

Vibrational investigations of guanine, thioguanine and their singly charged cations and anions

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Abstract: The complete vibrational studies have been done with help of quantum mechanics for the neutral Guanine (Gua) and Thioguanine (TGua) molecules and their singly charged cations and anions employing the B3LYP/6-311++G** method. Neutral Thioguanine and cations of Guanine and Thioguanine show planar structures and belong to C_s point group symmetry while the neutral Guanine and anions of Guanine and Thioguanine possess non-planar structure with C_1 point group symmetry. Vibrational studies of ionic radicals of Gua and its thio- derivative are not available in literatures. Such extensive studies have been attempted for the first time. The normal modes of all the species have been assigned on the basis using potential energy distributions (PEDs) using GAR2PED software. The PEDs have also been calculated to make a conspicuous assignment as animation available in GaussView is not a guarantee for correct normal mode assignment. Charge transfer occurs in the molecule have been shown by the calculated highest occupied molecular orbital—lowest unoccupied molecular orbital (HOMO–LUMO) energies. The mapping of electron density iso-surface with electrostatic potential, has been carried out to get the information about the size, shape, charge density distribution and site of chemical reactivity of the molecule. The electronic properties HOMO and LUMO energies have been measured. The energy gap from HOMO to LUMO of the Gua is 5.0547 eV and TGua 4.0743 eV.

Keywords: Guanine; Thioguanine and their cations and anions; DFT studies; PEDs; HOMO–LUMO and MEP

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1. Introduction

Guanine (Gua) is one of the important building blocks of nucleic acids and has distinct characteristics among all nucleic acid bases. Pharmaceutically it is used as an anti-metabolite of folic acid such as amino protein and methoprexate and is most effective in the treatment of leukemia in children. In addition, nucleic acids i.e. RNA and DNA are the central molecules in the storage and transmission of the genetic information. Interestingly, sulfur is a very reactive element and it is used as chemical warfare agent. Thioguanine (TGua) interferes with the conversion of physiologic purines into nucleic acid, that is, it first converts into deoxyribonucleotide that blocks DNA synthesis. TGua is known as metabolic inhibitor with antitumor and antineoplastic activity used in cancer

research [1–4]. These molecules have maximum number of tautomers in different environments.

The cationic and anionic radicals are intermediates in a number of chemical reactions. Therefore, data of their structures are useful for studying the mechanism and kinetics. Electron propagator theory of Gua and its cations is given by Dolgounitcheva et al. [5]. The structure and bonding of Gua–Cu (neutral, anionic, cationic) have been discussed on the basis of the calculated structures and energies by Martinez [6]. Theoretical quantum chemical study of tautomerism and proton transfer in 6, 8-Dithioguanine has been made by Zhanpeisov et al. [7]. Shukla and Leszczynski [8] have explained the spectral origins and ionization potentials of Gua tautomers.

A first principle study of Gua crystal has been made by Ortmann et al. [9]. The structural and electronic properties of Gua and guanosine have been investigated theoretically by Erkoc and Erkoc [10]. The crystal structures of Gua monohydrate [11] and TGua [12] have been determined by three dimensional diffractometer method. A comparative

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study of electronic structures and spectra of 8-bromoGua with Gua has been made by Mishra and Mishra [13]. Alhambra et al. [14] have investigated the tautomerism of neutral and protonated TGua in the gas phase and in aqueous solution with the help of an ab initio method. A brief discussion of protonated and deprotonated Gua and TGua molecules has been reported by Zhang et al. [15]. Vibrational spectra of Gua [16], the IR and Raman spectra of 15-N and D-substituted Gua [17]; harmonic force constant, in-plane vibrational modes of Gua with the help of ab initio method [18] and Out-of-plane vibrational modes of Gua [19] have been reported by various workers. IR spectroscopic analysis of Gua in an organ matrix suggested presence of both the keto and enol tautomers in equal proportions [20]. Florian and co-worker have suggested that the keto N₉H dominates in polar solvent but in gas phase keto N₇H tautomer is more stable and they have also investigated the IR and Raman spectra of polycrystalline Gua in light of the scaled quantum mechanical force field [21, 22]. IR and Raman spectra of alkylated Gua derivatives [23] and IR spectra of TGua tautomers [24] have been studied by Kasende and co-worker. Gunashekar et al. [25, 26] have carried out normal coordinate analysis of TGua. A brief discussion on the vibrational modes of TGua has been reported by our group [27]. Computational and matrix-isolation FT-IR studies of the tautomeric and vibrational properties of methylated Gua have been made by Schoone et al. [28]. Brauer et al. [29] have studied vibrational spectra of the Gua—Cyt base pair. Coulombeau et al. [30] have analyzed the vibrational mode of Gua by neutron inelastic scattering. A comparative study of IR spectra of 9-ethyl Gua, guanosine and deoxyguanosine has been made by Riziq et al. [31]. Many workers have studied the spectra of this molecule in the solid state and in solution phase and they have also carried out ab initio quantum mechanical calculations of the vibrational spectra of Gua [32–35].

For a proper understanding of vibrational spectra of the studied molecules, a reliable assignment of the experimental IR and Raman frequencies is essential. Therefore, in the present work we represent the detailed analysis of our investigation on the study of vibrational characteristics of Gua and TGua and their respective radicals which could be very helpful in understanding the biochemical and biophysical properties of nucleic acid bases.

Recently, similar investigations have been carried out by our group on the vibrational spectra of the radical cations and anions of thio-derivatives of nucleic acid bases [36, 37] and a brief spectroscopic analysis of vitamins and organic superconductors are also studied [38–43]. However, no such study seems to have been reported in literatures, on the vibrational characteristics of the radicals of Gua and TGua.

2. Computational details

DFT calculations for Gua and TGua and their corresponding radicals were performed using the GAUSSIAN 03 program [44] using the Becke-3-Lee-Yang-Parr (B3LYP) functional [45, 46] supplemented with the standard 6-31+G** and 6-311++G** basis sets (referred to as small and large basis sets, respectively) for the fully optimized geometry by assuming C_s point group symmetry. The labeling of atoms for the studied molecules is shown in Fig. 1. The ab initio calculations predicted the neutral Gua and TGua molecules as well as the anions of Gua to possess planar structures with C₁ point group symmetry while the cations of Gua and TGua possess C_s point group symmetry.

These calculations were carried out to compute the optimized molecular geometries, APT charges and fundamental vibrational frequencies along with their corresponding intensities in IR spectrum, Raman activities and depolarization ratios of the Raman bands for the studied species for the Gua and TGua molecules.

The assignments of the normal modes of vibration for all the molecules were made by visual inspection of the individual mode using the Gauss View software [47]. The frequency calculations indicated that they were now at energy minima. In this way, the stationary points of all the structures were obtained at the same theoretical level of B3LYP/6-311++G** which was a prerequisite for the geometric and energetic comparisons.

3. Results and discussion

3.1. Molecular geometries and atomic polar tensors (APT) charges

The optimized geometrical parameters (bond lengths and bond angles) for the Gua, TGua and their radicals calculated at the B3LYP/6-311++G** level along with the experimental parameters for the Gua and TGua molecules are collected in Table 1 and shown in Fig. 2.

