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Scaled Quantum Mechanical Force Fields and Vibrational Spectra of Solid-State Nucleic Acid Constituents. 4. N7-Protonated Guanine

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Vibrational spectra of polycrystalline guanine and single crystals of guaninium chloride monohydrate and guaninium chloride dihydrate have been studied in the 300–1800-cm⁻¹ frequency region. N7 protonation completely changes the appearance of Raman spectrum of guanine in the 1000–1600-cm⁻¹ region, whereas differences in crystal structures cause only systematic 5–20-cm⁻¹ frequency shifts here. The interpretation of the spectra was performed using the scaled *ab initio* STO-3G force field. A general set of scale factors for in-plane STO-3G force fields of purine derivatives based on the linear relationship between the C–N and C–C stretching scale factors and the corresponding diagonal STO-3G force constants has been proposed. The 2% agreement between the predicted and the experimental frequencies of N7-protonated guanine has been obtained.

Introduction

The biological implications of protonation of nucleic acids (NA) bases have generally been acknowledged.^{1,2} The N7 position of guanine represents, for its good accessibility in the DNA major groove and high proton affinity,³ a very important protonation site of NA bases in regard to the DNA conformational changes induced by a cation attack.² Protonation of guanine at the N7 nitrogen was observed to induce an anti-to-syn rotation of guanine.⁴ In the resulting Hoogsteen-type G–C base pair, guanine acts, owing to greater cytosine basicity, as a proton donor which results in the proton transfer to the N3 position of cytosine.⁵ The N7-protonated guanine has also been shown to play a role in formation of triple stranded DNA helix.⁶

Raman spectroscopy which represents a valuable tool for studying a secondary structure of nucleic acids as well as their interactions with other molecules and ions in aqueous solutions^{7,8} can take advantage of a clear manifestation of guanine protonation in vibrational spectra, evidenced by the IR spectra of guanylic acid,⁹ Raman spectra of guanine and 5'-GMP in aqueous solution at pH 0.5,¹⁰ Raman pH profiles for 5'-GMP,¹¹ a Raman study of self-aggregation of 5'-rGMP at low pH,¹² and Raman pH-dependent structure of calf thymus DNA.¹³ The previously published data however do not provide complete information needed for theoretical interpretation of the spectra. For this purpose we have studied a structurally well defined single crystal of guaninium chloride monohydrate¹⁴ and guaninium chloride dihydrate,¹⁵ containing N7-protonated guanine as well as the polycrystalline neutral guanine using Raman and IR spectroscopies. The use of two different crystals enabled us to determine the sensitivity of particular vibrational bands to weak intermolecular interactions.

We have interpreted the measured spectra using the scaled *ab initio* STO-3G force field. By means of scaling procedure, quantum mechanical force constants expressed in internal coordinates are multiplied by the few scale factors close to 1.0, to compensate for errors originating from the neglecting of electron correlation, finiteness of basis set, anharmonicity, and the influence of intermolecular interactions.¹⁶ A significant feature of scale factors is their good transferability among related molecules.^{17,18} The main obstacle to the transferability of the STO-3G scale factors of NA bases turned out to be the choice of the C–N and C–C stretching scale factors, strongly dependent on the bond order, and of the N–H and C–H bending scale factors, influenced by intermolecular interactions and coupled with the values of C–N and C–C stretching scale factors. All the C–N stretching scale factors cannot be, because of their large numbers, calculated in the least-squares fit to the experimental data independently. Therefore, in our previous studies on vibrational spectra of neutral and protonated adenine,^{19,20} 2-aminoadenine,²¹ and guanine²² we

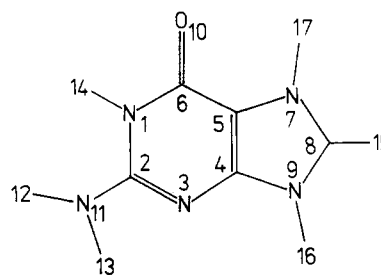


Figure 1. Atomic numbering for N7-protonated guanine.

have formed the C–N, C=N, C–C, and C=C stretching force constants groups, each group having a common scale factor. However, when the refined scale factors are transferred to a related molecule the question on criteria for grouping the ring stretching force constants of new molecule arises. Recently we have collected enough results from fitting procedures^{19,21,22} to be able to develop a linear relationship between STO-3G ring stretching force constants and scale factors, resulting in the well defined set of scale factors applicable for all purine derivatives. The mentioned linear function and general set of scale factors is presented in this paper and is tested in the calculation of in-plane vibrational frequencies and assignment of N7-protonated guanine.

