19)+S65(16)+S61(12)
	1033	1035	S65(23)+S67(15)+S62(10)
	1005	1014	S65(14)+S62(12)
973(s)	979	979	S71(33)+S38(10)
905(w)	928	904	S10(14)+S5(10)+S12(10)+S37(10)
865(w)	856	865	S44(25)+S53(19)+S57(11)+S41(10)
802(m)		828	S70(20)+S53(19)+S34(10)
778(m)	788		
725(m)			
690(w)		714	S15(18)+S24(14)+S53(10)
638(w)		634	S12(28)+S17(14)+S29(12)
		614	S41(12)+S38(11)+S53(10)
	584		
		555	S86(26)+S78(15)+S74(11)
		505	S15(20)+S16(17)+S13(17)+S24(10)
	499		
		486	S76 (28)

Table 3. Comparison between the experimental and calculated wavenumbers (cm^{-1}) of 5′-dGMP. R (Raman): Small and Peticolas (1971); I.R. (Infrared); (vs): very strong, (s): strong, (m): medium; w: weak and (sh): shoulder. The expressions of the *S* coordinates are reported in Tables 1 a, b and c

Table 4. Comparison between the experimental and calculated wavenumbers (cm^{-1}) of 5′-dGMP-d1 (C8-deuterated) and 5′-dGMP-d4 (C8, N1 and N2-deuterated). See footnote of Table 3

5'-dGMP-d1			5'-dGMP-d4		
EXP. IR	CAL.	ASSIGNMENTS (PED %)	EXP. IR	CAL.	ASSIGNMENTS (PED %)
	1700	S3(44)+S11(31)			
1697(vs)	1698	S8(63)+S5(12)			
			1686(vs)	1688	S3(49)+S11(27)+S8(12)
1660(m)	1666	S5(22)+S17(14)+ S26(14)+S18(11)+ S23(11)	1660(sh)	1668	S19(19)+S26(16)+S18(14)+ S11(11)+S3(11)
1605(m)	1619	S11(23)+S19(17)+ S17(12)+S5(11)	1605(sh)	1601	S17(24)+S23(22)+S27(15)+ S11(10)
1585(m)	1583	S27(46)+S5(14)+ S23(10)	1585(m)	1589	S5(34)+S27(27)
1523(m)	1510	S18(22)+S26(18)+ S17(13)	1528(m)	1510	S18(23)+S19(12)+S17(11)+ S23(10)
1460(m)	1465	S26(44)+S19(28)	1460(m)	1460	S19(33)+S26(32)
	1433	S42(18)+S56(11)+ S54(10)	1430(m)	1432	S42(18)+S56(12)+S54(10)+ S51(10)
1420(w)	1421	S21(12)+S17(10)+ S23(10)		1418	S23(18)+S17(11)+S48(10)
1380(sh)	1384	S28(14)+S11(14)+ S28(13)			
1360(m)	1371	S26(12)+S20(12)+ S11(11)			
1315(w)	1325	S66(49)+S46(12)		1325	S66(49)+S46(13)
			1215 (broad)	1185	S8(21)+S44(11)
1120(sh)	1120	S72(18)+S62(10)+ S34(10)	1120(sh)	1112	S72(19)+S44(11)
1085(vs)	1083	S73(76)	1085(vs)	1083	S73(65)
975(s)	978	S71(36)+S38(10)	975(s)	978	S71(37)+S38(10)
865(w)	865	S44(25)+S53(20)+ S57(11)	865(w)	865	S44(22)+S53(19)+S57(10)
802(m)	827	S53(17)+S70(14)	802(m)	827	S53(16)+S70(15)
778(m)			778(m)		
724(w)			724(w)		
690(w)	712	S24(13)+S53(13)+ S15(12)+S13(10)	690(w)	719	S14(20)+S53(10)+S12(10)