The optimized bond lengths C₄–N₃, N₁–C₆ and C₅–C₆ for TGua are slightly (0.006, 0.021 and 0.005 Å) shorter than those in Gua molecule. Shortening of these bonds is due to the substitution of S atom (–0.678) in place of O atom (–0.933) at the site C₂ which changes the nature of charge at the sites of the Gua molecule. However, the C₂–N₃/C₄–C₅ bond lengths are longer by 0.004/0.007 Å for TGua as compared to the Gua molecule. Due to attachment of the S atom in place of the O atom, the atomic charges on sites are redistributed, due to which the geometrical parameters of molecules are expected to be changed from the parent molecule. The electronic charge has been distributed over

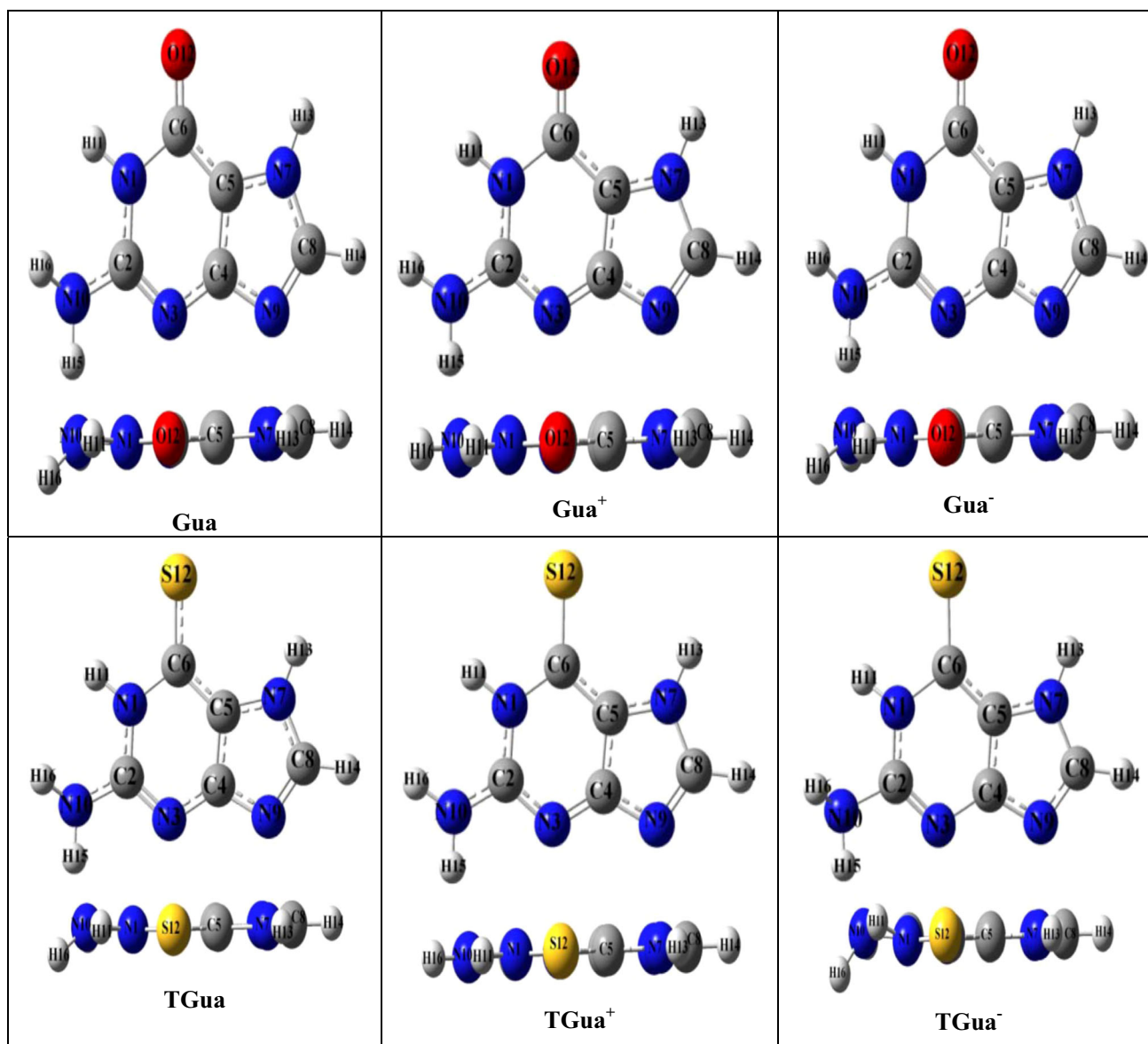


Fig. 1 Atomic Numbering scheme and Front and Lateral view of the Studied Molecules

the C₂, C₅, C₆ and H₁₁ sites (these sites are positive in nature) and atomic charges are decreased by 0.051, 0.165, 0.885 and 0.028 atomic unit in the TGua molecule. On the other hand in the TGua molecule, the electronegative N atom withdraws the electron from the C atoms which increase their positive nature than those of the Gua molecule. Thus the atomic charges are increased by 0.038, 0.033, 0.096 and 0.003 atomic unit on the N₁, N₃, C₄, and N₇ sites respectively in TGua molecule. It could be seen from the Table 1 that the calculated bond lengths of TGua are not much different from those of Gua except C₅–C₆ and N₁–C₆ which are shorter by 0.019 and 0.021 Å in going from Gua to TGua. Due to negative charges on the C₅ and N₁ sites pulled the electron from the C₆ site towards itself.

APT atomic charge (in electron unit) at each atomic site of the studied species at the same level are collected in Table 2 and these APT charges are pictorially shown in Fig. 3.

Due to removal of one electron from the neutral Gua and TGua molecules, the optimized geometries are modified. Atomic charges have also been redistributed on each atomic site upon the radicalization process. Due to removal of an electron in going from Gua to in Gua⁺ the APT charges on the C₂, N₃, C₅, C₈, H₁₁, O₁₂, and H_{13/14/15/16} sites increase while decrease on the N₁, C₄, C₆, N₇, N₉, N₁₀. In case of TGua⁺ the APT charges on the N₁, C₂, N₃, C₅, C₈, H₁₁, S₁₂, and H_{13/14/15/16} are found to increase while decrease on the C₄, C₆, N₇, N₉, N₁₀.

Table 1 Experimental and calculated structural parameters^a of Gua, TGua and their cations and anions

Definitions	Guanine				TGuanine			
	Gua		Gua ⁺	Gua ⁻	TGua		TGua ⁺	TGua ⁻
	Cal	Exp [11]			Cal	Exp [12]		
r (N ₁ -C ₂)	1.381	1.371	1.366	1.384	1.380	1.363	1.367	1.376
r (C ₂ -N ₃)	1.301	1.315	1.352	1.309	1.305	1.327	1.344	1.294
r (N ₃ -C ₄)	1.365	1.364	1.318	1.361	1.359	1.355	1.317	1.390
r (C ₄ -C ₅)	1.394	1.382	1.435	1.397	1.401	1.395	1.445	1.414
r (C ₅ -C ₆)	1.425	1.405	1.447	1.422	1.406	1.376	1.401	1.388
r (C ₆ -O ₁₂ /S ₁₂)	1.222		1.205	1.230	1.672	1.690	1.674	1.723
r (C ₆ -N ₁)	1.418	1.398	1.424	1.416	1.397	1.411	1.400	1.448
r (N ₇ -C ₅)	1.378	1.405	1.339	1.381	1.375	1.372	1.353	1.379
r (C ₈ -N ₇)	1.364	1.314	1.404	1.362	1.363	1.344	1.388	1.391
r (N ₉ -C ₈)	1.317	1.369	1.299	1.320	1.319	1.335	1.306	1.329
r (N ₉ -C ₄)	1.371	1.364	1.377	1.376	1.369	1.364	1.369	1.357
r (C ₂ -N ₁₀)	1.380		1.328	1.371	1.376	1.319	1.334	1.409
α (C ₅ -C ₆ -N ₁)	109.0		109.8	109.3	109.8		111.8	110.3
α (C ₆ -N ₁ -C ₂)	125.3		124.9	125.3	125.1		124.5	122.7
α (N ₁ -C ₂ -N ₁₀)	115.8		119.8	115.8	116.0		119.5	114.3
α (N ₁ -C ₂ -N ₃)	124.2		123.8	123.8	124.1		123.1	126.3
α (N ₁₀ -C ₂ -N ₃)	120.0		116.4	120.3	119.9		117.4	119.4
α (C ₂ -N ₁₀ -H ₁₆)	117.7		123.8	118.1	118.3		123.9	112.8
α (C ₂ -N ₁₀ -H ₁₅)	112.7		117.5	113.7	113.2		117.5	109.3
α (H ₁₆ -N ₁₀ -H ₁₅)	114.0		118.7	113.7	114.5		118.6	111.1
α (C ₅ -C ₄ -N ₃)	124.2		123.8	124.3	123.6		123.3	122.1
δ (C ₈ -N ₇ -C ₅ -C ₆)	179.0		180.0	179.2	179.4		180.0	180.0
δ (H ₁₃ -N ₇ -C ₅ -C ₄)	180.0		180.0	178.2	180.0		180.0	179.2
δ (N ₇ -C ₅ -C ₆ -N ₁)	179.4		180.0	179.3	180.0		180.0	179.1
δ (C ₄ -C ₅ -C ₆ -O ₁₂)	179.0		180.0	178.4	179.4		180.0	178.5
δ (C ₅ -C ₆ -N ₁ -C ₂)	0.1		0.0	0.3	0.6		0.0	3.8
δ (O ₁₂ -C ₆ -N ₁ -C ₂)	180.0		180.0	179.4	180.0		180.0	176.0
δ (C ₆ -N ₁ -C ₂ -N ₃)	0.1		0.0	1.3	0.4		0.0	6.0
δ (H ₁₁ -N ₁ -C ₂ -N ₃)	175		180.0	176.3	176.0		180.0	161.2
δ (N ₁ -C ₂ -N ₁₀ -H ₁₆)	35.8		0.0	28.3	33.4		0.0	46.2
δ (N ₃ -C ₂ -N ₁₀ -H ₁₅)	11.0		0.0	16.3	11.1		0.0	9.9
δ (N ₁ -C ₂ -N ₃ -C ₄)	0.8		0.0	1.2	0.5		0.0	4.3
δ (N ₁₀ -C ₂ -N ₃ -C ₄)	176.5		180.0	177.1	176.8		180.0	175.4