Methods

Raman spectra were measured in the 300–1800-cm⁻¹ region with a 2-cm⁻¹ spectral step using a modular UV–vis spectrometer described elsewhere.²³ A 514.5-nm line of Ar ion laser was used to excite the spectra. The Raman spectrum of guaninium chloride dihydrate shown in Figure 5 represents a sum of the (*yy*) and (*xy*) components of polarized single crystal spectra. For recording Raman spectra of polycrystalline samples of guanine (Calbiochem) and guaninium chloride monohydrate the powder was pressed into a rotating cell and a holographic notch filter was employed to suppress the stray light. Raman spectra of guaninium chloride monohydrate were also recorded in the 100–300- and 2800–3500-cm⁻¹ frequency regions. IR spectrum of guaninium chloride monohydrate was obtained from a KBr pellet by using a Perkin Elmer 684 spectrometer.

The *ab initio* harmonic force constants of N7-protonated guanine were computed by means of the GAMESS quantum chemical program²⁴ as second analytic derivatives of the total HF SCF STO-3G energy in the STO-3G optimized geometry.³ The transformation of force constants from Cartesian into a standard set of internal coordinates,^{19–22,25,26} scaling procedure,¹⁹ and calculation of vibrational frequencies, normal modes, and distribution of potential energy¹⁹ was performed with our program

TABLE I: Scale Factors of STO-3G Force Fields of Purine Derivatives

internal coordinate ^a	molecule ^b	scale factor ^c	general set of scale factors ^e
CN stretching	Ade	0.82 (8.41)	SF = -0.031FC + 1.08
	Gua	0.77 (10.32)	
		0.85 (8.09)	
	AA	0.70 (11.35)	
		0.86 (7.55)	
CC stretching	Ade	0.79 (8.86)	SF = -0.027FC + 1.02
	Gua	0.74 (12.16)	
		0.72 (8.27)	
	AA	0.69 (9.55)	
		0.85 (6.75)	
CO stretching	Gua	0.74 (10.41)	0.63
	Ade	0.77 (8.21)	
		0.77 (9.50)	
CH,NH stretch	Gua	0.63	0.61
	Ade	0.65	
		0.57	
deformation of six-memb ring	AA	0.60	0.91
	Ade	0.96	
	Gua	0.91	
deformation of five-memb ring	AA	0.90	0.81
	Ade	0.88	
	Gua	0.81	
C-NH ₂ bending	AA	0.90	1.20
	Ade	0.96	
	Gua	1.20	
C=O bending	AA	0.90	1.20
	Gua	1.20	
	Ade	0.85	
NH ₂ scissoring	Gua	0.82	0.84
	AA	0.85	
	Ade	0.92	
NH ₂ rocking	Gua	0.91	
	AA	0.72	
	Ade	0.90	
NH bending	Gua	0.81	
	AA	0.82	
	Ade	0.80	
CH bending	Gua	0.90	
	AA	0.82	
	Ade	0.58	
stretch-stretch ^d	Gua	0.97	0.56, 0.97
	AA	0.54	
	Ade	1.26	
stretch-bend ^d	Gua	1.08	1.26, 1.08
	AA	1.26	
	Ade	0.70	
bend-bend ^d	Gua	0.89	0.68
	AA	0.44	

^a For definition see ref 19. ^b Ade, adenine,¹⁹ Gua, guanine,²² AA, 2-aminoadenine.²⁷ ^c Corresponding unscaled STO-3G force constants (for C-C bonds) and mean values of force constants (for C-N bonds) are given in parentheses: SF, scale factor; FC, force constant [mdyn/Å]. ^d Scale factors of interaction force constants. ^e Two alternative sets of scale factors of interaction force constants are given, for discussion see text.

SQMVB without using any experimental information about N7-protonated guanine.