1200–850 cm^{-1} spectral region. The infrared spectra in this region mainly consists of an intense, broad and badly resolved band peaking at 1085 cm^{-1}, with an important shoulder at about 1135 cm^{-1} in 5′-dGMP and at ~ 1120 cm^{-1} in the deuterated analogs. Results of the calculations indicate that the two components of this band should arise from the degeneracy removal in PO$_3$-degenerate stretching modes. However, a certain number of the vibration modes masked by this band have been observed in the Raman spectra (Table 3). These bands situated at 1061, 1033 and 1005 cm^{-1} have been assigned to the sugar vibration modes. The intense band situated at 973 (I.R.) or 979 (*R*) cm^{-1} reveals a coupling between PO$_3$-symmetric stretching and sugar vibrations. This region includes two weak infrared bands at 905 and 865 cm^{-1}, assigned to the guanine and sugar modes, respectively.

850–600 cm^{-1} spectral region. The low frequency base and sugar vibration modes give rise to the less intense absorption bands in this region. The broad band at 802 cm^{-1} (undeuterated) is attributed to the ν(P-O5′) stretching mode coupled with the sugar vibrations (Fig. 1). The infrared bands at 690 and 638 cm^{-1} are assigned to the planar vibration modes of guanine. The former, observed at 683 cm^{-1} in Raman spectra, is attributed to the breathing mode of the guanine-residue. The latter, which includes the δ(C8-H) bending coordinate in its PED (Table 2), disappears completely upon C8-deuteration. The calculations fail to predict the infrared bands at 778 cm^{-1} and 725 cm^{-1}. We think that they both arise from the out-of-plane cyclic vibrations of guanine. Both of them are unaffected by deuteration. It should be mentioned that a similar band, situated at 778 cm^{-1} in the *B* form and 784 cm^{-1} in the *Z* form of poly(dG-dC) · poly(dG-dC) infrared spectra, is assigned to the non-planar vibration modes of the guanine-residue on the basis of our former calculations (Ghomi et al. 1984).

Below 600 cm^{-1}. Only two Raman bands at 584 and 499 cm^{-1} are present in this spectral region. The present calculations permit us to interpret them as arising from the sugar-phosphate and base-residue vibration modes.

B. Guanosine-moiety in B and Z forms of DNA

Taking account of the good agreement between the experimental and calculated results in 5′-dGMP, we have tried to test the force field obtained in the case of the guanosine-moiety found in right and left-handed poly(dG-dC) · poly(dG-dC). A dynamical model consisting of a guanine associated with a 2′-deoxyribose molecule limited to its O3′ and O5′ terminals has been taken into consideration. In order to construct the *B* and *G* matrices corresponding to the *B* form, the coordinates of the wrinkled *B* DNA (Arnott et al. 1983) were used. For the *Z* form, the crystalline coordinates of the Z_I-form (Wang et al. 1981) have been introduced. The redundancy was entirely removed (see Theory), and the force field was supposed to be invariant whatever the conformation (*B* or *Z*) studied. The calculated wavenumbers, particularly those corresponding to the guanine-residue are compared to the Raman (Pohl et al. 1973; Thamann et al. 1981; Benevides and

EXPERIMENTAL					CALCULATED ASSIGNMENT (PED %)	
(a)	(b)	(c)	(d)	(e)		
1574(0.35)	1574(0.46)	1576(0.60)	1575	1575(m)	1560	S27(22)+S8(22)+ S10(10)
1530(0.04)	1533(0.04)	1530(0.20)		1528(m)	1520	S17(34)+S5(16)+ S8 (14)+S11(13)
1487(0.75)	1485(0.69)	1488(1.0)	1488	1488 (sh)	1481	S11(30)+S19(24)
1380(0.17)		1385(0.1)		1374(m)	1375	S1(35)+S20(11)
681(0.28)	681(0.26)	682(0.3)	682		690	S15(28)+S24(20)