^a *r*, bond lengths (Å); α, bond angles (°); δ, dihedral angle (°)

The bond lengths N₁-C₂/C₂-N₁₀ are shortened by 0.015/0.052 Å for Gua⁺ and 0.013/0.042 Å for TGua⁺ due to increase of the atomic charges on the C₂ site which attracts the N₁ and N₁₀ atoms towards itself. Due to loss of electronic charge from the N₃ site, the atomic charges increase which repels the electropositive atom C₂. Therefore, the magnitude of bond length C₂-N₃ for the cationic species is greater by 0.051/0.039 Å for Gua⁺/TGua⁺ than that in their neutral molecules. Both the electropositive atoms C₄ and C₅ repel each other due to increase in their atomic charges and the C₄ site is being attracted by the

electronegative N₃ and N₉ atoms. Therefore, the magnitude of the common bond C₄-C₅ of pyrimidine ring and imidazole ring is lengthened by 0.041/0.044 Å in Gua⁺/TGua⁺ and N₃-C₄ bond is shortened by 0.047/0.042 Å in Gua⁺/TGua⁺ than those in neutral Gua and TGua. Due to redistribution of APT charges, the atomic charge decreases on C₆ site which is attached with electronegative O atom and increases on the C₅ site which is attracted by the electronegative atom N₇ in the ring. Thus, the bond lengths C₆=O₁₂/C₅-N₇/C₈-N₉ are shortened by 0.016/0.039/0.018 Å and the C₅-C₆ bond length is elongated by

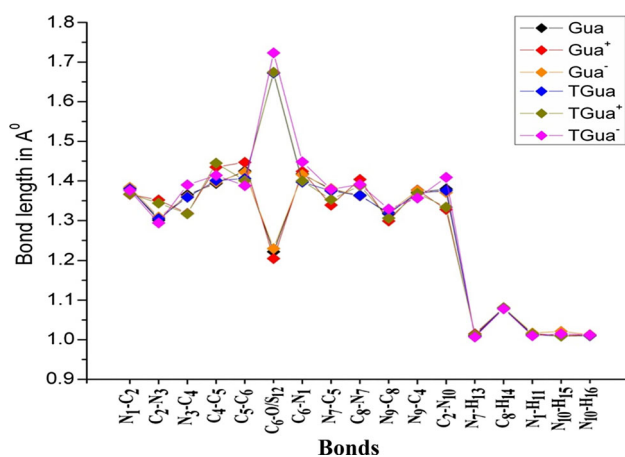


Fig. 2 Variations of Bond Lengths in different Molecules

Table 2 APT Charges* at various atomic sites of Gua, TGua and their cations and anions

Atom	Guanine			Thioguanine		
	Gua	Gua ⁺	Gua ⁻	TGua	TGua ⁺	TGua ⁻
N ₁	-0.646	-0.649	0.829	-0.608	-0.517	-0.680
C ₂	1.075	1.178	-1.878	1.018	1.069	0.917
N ₃	-0.769	-0.510	1.222	-0.736	-0.526	-0.613
C ₄	0.687	0.434	-0.977	0.783	0.661	0.019
C ₅	-0.277	0.180	-0.432	-0.364	0.165	0.019
C ₆	1.266	0.928	-0.690	0.993	0.108	0.574
N ₇	-0.403	-0.528	1.349	-0.400	-0.549	-0.216
C ₈	0.313	0.470	0.027	0.310	0.657	-0.263
N ₉	-0.528	-0.479	0.634	-0.536	-0.599	0.004
N ₁₀	-0.775	-0.767	2.008	-0.781	-0.818	-0.583
H ₁₁	0.211	0.252	-0.620	0.202	0.230	0.161
O/S ₁₂	-0.933	-0.600	0.454	-0.678	0.096	-0.855
H ₁₃	0.257	0.311	-1.110	0.255	0.271	0.206
H ₁₄	0.078	0.143	-0.331	0.084	0.138	0.042
H ₁₅	0.228	0.326	-0.481	0.236	0.332	0.175
H ₁₆	0.217	0.309	-1.004	0.221	0.282	0.094

* in electron unit

0.022 Å for the Gua cation. The bond length C₅-N₇/C₈-N₉ are shortened by 0.022/0.013 Å in TGua⁺ than that of TGua.

Changes in bond angles in Gua⁺ are insignificant while in TGua⁺ some changes are noticed. The angles N₃-C₂-N₁₀ and C₅-C₆-O₁₂/S₁₂ decrease by 1.6° and 3.6° for Gua⁺ and 1.9° and 2.5° for TGua⁺ as compared to their respective neutral species. It could be noticed from the Table 1 that angles N₁-C₂-N₁₀, C₂-N₃-C₄, C₂-N₁₀-H₁₅ and H₁₆-N₁₀-H₁₅ increase by 4.0°, 1.2°, 4.8° and 4.7° for Gua⁺ and 3.5°, 1.6°, 4.3° and 4.1° for TGua⁺. The angles C₅-N₇-H₁₃, C₆-C₅-N₇ and N₁-C₆-C₅ increase by 1.2°,

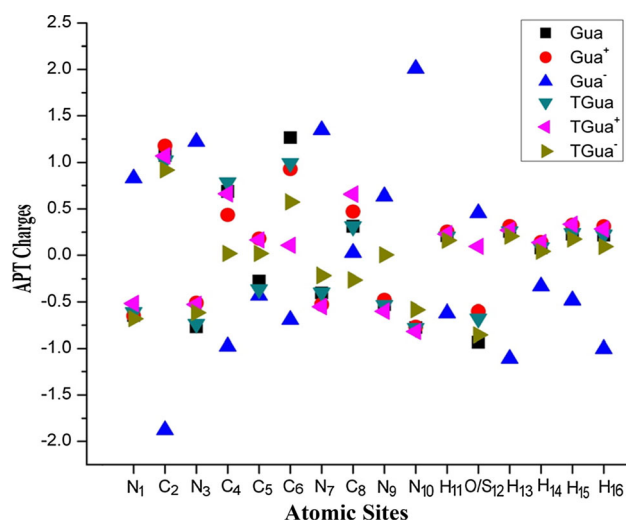


Fig. 3 Variations of APT Charges at various Atomic Sites

2.2° and 2.0° for and the angles C₈-N₇-H₃, C₄-C₅-C₆ and N₁-C₂-N₃ decrease by 1.3°, 1.8° and 1.0° in going from TGua to TGua⁺ respectively. It is also found that the angles N₇-C₈-H₁₄, C₂-N₁₀-H₁₆ and N₃-C₄-N₉ are increased by 1.0°, 6.1° and 1.0° in going from Gua to Gua⁺ radical respectively. Both the H atoms of the NH₂ group are pushed out-of-plane with respect to the molecular plan in case of neutral molecules. The radicalization of the neutral Gua and TGua molecules, causes both the H atoms to pull inside the molecular plane and the changes in the dihedral angles N₁-C₂-N₁₀-H₁₆/N₃-C₂-N₁₀-H₁₅ are noticed by 35.8°/11.0° for the Gua⁺ and 33.4°/11.1° for the TGua⁺ cations.