Results and Discussion

Scale Factors and Force Field. The mean values of C-N stretching force constants, together with the corresponding scale factors (SF) obtained by the least-squares fit to the experimental frequencies of crystalline adenine,¹⁹ guanine,²² and 2-aminoadenine,²¹ are presented in Table I and Figure 2. A linear least-squares approximation (Figure 2) of the equally weighted data resulted in the function

$$\text{SF}^{\text{CN}} = -0.0307\text{FC} + 1.083 \quad (1)$$

for C-N stretching scale constants, where force constants (FC) are given in mdyn/Å.

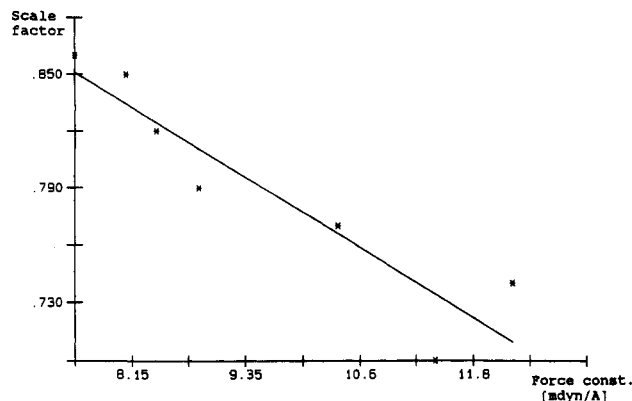


Figure 2. Linear approximation of the C-N stretching force constants vs scale factors dependence.

A similar relation can be assumed also for the C-C stretching scale factors. For them, however, the uncertainty of the least-squares fit to experimental frequencies is two times higher (~ 0.04) than that of C-N scale factors, and coupling with the N-H and C-H bending scale factors appears. It can account for the inconsistency of their adenine values with the values obtained for 2-aminoadenine and guanine. In the present study we therefore propose the linear function based on the 2-aminoadenine and

$$\text{SF}^{\text{CC}} = -0.0274\text{FC} + 1.021 \quad (2)$$

guanine data. We intend to improve the wide applicability of this dependence by including further data from pyrimidine bases, in the next paper in this series. Since a different grouping of the bending vibrations of the six- and five-membered rings (D6R, D5R) and the amino group (DCNH₂) have been assumed for adenine, 2-aminoadenine, and guanine, a rather inconsistent set of scale factors has been obtained for them (Table I). For the proposed general set of scale factors of purine derivatives we have accepted the same type of grouping as in the case of guanine since it leads to the best agreement with experimental data. An interesting result comes from the comparison of the mean values of scale factors of rocking and scissoring vibrations of amino groups (NH₂R, NH₂S) and DNH and DCH bending vibrations which all turned out to be 0.84. The single scale factor common for all C-H and N-H in-plane bending vibrations can, consequently, be determined. The rather dissimilar values of this scale factors calculated previously were partly connected with the inconsistent grouping of stretching scale factors, partly with differences in molecular environments. Unfortunately, such an unifying approach as for the N-H and C-H bending vibrations cannot be applied to the scale factors of interaction force constants. Each of the stretch-stretch, stretch-bend, and bend-bend groups of interaction force constants have been scaled by the common scale factor. The resulting three scale factors however turned out not to be transferable between adenine (2-aminoadenine) and guanine. The most striking difference has been obtained between the ab initio stretch-stretch interaction force constants of adenine and guanine, the adenine values being almost twice as large as that of guanine (Table I). Such significant inconsistency of the STO-3G force fields we prescribe mainly to the effect of exocyclic oxygen. Consequently, the two alternative sets of scaling factors of interaction force constants for purine derivatives with and without a carbonyl group are proposed in Table I.

Vibrational Spectra. Raman spectra of polycrystalline powders of guanine and guaninium chloride monohydrate, single crystal of guaninium chloride dihydrate, and IR spectrum of guaninium chloride monohydrate are presented in Figures 3-6 respectively. The spectral data are compared and interpreted in Table II. Our Raman spectrum of guanine closely resembles the spectrum obtained by M. Majoube.²⁷ Sufficiently intensive Raman bands of crystalline protonated guanine perfectly coincide with the low pH spectrum of its water solution,¹⁰ which demonstrates the applicability of solid-state studies for aqueous solutions. There are only