Table 5. Comparison between the experimental and calculated wavenumbers (cm^{-1}) corresponding to the guanosine-moiety in B-DNA. In parenthesis the relative intensities are noted. (a) Raman spectrum of aqueous poly(dG-dC) · poly(dG-dC) on 0.1 *M* NaCl (Thamann et al. 1981). (b) Raman spectrum of aqueous d(CG)$_3$ · d(CG)$_3$ in 0.1 *M* NaCl (Thamann et al. 1981). (c) Raman spectrum of poly(dG-dC) · poly(dG-dC) in 0.1 *M* NaCl (Pohl et al. 1973). (d) Raman spectrum of poly(dG-dC) · poly(dG-dC) in 0.1 *M* NaCl (Benevides and Thomas 1983). (e) Infrared spectrum of the thin films of poly(dG-dC) · poly(dG-dC) (Taboury et al. 1984). The expressions of the non-redundant *S* coordinates are reported in Table 1 a

EXPERIMENTAL						CALCULATED ASSIGNMENTS (PED %)	
(a)	(b)	(c)	(d)	(e)	(f)		
1574(0.39)	1580(0.37)	1572(0.33)	1580(0.5)	1578	1580(sh)	1578	S5(23)+ S17(19)+ S27(16)
1533(0.12)	1535(0.12)	1530(0.11)	1538(0.2)		1527(m)	1520	S17(26)+ S27(17)+ S8(12)+ S19(10)
1485(0.71)	1482(0.68)	1481(0.75)	1487(1.0)	1483	1482(sh)	1484	S11(37)+ S19(16)+ S23(11)
1358(0.30)	1355(0.30)	1358(0.2)	1360(0.3)	1355	1354(m)	1359	S21(15)+ S1(12)+ S27(10)
1320(0.63)	1320(0.57)	1326(0.18)	1310(0.8)	1316	1318(m)	1311	S20(11)+ S11(10)
625(0.19)	625(0.27)	623(0.3)	627(0.4)	625		630	S24(12)+ S17(11) S15(10)

Table 6. Comparison between the experimental and calculated wavenumbers (cm^{-1}) corresponding to the guanosine-moiety in Z-DNA. In parenthesis the relative intensities are noted. (a) Raman spectrum of crystalline d(CG)$_3$ · d(CG)$_3$ (Thamann et al. 1981). (b) Raman spectrum of aqueous poly(dG-dC) · poly(dG-dC) in 4 *M* NaCl (Thamann et al. 1981). (c) Raman spectrum of aqueous d(CG)$_3$ · d(CG)$_3$ in 4 *M* NaCl (Thamann et al. 1981). (d) Raman spectrum of aqueous poly(dG-dC) · poly(dG-dC) in 4.4 *M* NaCl (Pohl et al. 1973). (e) Raman spectrum of aqueous poly(dG-dC) · poly(dG-dC) in 4 *M* NaCl (Benevides and Thomas 1983). (f) Infrared spectrum of thin films of poly(dG-dC) · poly(dG-dC) (Taboury et al. 1984). The expressions of the non-redundant *S* coordinates are reported in Table 1 a

Thomas 1983) and infrared (Taboury et al. 1984) peak positions for the *B* and *Z* forms (Tables 5 and 6). The comparison was made only for the bands situated below 1600 cm^{-1} which should not considerably be affected by the base-stacking effect. It is shown that the calculated results are capable of accounting for the behaviour of the characteristic infrared and Raman bands altered by the *B* → *Z* conformational transition.

Discussion

In a former publication (Ghomi et al. 1984), it was shown that a modified Urey-Bradley force field could account for the changes of certain infrared and Raman bands in DNA's undergoing the *B* → *Z* transition. In our dynamic model, formed by CpG and GpC sequences, the hydrogens were neglected and the force constants were supposed to be invariant whatever the conformation (*B* or *Z*) studied. The most important conclusion of these preliminary calculations was that only the predominant factor of the conformational change, i.e. variation in torsion angles, was responsible of the modification in the shape of the vibrational spectra.