Adding one electron to the neutral Gua and TGua molecules leads to atomic charges redistribution on each atomic sites as a result of which molecular structures are slightly changed in the anionic species as compared to their respective neutral molecules. Due to attachment of an electron the APT charges on the N₁, N₃, N₇, N₉, N₁₀ and O₁₂ sites increase while decrease on the C₂, C₄, C₅, C₆, C₈, H₁₁ and H_{13/14/15/16} sites in going from Gua to the Gua⁻ anion. In case of TGua⁻ the APT charges on the N₃, C₅, N₇, N₉, and N₁₀ are found to increase by decreased on the N₁, C₂, C₄, C₆, C₈, H₁₁, S₁₂, and H_{13/14/15/16}.

The bond lengths C₂-N₃ and C₄-N₉ are elongated slightly in Gua⁻ and reverse of this is found with TGua⁻. The bond lengths C₄-C₅ and C₆=O₁₂/S₁₂ increase slightly 0.003 and 0.008 Å in Gua⁻ while these are lengthened by 0.013 and 0.051 Å in TGua⁻ as compared to their respective neutral Gua and TGua molecules. Enhancements are noticed in the above bond lengths due to decrease the atomic charges on the C₄ and C₆ sites. It could be noticed that the O atom has positive charge and C₆ atom has negative charges in Gua⁻ radical contrary to the case of all

the other molecules studied in the present case. The N₁–C₆ bond length is shortened (by 0.002 Å) in Gua[−] and elongated (by 0.051 Å) in TGua[−] as compared to their respective neutral molecules. In the anionic radical of TGua, the bond lengths N₃–C₄, C₈–N₇, C₈–N₉ and C₂–N₁₀ are lengthened as compared to its neutral molecule. Increased atomic charges on N atoms and decreased atomic charges on C atoms result in small changes in above bond lengths in the anionic radical.

It could be seen from the Table 1, in going from the Gua to Gua[−] only one angle C₆–N₁–H₁₁ has increased by 1.0°. The angles N₁₀–C₂–N₃, C₅–C₄–N₉, C₄–C₅–C₆, C₅–N₇–H₁₃ and N₉–C₈–H₁₄ increase by 2.2°, 1.0°, 1.2°, 1.4°, 1.1° and 1.7° in the TGua[−] radical as a result of radicalization. The angles C₆–N₁–C₂, N₁–C₂–N₁₀, N₃–C₄–C₅, N₇–C₅–C₄, N₉–C₈–N₇, N₁–C₆–S₁₂, C₂–N₁₀–H₁₅, C₂–N₁₀–H₁₆ and H₁₅–N₁₀–H₁₆ decrease by 2.5°, 1.7°, 1.5°, 1.0°, 1.8°, 2.2°, 3.9°, 5.5° and 3.4° in the TGua[−] radical. The dihedral angles N₁–C₂–N₁₀–H₁₆/N₃–C₂–N₁₀–H₁₅ are found to be 28.3°/16.3° in Gua[−] and 46.2°/9.9° in TGua[−]. In the TGua[−] radical, the H atom of the N₁H bond is found to be out-of-plane by the dihedral angle 20.0°. It is also to be noted that both the H atoms of the amino group in Gua[−] and TGua[−] species are pushed out-of-plane of purine more compared to their respective neutral molecules.

3.2. Vibrational analysis

The cations of Gua and TGua show planar structures with the C_s point group symmetry and all the 42 normal modes are distributed between the two species a' and a'' as: 29a' (in-plane) + 13a'' (out-of-plane). The neutral molecules and anions of Gua and TGua possess non-planar structures with C₁ point group symmetry and all the 42 normal modes are distributed as: 42a.

From the quantum chemical calculations one obtains the Raman activities (S_i) which can be used to calculate the corresponding Raman intensities (I_i) using the following relation [48, 49].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i/kT)]} \quad (1)$$

where ν_0 is the exciting frequency (in cm^{−1} units); ν_i is the vibrational wavenumber of the *i*th normal mode, *h*, *c* and *k* are the fundamental constants and *f* is a suitable chosen common normalization factor for all the peak intensities. The computed IR and Raman spectra for the Gua, TGua and their corresponding radical cations and anions are depicted in Figs. 4 and 5.

The calculated vibrational frequencies, scaled frequencies, the IR intensities, Raman scattering activities, observed frequencies of IR and Raman spectra and

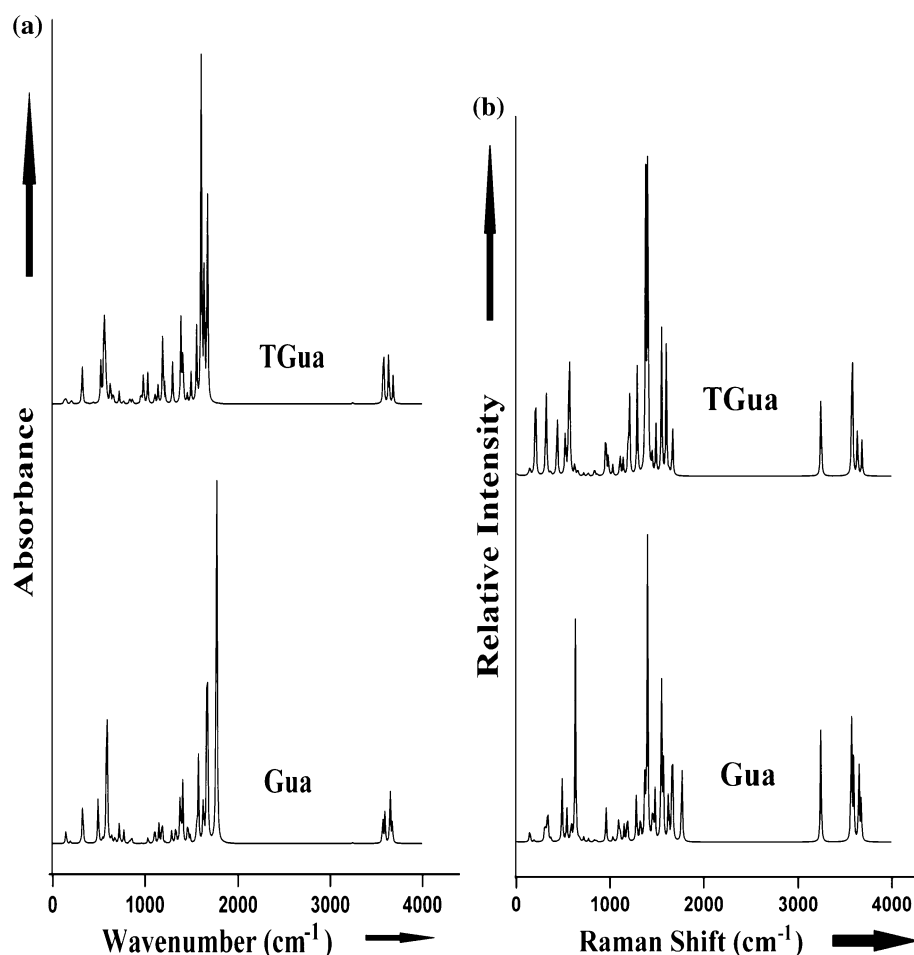
proposed normal modes assignment based on visual Gauss View software are collected in Table 3 for Gua, TGua and their ionic radicals and the PEDs for all the modes of all the studied molecules are collected in Table 4.