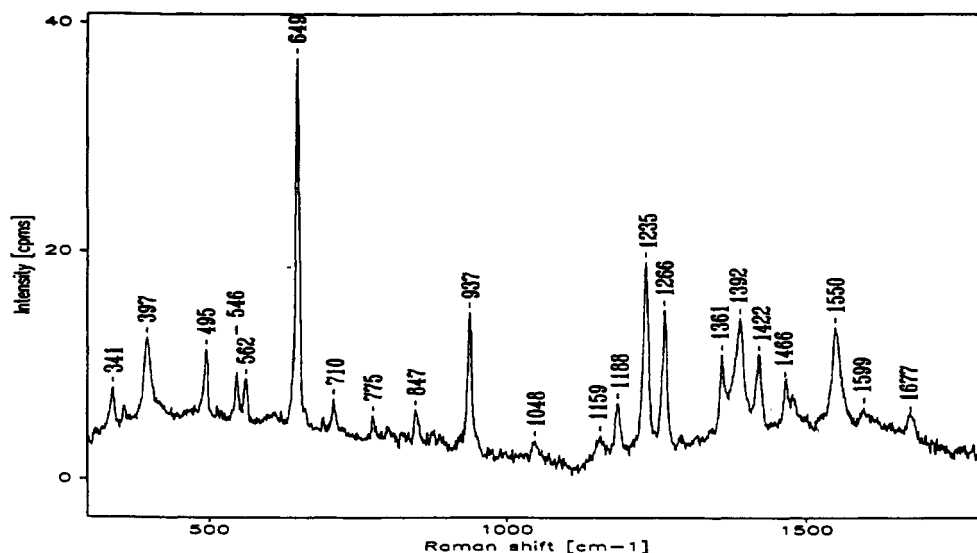


Figure 3. Raman spectrum of polycrystalline neutral guanine.

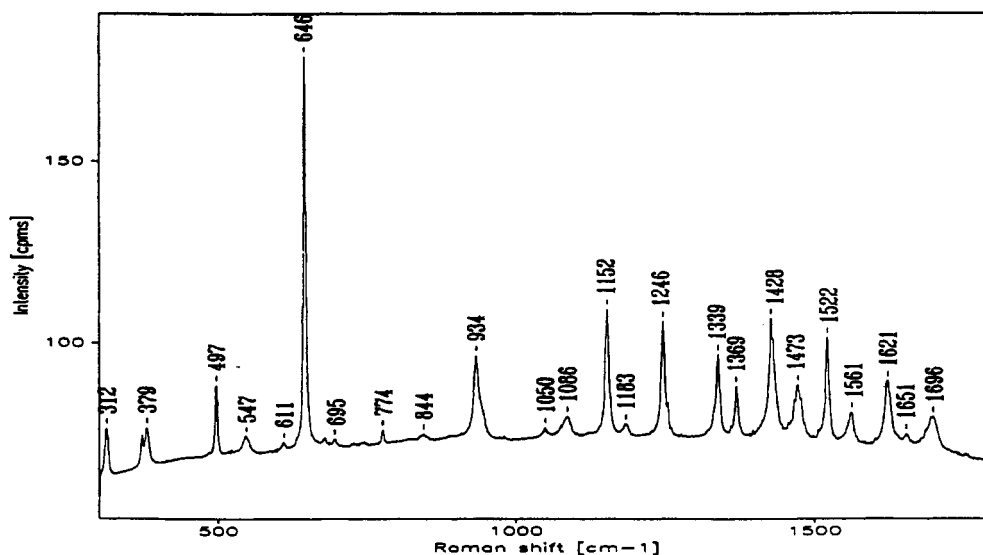


Figure 4. Raman spectrum of polycrystalline N7-protonated guanine (guaninium chloride monohydrate).