In the present work, which considers the hydrogens, a valence force field was used in order to give a more faithful representation of the observed vibrational spectra. The 5′-dGMP force field, adapted by taking account of the experimental data on this molecule, has been applied in the case of the guanosine-moiety in *B* and *Z* forms of poly(dG-dC) poly(dG-dC). The good agreement between the experimental and calculated results, justifies the idea that the force field does not depend upon mononucleoside conformation. On the other hand, this theoretical study permits us to classify the vibration modes which are conformation sensitive and especially those modified by the *B* → *Z* structural transition. In 5′-dGMP, a low anti guanine-residue ($\chi_{CN} = 236.9°$) is associated with a 2′-deoxyribose with an O1′-endo, C4′-exo conformation (Young et al. 1974). In the wrinkled *B* form, the X-ray patterns are in agreement with a high anti guanine ($\chi_{CN} = 286.3°$) connected to a C2′-endo sugar (Arnott et al. 1983). The choice of the crystalline Z_I form geometrical data instead of those relating to the Z_{II}-form (Wang et al. 1981) is due to the inability of the latter form to account for the dichroic infrared spectra (Pilet and Leng 1982). Indeed the Z_{II} conformation failed to predict the angle between the transition dipole moment of the PO_2^- symmetric stretching mode and the double helix axis (Taillandier et al. 1983). However, the geometrical difference between the Z_I and Z_{II} forms, occurring principally in the phosphodiester chain, becomes completely negligibe in regard to the guanosine-moiety. The Z_I form considered here presents a base syn conformation ($\chi_{CN} = 66.7°$) with a C3′-endo sugar (Wang et al. 1981). The characteristic bands of the guanine-residue observed at ~1580, ~1535 and ~1480 cm^{-1} in 5′-dGMP are also observed in *B* and *Z* form spectra (Tables 3–6). The shift of the last two bands upon C8-deuteration in 5′-dGMP (Table 4) and their alteration upon Co^{2+} metal-ion binding at the C8-site of the guanine-residue (Taboury et al. 1984) are in good agreement with the calculated assignments for the corresponding vibration modes. The guanine-residue 1385 cm^{-1} band observed in 5′-dGMP, involving the C1′-N9 glycosidic bond-stretch, is one of the infrared bands most sensitive to base conformation. The corresponding mode situated at 1374 cm^{-1} in the *B* form (Table 5) is shifted to 1354 cm^{-1} in the *Z* form (Table 6). The guanine-residue breathing mode at 690 cm^{-1} (Nishimura et al. 1984) should be considered as a Raman characteristic line altered by the same conformational transition. The corresponding mode at 685 cm^{-1} in the *B* form is found at 625 cm^{-1} in the *Z* form (Tables 5 and 6). The calculated results account for this change and are in good agreement with the experimental assignments made by Nishimura et al. (1983).

In conclusion, the guanine 1374 cm^{-1} band (*B* form) shifted to 1354 cm^{-1} (*Z* form), involving mainly the C1′-N9 stretching coordinate, induces a relatively important dipole moment variation and can be considered as a good marker in recognizing the *B* and *Z* forms by infrared spectroscopy. In contrast, the breathing character of the guanine-residue 685 cm^{-1} mode (*B* form) shifted drastically to 625 cm^{-1} (*Z* form), makes its observation in infrared spectra difficult, but causes a strong variation of the electronic polarizability. This is why Pohl et al. (1973) and Thamann et al. (1981) in their original work on Raman spectra of the low and high salt forms of poly(dG-dC)·poly(dG-dC) and d(CG)$_3$·d(CG)$_3$ presented this mode as an excellent marker for the right and left handed structures.

To follow the general ideas presented above, a theoretical work based on the changes of the vibration modes of DNA chains as a function of all possible values of the conformational angles, is now in preparation. The results obtained will permit us to classify the conformational transition dependent vibration modes in mononucleosides and phosphate-backbone.

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