3.2.1. Neutral molecules

For the Neutral Molecules As could be seen from the Table 3 several of the normal modes show small variations in going from Gua to TGua. We have assigned all these frequencies in light of the PEDs (Table 4). In the present chapter only those modes of the neutral Gua and TGua molecules have been discussed which either are controversial or change considerably in going from one molecule to another. Replacement of O atom by S atom at the C₆ site of the Gua molecule results in significant changes in vibrational characteristics for some of the modes.

3.2.1.1. Ring modes The molecules under the present study are systems of two heterocyclic rings, a six membered pyrimidine ring and a five membered imidazole ring. The purine ring has 21 ring modes as 10 ring stretching, 5 in-plane bending and 6 out-of-plane deformation modes. The ring stretching modes have been identified as ν_{34} , ν_{33} , ν_{32} , ν_{31} , ν_{30} , ν_{29} , ν_{26} , ν_{23} , ν_{22} and ν_{13} (Table 3). The highest ring stretching mode has been calculated to be 1568/1633 cm^{−1} for Gua/TGua molecules. The IR intensity for the ν_{34} mode is increased 1.5-fold and Raman activity is decreased by a factor of ~1/15 in going from Gua to TGua. The mode ν_{34} has been observed by Delabar and Majoube [17] at 1565 cm^{−1} with strong intensity in IR spectrum for Gua. Gunasekaran et al. [26] assigned an IR band 1625 cm^{−1} with medium intensity and a Raman band 1620 cm^{−1} with very strong intensity. Earlier these frequencies are assigned to the scissoring mode of the NH₂ group [26] but we reassign these to the ring stretching mode (ν_{34}) in light of the present calculations. The ring stretching modes ν_{33} , ν_{32} , ν_{31} , ν_{30} and ν_{29} do not show large variation in going from the Gua to TGua molecules. It could be noticed from the Table 3 that the IR intensities for the ring stretching modes ν_{33} , ν_{32} , ν_{23} , ν_{22} and ν_{13} increase by factors of ~5, ~4, ~25, ~10 and ~20 for TGua as compared to the Gua molecule. The Raman intensities increase by factors of ~4, ~4, ~10 for ν_{29} , ν_{26} , ν_{22} respectively and decrease by a factor of ~1/2 for the ν_{23} mode in TGua as compared to those of Gua. The ν_{26} and ν_{22} modes for TGua increase by 22 and 160 cm^{−1} as compared to that of the Gua molecule. The frequencies for these modes (ν_{26} and ν_{22}) are observed at 1174 (IR)/1042(R) cm^{−1} and 1188 (IR)/1052(R) cm^{−1} respectively for Gua [23]. However, the ν_{26} mode is assigned at 1225 cm^{−1} (IR)/1229 cm^{−1} (R) for TGua [26] and the observed IR frequency 1201 cm^{−1} is assigned to the ν_{22}

Fig. 4 Calculated IR and Raman spectra of Gua and TGua molecules



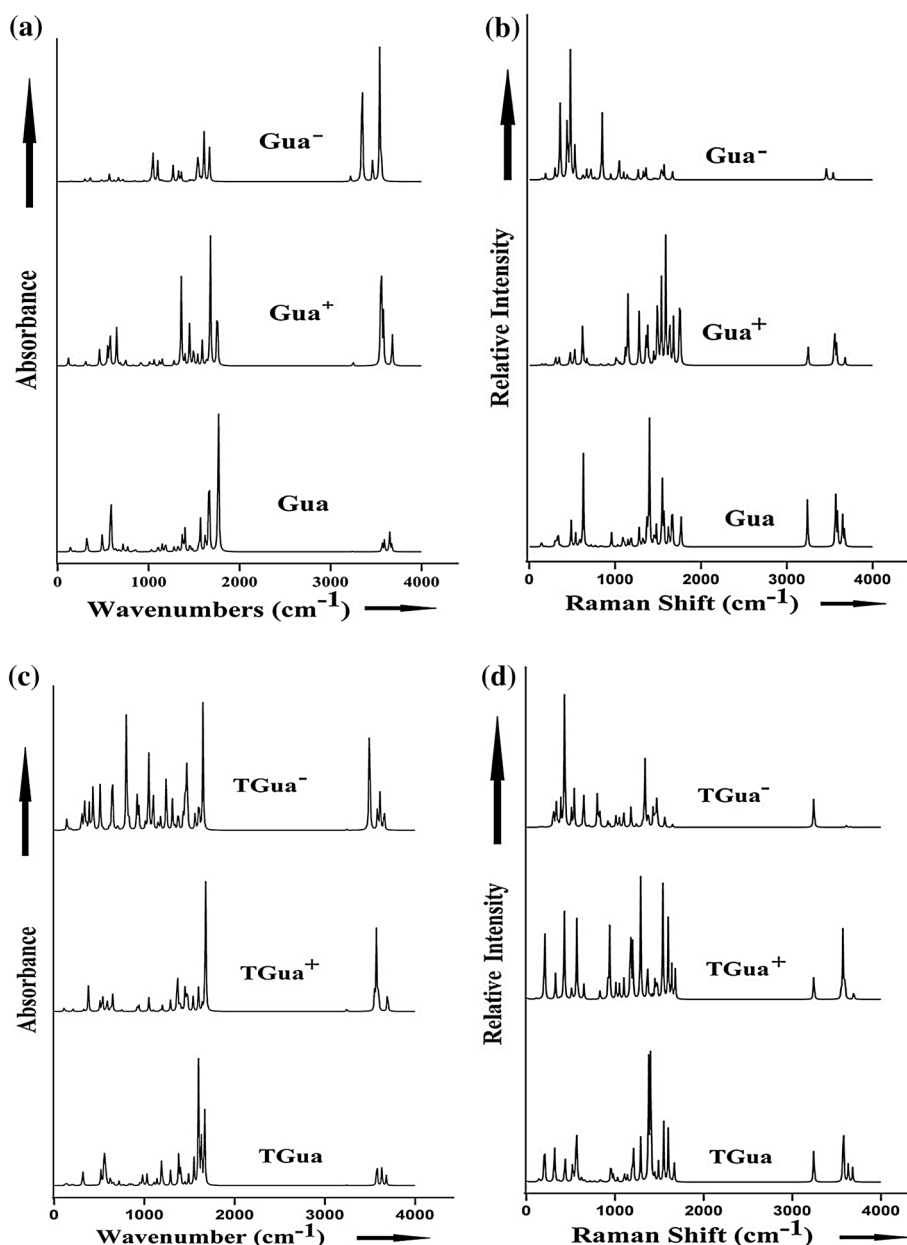
mode for TGua [24]. The ν_{23} and ν_{13} modes decrease by 59 and 64 cm^{-1} in going from Gua to TGua. The frequencies for these two modes are observed at 1032 and 570 cm^{-1} for TGua by Kasende et al. [24] in the IR spectrum. The lowest ring stretching ν_{13} mode is assigned at $601/602\text{ cm}^{-1}$ with weak intensity in the IR/Raman spectra for Gua by Delabar and Majoube [17].

The in-plane bending modes of the purine ring are identified as the modes ν_{21} , ν_{19} , ν_{15} , ν_{10} and ν_8 . The IR intensities for all these modes increase by factors of ~ 20 , ~ 2 , ~ 2 and ~ 3 except that of the ν_8 mode for the TGua molecule as compared to the Gua molecule. The Raman activities for modes ν_{21} and ν_{19} are enhanced twofold in going from Gua to TGua. It could be noticed that the lowest in-plane ring bending mode (ν_8) for TGua shifts downward by 53 cm^{-1} . This mode is observed at 490 cm^{-1} with medium IR band for Gua. However, Gunasekaran et al. [26] have observed this mode at $424/410\text{ cm}^{-1}$ with medium/weak intensities in the IR/Raman spectra respectively for TGua by Delabar and Majoube [17]. The mode ν_{21} could be observed at $950/940\text{ cm}^{-1}$ with strong intensity in the IR/Raman spectra of Gua [17] which corresponds especially to the

imidazole ring stretching. For TGua this mode is observed at 942 cm^{-1} in the IR spectrum by Kasende et al. [24] and 945 cm^{-1} in Raman spectrum by Gunasekaran et al. [26]. The ν_{19} mode corresponding to the pyrimidine ring is calculated to have frequency 834 and 835 cm^{-1} for the Gua and TGua molecules respectively. This mode is observed at 838 cm^{-1} with medium IR intensity for Gua [17] and 838 cm^{-1} with medium intensity in Raman spectrum for TGua [26]. The calculated frequencies for the ν_{15} and ν_{10} modes are found to be $674/539$ and $655/524\text{ cm}^{-1}$ for the Gua/TGua molecules. The mode ν_{15} could be assigned at 654 cm^{-1} with medium intensity in the IR spectrum for Gua [17] and at 656 cm^{-1} with medium intensity in the Raman spectrum for TGua [26]. The observed frequencies $541/547\text{ cm}^{-1}$ are assigned to the ν_{10} mode with weak intensities in IR/Raman spectra for Gua [17].