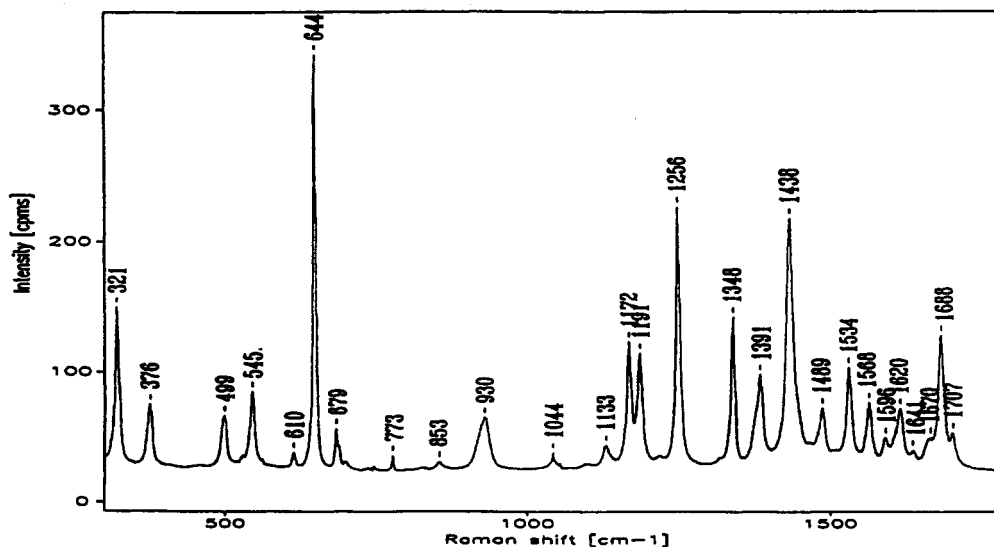


Figure 5. Raman spectrum of the single crystal of guaninium chloride dihydrate.

slight differences between Raman spectra of protonated and neutral base below 1000 cm^{-1} . The two strong 649- and 937-cm^{-1} guanine bands retain high intensity and are shifted downwards about 3 cm^{-1} . Since the protonation substantially affects the values

of ring stretching force constants¹⁹ (Table III), the more pronounced changes caused by protonation can be expected in the $1100\text{--}1800\text{-cm}^{-1}$ region. Actually, the spectral features are very dissimilar, with no protonation invariant Raman band. Except

TABLE II: Raman and Infrared Spectra of N7-Protonated Guanine and Their Interpretation

Raman ^a	Raman ^b	IR ^b	calcd	interpretation ^c
	123 m			intermolecular vibration
	206 m			out-of-plane vibration
321 s	312 m		298	D6RE2 (25), D5R (21), DC6O (16), C5C6 (14), C5N7 (5)
	369 sh			out-of-plane vibration
376 m	379 m	382 vs	380	DC2N (48), DC6O (21), C6N1 (8), N3C4 (6)
499 m	497 m	504 s	495	D6RE1 (69), C2N11 (6)
		528 s		out-of-plane vibration
545 m	547 w	~557 sh	552	D6RE2 (53), C5C6 (10), D6RE1 (8), DC2N (7)
610 vw		608 s		out-of-plane vibration
644 vs	646 vs	643 w	626	C5C6 (17), D6RE1 (13), N1C2 (12), N3C4 (10), D6RTr (9), C6N1 (7)
679 w	679 vw	686 s		out-of-plane vibration
	695 vw	712 m	715	DC6O (31), DC2N (24), D5R (10), D6RTr (8), C5C6 (6), DNH2R (6)
		738 vw		out-of-plane vibration
773 vw		770 m		out-of-plane vibration
		835 vs		out-of-plane vibration
853 vw	844 vw	848 sh	844	D6RTr (34), D5R (14), N3C4 (12), C5N7 (8), D6RE1 (7), C2N3 (6)
		~896 w		out-of-plane vibration
~930 m	934 s	934 w	948	D5R = (85)
	~950 sh	950 w		out-of-plane vibration
1044 vw	1050 vw		1044	C2N3 (29), N1C2 (19), D6RTr (10), DC6O (9), C2N11 (7)
	1086 w	1069 m	1075	DNH2R (40), D5R (13), C2N3 (13), DC8H (8), N9C4 (7)
1133 w		1112 m	1133	DC8H (25), DNH2R (24), N9C4 (14)
1172 m	1152 s	1148 m	1152	C8N9 (37), DN9H (19), DC8H (17), C6N1 (8)
1191 m	1183 vw	1179 m	1162	C6N1 (30), N7C8 (17), N3C4 (13), DC6O (7), C2N3 (7), N1C2 (6)
1256 s	1246 s	1241 m	1242	DN7H (21), N9C4 (16), C6N1 (14), DN9H (7), N7C8 (7), DC8H (6)
		1263 vw		overtone
1348 m	1339 s	1339 w	1300	C5N7 (32), N3C4 (11), C5C6 (11), N9C4 (8), C2N3 (8), C8N9 (6)
1391 m	1369 m	1367 s	1364	DN9H (23), DN7H (18), C8N9 (12), N3C4 (9), N7C8 (8), C6N1 (6)
		1398 s	1379	C4C5 (29), C8N9 (18), N9C4 (13), DC8H (7), D5R (7), D5R = (6)
1448 s	1428 s		1400	DN1H (43), C2N11 (26), C6O (11)
1489 m	1473 m	1470 m	1473	N7C8 (37), DN7H (10), DC8H (8), N1C2 (7), N3C4 (6), D5R (6)
1534 m	1522 s	1513 s	1500	N1C2 (28), C2N3 (12), DC8H (9), DC2N (8), N7C8 (7), C8N9 (7)
1568 m	1561 w	1555 s	1596	C2N11 (14), C2N3 (13), DN1H (10), D6RE2 (10), C6O (7), N3C4 (7)
1596 w				water bending vibration
1620 m	1621 m		1618	DN7H (15), C5N7 (13), C4C5 (11), D6RTr (10), C8N9 (9), C6O (8)
1641 vw	1651 vw	~1657 vs		water bending vibration
1670 sh			1673	DNH2S (15), DN1H (15), C6O (12), C4C5 (8), N3C4 (8), C2N3 (7)
1688 s	~1696 m		1681	DNH2S (70), C6O (10), C2N11 (7)
1707 vw		~1708 vs	1704	C6O (33), C4C5 (13), C5C6 (7), D6RTr (6), DNH2S (6), C6N1 (6)
			2822	C8H (97)
			3046	NH13 (49), NH12 (49)
			3064	N7H (69), N9H (30)
			3090	N9H (67), N7H (28)
	~3113 m		3101	N1H (96)
	~3399 m		3255	NH12 (50), NH13 (50)

^aSingle crystal of guanine hydrochloride dihydrate (Figure 5). ^bCrystalline (powder) sample of guanine hydrochloride monohydrate (Figures 4 and 6). ^cPotential energy distribution [%] is given for in-plane vibrational modes, deformational internal coordinates are marked by the first "D" letter, for their definition see refs 19 and 22. ^dFrequencies are given in [cm⁻¹], intensities are abbreviated as vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; ~, broad.

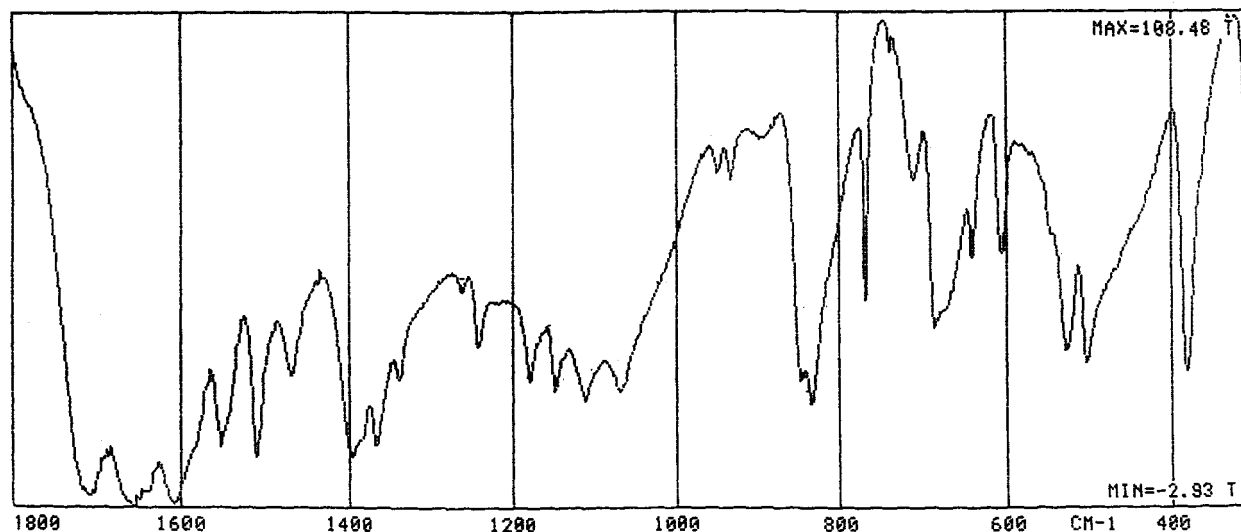


Figure 6. IR spectrum of polycrystalline N7-protonated guanine (guaninium chloride monohydrate).