The purine ring has 6 non-planar modes (ν_{18} , ν_{14} , ν_7 , ν_3 , ν_2 and ν_1) out of which three modes correspond to the pyrimidine ring and two modes correspond to the imidazole ring and one is the butterfly type motion (ν_2), during which the two ring move like the wings of a butterfly. The mode ν_2 is calculated to be 148 and 126 cm^{-1} for the Gua

Fig. 5 Calculated IR and Raman spectra of Gua, TGua and its ions



and TGua respectively. The experimental Raman frequency 115 cm^{-1} with medium intensity for TGua [26] could be assigned to the butterfly mode (ν_2). The calculated IR intensity is decreased by factors of $\sim 1/3$ and $1/10$ for the mode ν_{18} and ν_{14} . These two modes (ν_{18}/ν_{14}) are calculated to be $770/641$ and $766/662\text{ cm}^{-1}$ for Gua and TGua respectively. The bands $778/775$ and $645/651\text{ cm}^{-1}$ for Gua appear in IR/Raman spectra [17] corresponding to the ν_{18} and ν_{14} modes. However, for TGua the frequency 645 cm^{-1} with medium intensity in Raman band [26] corresponds to the ν_{14} mode. The non-planar ring deformation modes (ν_3/ν_1) are found to be $191/142\text{ cm}^{-1}$ for Gua and $195/145\text{ cm}^{-1}$ for the TGua molecule. The

frequency observed at 150 cm^{-1} with medium and weak intensity in Raman spectrum could be assigned to the ν_1 mode for TGua [24].

3.2.1.2. N-H/C-H modes The C-H band has a stretching mode (ν_{38}), an in-plane bending mode (ν_{27}) and an out-of-plane bending mode (ν_{20}). From the Table-6.3 it could be seen that no changes are noticed in the vibrational frequencies of the C-H modes after replacing the O atom by S atom at the C_6 site. Gua and TGua have two N-H bonds, N_1 -H and N_7 -H, with the 2 stretching (ν_{41} and ν_{40}), 2 in-plane bending (ν_{28} and ν_{24}) and 2 out-of-plane bending (ν_{12} and ν_9) modes. The stretching modes ν_{41}/ν_{40} are calculated

Table 3 Experimental and Calculated Vibrational frequencies for Gua, TGua and their cations and anions

Modes	Guanine				Thioguanine				Assignments				
	Gua		Gua ⁺		Gua ⁻		TGua		TGua ⁺		TGua ⁻		
	Cal freq	(^a)Scaled freq Exp [17]	Cal freq	(^a)Scaled freq Exp [24, 26]	Cal freq	(^a)Scaled freq Exp [24, 26]	Cal freq	(^a)Scaled freq Exp [24, 26]	Cal freq	(^a)Scaled freq Exp [24, 26]	Cal freq	(^a)Scaled freq Exp [24, 26]	
V ₁	142 (21, 0) 0.69	139	118 (28, 0) 0.75	143 (10, 359) 0.67	145 (12, 0) 0.71	142	150 (R, w)	140 (2, 0) 0.75	141 (17, 102) 0.74			φ (ring) a''	
V ₂	148 (4, 0) 0.73	145	151 (2, 0) 0.75	152 (20, 559) 0.59	126 (10, 0) 0.72	123	115 (R, m)	113 (19, 0) 0.75	100 (0, 10) 0.48			φ (ring) a''/Butter fly	
V ₃	191 (4, 0) 0.33	187	191 (3, 0) 0.75	191 (3, 3710) 0.74	195 (3, 0) 0.25	191		209 (6, 0) 0.75	161 (4, 214) 0.33			φ (ring) a''	
V ₄	305 (3, 1) 0.35	398	307 (19, 2) 0.70	301 (175, 103.48) 0.30	205 (7, 6) 0.67	200		207 (7, 12) 0.73	186 (3, 253) 0.53			β (CO/S) a'	
V ₅	324 (90, 1) 0.75	317	461 (56, 0) 0.75	356 (309, 30.827) 0.745	316 (41, 5) 0.34	309		381 (118, 0) 0.75	337 (52, 24.859) 0.35			τ (NH ₂) a''	
V ₆	336 (2, 3) 0.57	329	347 (5, 3) 0.74	339 (2, 1458) 0.749	323 (41, 4) 0.30	316		329 (10, 6) 0.50	310 (10, 753) 0.43			β (C-NH ₂) a'	
V ₇	367 (1, 0) 0.69	359	302 (0, 0) 0.75	361 (28, 67.241) 0.60	365 (1, 0) 0.74	357		322 (0, 0) 0.75	306 (20, 16.392) 0.33			φ (ring) a''	
V ₈	489 (4, 5) 0.54	478	476 (3, 8) 0.40	493 (67, 109.923) 0.30	436 (3, 8) 0.42	426		428 (0, 30) 0.38	412 (7, 498) 0.27			α (ring) a'	
V ₉	492 (83, 1) 0.69	481	649 (135, 1) 0.75	444 (8, 114.443) 0.73	519 (54, 1) 0.75	508		626 (25, 1) 0.75	389 (41, 26.580) 0.34			γ (NH) a''	
V ₁₀	539 (6, 3) 0.75	527	527 (3, 9) 0.51	532 (91, 14.617) 0.26	524 (16, 5) 0.20	513		513 (7, 5) 0.20	511 (16, 22.573) 0.33			α (ring) a'	
V ₁₁	586 (279, 1) 0.58	572	576 (153, 0) 0.75	479 (92, 205.685) 0.35	555 (184, 4) 0.09	543		509 (40, 0) 0.74	802 (194, 78.246) 0.33			ω (NH ₂) a''	
V ₁₂	586 (69, 1) 0.75	573	550 (62, 0) 0.75	569 (485, 69.487) 0.41	624 (45, 2) 0.37	610		649 (70, 1) 0.75	432 (71, 154.928) 0.34			γ (NH) a''	