for the force constants changes, further reason for such drastic changes results from the calculated delocalized character of the bending vibration of "proton" (DN7H). The C=O stretching

band is upshifted by protonation to the 1708 cm⁻¹ band as evidenced also by IR spectrum of guanylic acid⁹ where a strong band appears at 1705 cm⁻¹. A substantial contribution to this normal

TABLE III: Effect of N7-Protonation on Diagonal Ring Stretching Force Constants of Guanine

internal coordinate	force constant ^a [mdyn/Å]	
	guanine ²²	H ⁺ at N7
N1C2	8.34	8.28
C2N3	10.93	9.50
N3C4	7.47	7.57
C4C5	10.41	10.72
C5C6	6.75	6.56
C6N1	6.72	7.10
C2N11	8.86	9.53
C5N7	7.46	8.15
N7C8	11.78	11.10
C8N9	8.58	10.19
N9C4	9.19	8.13
C6O	16.43	16.67

^a Unscaled STO-3G force constants.

vibration originates also from the C4=C5 stretching vibration, the force constant of which is reinforced by protonation (Table III).

An interesting piece of information about the influence of the crystal environment on guanine vibrational frequencies can be inferred from Figures 4 and 5 where Raman spectra of guanine monohydrate and dihydrate are compared. Here it should be noted that the presented Raman spectrum of single crystal (Figure 4) represents the sum of only two components of the Raman tensor. As a result significant intensity variations can be encountered for the bands of the same frequency when the spectra on Figures 4 and 5 are compared. Analyzing the frequency information we can see that the molecules in crystals preserve their individuality. The spectral lines of protonated guanine embedded in the dihydrate crystal are only slightly systematically shifted to the higher frequencies in the 1150–1600-cm⁻¹ region, with regard to the spectrum of the other crystal. A closer inspection of the structural differences^{14,15} reveals that molecules of protonated guanine form similar NH2...N3 hydrogen-bonded pairs in both crystals. The length and type of the N7-H...O hydrogen bond is also the same in both systems. The N1-H...Cl and N9-H...O(H₂O) hydrogen bonds in the dihydrate crystal are replaced by the N1-H...O(H₂O) and N9-H...Cl hydrogen bonds in the monohydrate crystal. Consequently, the differences observed in the 1150–1600-cm⁻¹ region should, from the structural point of view, originate mainly from the N1-H and N9-H bending vibrations (DN1H, DN9H). The more detailed comparison of both spectra reveals that, as could be envisaged, they differ mainly for the normal modes with significant contribution of amino group rocking vibration (DNH2R). Above 1150 cm⁻¹ the largest shifts of 20 cm⁻¹ are observed for 1152-, 1369-, and 1428-cm⁻¹ normal modes with great calculated contribution of the DN1H and DN9H vibrational modes. Significant shifts of 4–22 cm⁻¹ observed for all vibrations in the 1150–1600-cm frequency region clearly demonstrate strong delocalization of the in-plane bending vibrations of hydrogens, in accordance with computed potential energy distribution. Such a good agreement of calculated interpretation with independent experimental data that have not been used for the refinement of force field supports the transferability and reliability of the proposed set of scale factors.

Conclusions

The general set of transferable STO-3G scale factors based on the linear scaling of stretching force constants enables a routine interpretation of vibrational spectra of various purine derivatives in solid state and solutions. The obtained very good agreement

of mutually independent sets of calculated and experimental in-plane vibrational frequencies of protonated guanine supports the wide transferability of the proposed scale factors. The poor quality of the STO-3G basis set manifests itself mainly in the limited transferability of the scale factors belonging to the interaction force constants. On the other hand, once the linear relationship and single common scale factor for all in-plane bending vibrations of hydrogens have been evidenced for a minimal basis set, one can rely on their validity for larger basis sets too. Finally, we believe that an implementation of a linear relationship between scale factors and stretching force constants in spectroscopic programs for normal coordinate treatment will result in a significant reduction of number of independently fitted parameters.

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Registry No. Guanine, 73-40-5; guanine monohydrate, 6027-81-2; guanine dihydrate, 18602-14-7.

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