Table 3 continued

Modes	Guanine				Thioguanine				Assignments		
	Gua		Gua ⁺		Gua ⁻		TGua		TGua ⁺	TGua ⁻	
	Cal freq	(^d)Scaled freq	Exp [17]		Cal freq	(^d)Scaled freq	Exp [24, 26]				
v ₁₃	630	616	601 (IR, m)	623	621	566	554	570 (IR, s)	569	540	v (ring) a'
	(4, 25)		602 (R, w)	(1, 26)	(89, 6524)	(100, 22)			(5, 34)	(3, 49,671)	
v ₁₄	0.07			0.09	0.747	0.10			0.08	0.32	
	641	627	645 (IR, m)	637	630	662	648	645 (IR, w)	587	613	φ (ring) a''
v ₁₅	(10, 0)		651 (R, vs)	(0, 0)	(1, 7262)	(0, 0)			(60, 1)	(6, 2257)	
	0.28			0.75	0.72	0.71			0.75	0.35	
v ₁₆	674	659	654 (IR, m)	671	668	655	641	656 (R, m)	650	640	α (ring) a'
	(13, 0)			(3, 4)	(294, 27,234)	(21, 1)			(7, 7)	(31, 4375)	
v ₁₇	0.73			0.62	0.25	0.64			0.68	0.41	
	719	704	703 (IR, m)	723	706	719	704	693 (IR, m)	719	647	γ (C-NH ₂)
v ₁₈	(33, 0)		712 (R, vw)	(1, 0)	(106, 16,088)	(19, 1)		719 (R, w)	(3, 0)	(77, 66,075)	a''
	0.71			0.75	0.22	0.75			0.75	0.33	
v ₁₉	734	718	726 (IR, vw)	689	720	583	570	565 (IR, m)	537	357	γ (CO/S) a''
	(6, 0)			(9, 1)	(113, 22,028)	(26, 1)		564 (R, m)	(90, 0)	(12, 3887)	
v ₂₀	0.72			0.75	0.33	0.49			0.75	0.33	
	770	753	778 (IR, s)	747	760	766	750		748	704	φ (ring) a''
v ₂₁	(22, 1)		775 (R, vw)	(27, 1)	(21, 5933)	(7, 1)			(8, 0)	(9, 4982)	
	0.51			0.75	0.36	0.74			0.75	0.33	
v ₂₂	834	816	838 (IR, m)	833	832	835	817	838 (R, m)	832	827	α (ring) a'
	(6, 1)			(4, 2)	(29, 12,987)	(13, 2)			(0, 6)	(19, 45,080)	
v ₂₃	0.55			0.29	0.41	0.38			0.41	0.33	
	855	837	850 (IR, s)	909	849	864	845		926	511	γ (CH) a''
v ₂₄	(14, 0)		850 (R, vw)	(9, 0)	(48, 197,630)	(11, 1)			(7, 0)	(53, 67)	
	0.75			0.75	0.74	0.75			0.74	0.47	
v ₂₅	958	937	950 (IR, s)	923	951	955	934	942 (IR, m)	922	937	α (ring) a'
	(1, 7)		940 (R, s)	(11, 2)	(75, 18,233)	(20, 15)		945 (R, m)	(19, 15)	(41, 10,415) 0.31	
v ₂₆	0.22			0.59	0.72	0.18			0.59		
	1033	986	1042 (IR, w)	1034	1025	1193	1139	1201 (IR, w)	1012	1012	v (ring) a'
v ₂₇	(12, 1)		1052 (R, vw)	(8, 7)	(207, 10,921)	(129, 9)			(2, 15)	(13, 37,500)	
	0.31			0.10	0.74	0.74			0.23	0.34	
v ₂₈	1088	1039		1121	1099	1029	983	1032 (R, w)	1176	1097	v (ring) a'
	(2, 5)			(17, 18)	(1345, 30,949)	(51, 3)			(10, 95)	(72, 61317) 0.34	
v ₂₉	0.39			0.42	0.52	0.16			0.24		

Table 3 continued

Modes	Guanine				Thioguanine				Assignments				
	Gua		Gua ⁺		Gua ⁻		TGua			TGua ⁺		TGua ⁻	
	Cal freq	(^a)Scaled freq	Exp [17]		Cal freq	(^d)Scaled freq	Exp [24, 26]			Cal freq	(^d)Scaled freq	Exp [24, 26]	
v ₂₄	1105	1055	1118 (IR, m)	1013	1047	1056	1100 (IR s)	1051	1048	1100 (IR s)	1048	β (NH)	
	(35, 5)			(19, 10)	(2475, 98,100)	(20, 8)	1112 (R, w)	(63, 13)	(130, 31,197)	0.36			
v ₂₅	0.09			0.68	0.33			0.37					
	1150	1098	1150 (IR, w)	1061	1143	1090	1143 (IR sh)	1100	1154	1143 (IR sh)	1100	ρ (NH ₂) a'	
	(32, 4)			(21, 3)	(133, 27,448)	(28, 5)		(6, 18)	(15, 1871)				
v ₂₆	0.50			0.71	0.74			0.36	0.42				
	1185	1132	1174 (IR, m)	1149	1175	1153	1225 (IR, m)	1201	1182	1225 (IR, m)	1201	ν (ring) a'	
	(52, 9)			(23, 79)	(44, 8230)	(9, 32)	1229 (R, m)	(28, 57)	(20, 72,232)				
v ₂₇	0.10			0.39	0.26			0.32	0.33				
	1282	1224	1261 (IR, s)	1282	1269	1232	1285 (IR, m)	1289	1242	1285 (IR, m)	1289	β (CH) a'	
	(23, 14)			(18, 73)	(1054, 48,739)	(63, 38)		(51, 137)	(93, 13,058)	0.40			
v ₂₈	0.73			0.39	0.39			0.24					
	1325	1265	1378	1378	1331	1320	1375 (IR, w)	1420	1311	1375 (IR, w)	1420	β (NH) a'	
	(39, 9)			(1, 59)	(114, 19,232)	(76, 17)		(10, 5)	(47, 14,688)				
v ₂₉	0.37			0.64	0.67			0.15	0.37				
	1373	1311	1375 (IR, s)	1359	1359	1318	1370 (IR, m)	1366	1337	1370 (IR, m)	1366	ν (ring) a'	
	(93, 24)			(309, 36)	(618, 63,232)	(67, 97)	1369 (R, m)	(230, 54)	(8, 329,547)				
v ₃₀	0.65			0.28	0.18			0.71	0.33				
	1399	1336	1390 (IR, sh)	1399	1327	1340		1395	1375				
	(104, 95)			(36, 6)	(691, 29,850)	(88, 151)		(52, 6)	(37, 78,016)				
v ₃₁	0.19			0.24	0.71			0.52	0.32				
	1455	1390	1464 (IR, s)	1451	1450	1383	1433 (IR, m)	1453	1455	1433 (IR, m)	1453	ν (ring) a'	
	(46, 14)			(142, 17)	(95, 7639)	(15, 8)	1439 (R, m)	(142, 32)	(86, 75,147)				
v ₃₂	0.60			0.47	0.71			0.27	0.33				
	1479	1412	1477 (IR, s)	1495	1475	1423	1480 (IR, m)	1475	1473	1480 (IR, m)	1475	ν (ring) a'	
	(12, 17)			(84, 156)	(155, 12,361)	(46, 21)	1482 (R, m)	(133, 35)	(119, 179,687)	0.33			
v ₃₃	0.39			0.17	0.28			0.18					
	1548	1478	1550 (IR, s)	1635	1546	1480	1539 (IR, m)	1540	1433	1539 (IR, m)	1540	ν (ring)	
	(24, 62)			(24, 117)	(1617, 119,775)	(113, 64)	1537 (R, m)	(65, 158)	(29, 107,043)	0.34	a'		
v ₃₄	0.23			0.39	0.37			0.24					
	1568	1497	1565 (IR, s)	1539	1536	1559	1625 (IR, m)	1641	1563	1625 (IR, m)	1641	ν (ring) a'	
	(156, 29)			(38, 140)	(1292, 63,445)	(252, 2)	1620 (R, m)	(33, 53)	(28, 156,764)	0.32			
	0.40			0.39	0.37			0.50					

Table 3 continued

Modes	Guanine				Thioguanine				Assignments		
	Gua		Gua ⁺		Gua ⁻		TGua		TGua ⁺	TGua ⁻	
	Cal freq	(d) Scaled freq	Exp [17]		Cal freq	(d) Scaled freq	Exp [24, 26]				
v ₃₅	1623	1550	1638 (IR, m)	1589	1571	1601	1529	1585 (IR, w)	1600	1605	σ (NH ₂)
	(88, 23)		1604 (R, vw)	(88, 212)	(204, 50,134)	(538, 62)		1590 (R, m)	(106, 116)	(58, 58,147)	
v ₃₆	0.14			0.27	0.58	0.09				0.31	ν (C-NH ₂) a'
	1665	1590	1675 (IR, vs)	1679	1608	1668	1593	1666 (IR, m)	1678	1649	
v ₃₇	(508, 57)		1678 (R, m)	(461, 87)	(3315, 91,614)	(382, 28)			(651, 51)	(185, 692,542)	0.33
	0.19			0.28	0.55	0.27			0.40		
v ₃₈	1767	1687		1755	1668	982	961	980 (R, m)	940	918	ν (CO/S) a'
	(820, 41)			(293, 205)	(2480, 334,917)	(52, 5)			(27, 54)	(54, 15,608)	
v ₃₉	0.32			0.35		0.71			0.60	0.32	ν (CH) a'
	3241	3095		3247	3218	3243	3097	3090 (IR, m)	3243	3243	
v ₄₀	(2, 127)			(15, 120)	0.30	(3, 134)		3098 (R, w)	(12, 128)	(2, 14,972)	ν _s (NH ₂) a'
	0.29			0.51		0.30			0.34	0.33	
v ₄₁	3567	3406		3548	3346	3572	3411	3390 (IR, m)	3551	3583	ν (NH) a'
	(47, 198)			(160, 60)	(9407, 0)	(44, 115)			(85, 35)	(36, 1389)	
v ₄₂	0.15			0.60	0.17	0.21			0.45	0.60	ν (NH) a'
	3591	3429		3557	3463	3578	3417	3460 (IR, w)	3594	3656	
v ₄₃	(53, 107)	0.20		(350, 211)	(1665, 252,882)	(64, 164)			(111, 118)	(38, 14,029)	ν _{as} (NH ₂) a'
	0.74			0.12		0.13			0.72	0.34	
v ₄₄	3648	3484		3579	3541	3632	3468	3540 (IR, w)	3694	3612	ν _{as} (NH ₂) a'
	(101, 119)	0.20		(174, 1218)	(8264, 301,330)	(88, 86)			(107, 49)	(64, 36,143)	
v ₄₅	3673	3508		3677	3560	3681	3515		0.72	0.32	ν _{as} (NH ₂) a'
	(39, 65)			(131, 59)	(950, 151,945)	(43, 60)					
v ₄₆	0.74			0.69	0.45	0.75					ν _{as} (NH ₂) a'

(a) The first and second numbers within each bracket represent IR intensity and Raman activity while the numbers above and below the bracket represent the corresponding calculated frequency and depolarization ratio of the Raman band respectively

(b) ν = stretching mode, α = deformation mode, φ = out-of-plane ring deformation mode, β = in-plane bending mode, γ = out-of-plane bending mode, δ = deformation mode, ρ_{||} = parallel rocking mode, ρ_⊥ = perpendicular rocking mode, τ = torsion mode

(c) vw very-weak, w weak, m medium, ms medium-strong, s strong, vs very-strong, vvs very-very strong

(d) Calculated frequencies below 1000 cm⁻¹ were scaled by the scale factor 0.9786 and those above 1000 cm⁻¹ by the scale factor 0.9550 for larger wave numbers Ref. [65]

Table 4 PEDs (Potential Energy Distributions)^s of Gua, TGua and their cations and anions

Modes	Guanine		Gua ⁺		Gua ⁻	
	Gua	PED	Gua ⁺	PED	Gua ⁻	PED
V ₁	51φ(ring) + 31φ(ring) + 5φ(ring) + 5γ(N ₁ H)		51φ(ring) + 35φ(ring) + 6φ(ring)		48φ(ring) + 39φ(ring) + 5φ(ring) + 4γ(N ₁ H)	
V ₂	46φ(ring) + 20γ(N ₁ H) + 18φ(ring) + 7φ(ring) + 6φ(ring)		38φ(ring) + 27γ(N ₁ H) + 27φ(ring) + 4φ(ring)		45φ(ring) + 21γ(N ₁ H) + 19φ(ring) + 12φ(ring)	
V ₃	62φ(ring) + 20γ(N ₁ H) + 9φ(ring) + 4φ(ring)		52φ(ring) + 14φ(ring) + 11φ(ring) + 8γ(N ₁ H)		62φ(ring) + 19γ(N ₁ H) + 10φ(ring)	
V ₄	30β(C₆O) + 14α(ring) + 8τ(NH ₂) + 7ν(ring) + 6α(ring) + 6β(C-NH ₂) + 4ν(ring) + 4α(ring)		38β(C₆O) + 18α(ring) + 11ν(ring) + 8α(ring) + 5α(ring)		38β(C₆O) + 15α(ring) + 8α(ring) + 7ν(ring) + 5ν(ring) + 5α(ring)	
V ₅	63τ(NH ₂) + 22ω(NH₂) + 4γ(N ₁ H) + 4ν(C-NH ₂)		48ω(NH₂) + 34τ(NH ₂) + 14γ(N ₁ H)		49τ(NH ₂) + 16ω(NH₂) + 12φ(ring) + 4β(C-NH ₂) + 4ν(C-NH ₂)	
V ₆	53β(C-NH₂) + 11β(C ₆ O) + 12ν(ring) + 6ρ(NH ₂) + 5φ(ring)		61β(C-NH₂) + 10β(C ₆ O) + 10ν(ring) + 6ρ(NH ₂) + 4ν(ring)		54β(C-NH₂) + 10ν(ring) + 10β(C ₆ O) + 6ρ(NH ₂) + 4ν(ring)	
V ₇	59φ(ring) + 13φ(ring) + 11φ(ring) + 8φ(ring)		62φ(ring) + 13φ(ring) + 9φ(ring) + 8φ(ring) + 6φ(ring)		54φ(ring) + 13φ(ring) + 10φ(ring) + 6φ(ring) + 5ω(NH ₂)	
V ₈	40α(ring) + 30α(ring) + 5ν(C-NH ₂) + 4ν(ring) + 4α(ring)		47α(ring) + 27α(ring) + 5α(ring) + 4ν(ring)		36α(ring) + 15α(ring) + 13ω(NH ₂) + 9γ(N ₁ H) + 5α(ring) + 4ν(ring)	
V ₉	62γ(N₇H) + 23φ(ring) + 12φ(ring)		64γ(N₇H) + 20γ(N ₁ H) + 10τ(NH ₂)		61γ(N₇H) + 20φ(ring) + 14φ(ring)	
V ₁₀	44α(ring) + 17α(ring) + 12ν(ring) + 4β(C-NH ₂) + 4α(ring)		46α(ring) + 17α(ring) + 13ν(ring) + 4ν(ring) + 4β(C-NH ₂)		40α(ring) + 12α(ring) + 11γ(N ₁ H) + 5ν(ring) + 4ν(ring) + 4ν(C-NH ₂)	
V ₁₁	42ω(NH₂) + 33γ(N ₁ H) + 7ν(C-NH ₂) + 4α(ring) + 4γ(C ₆ O)		36φ(ring) + 28ω(NH₂) + 13γ(N ₇ H) + 12τ(NH ₂) + 10φ(ring) + 7φ(ring) + 4γ(N ₁ H)		34ω(NH₂) + 15γ(N ₁ H) + 13ν(C-NH ₂) + 7α(ring) + 7φ(ring)	
V ₁₂	41γ(N₁H) + 26ω(NH ₂) + 9γ(C-NH ₂) + 5φ(ring) + 4φ(ring)		31γ(N₇H) + 20φ(ring) + 18ω(NH ₂) + 16φ(ring) + 8γ(N ₁ H) + 7γ(C ₆ O) + 15τ(NH ₂)		49γ(N₁H) + 18ω(NH ₂) + 6γ(C-NH ₂) + 4τ(NH ₂)	
V ₁₃	18α(ring) + 14ν(ring) + 18ν(ring) + 10ν(ring) + 8ν(ring) + 6ν(ring) + 5ν(C-NH ₂) + 5α(ring)		18α(ring) + 16ν(ring) + 6ν(ring) + 10ν(ring) + 18ν(ring) + 6ν(ring) + 6ν(C-NH ₂) + 5γ(C ₆ O)		14α(ring) + 14ν(ring) + 15ν(ring) + 6ν(ring) + 6φ(ring) + 5ν(ring) + 5γ(N ₁ H) + 5α(ring) + 4ν(C ₆ O)	
V ₁₄	41φ(ring) + 21φ(ring) + 12φ(ring) + 8γ(N ₁ H) + 5φ(ring) + 5γ(C ₆ O)		30φ(ring) + 20γ(N ₁ H) + 19γ(N ₇ H) + 10τ(NH ₂) + 7φ(ring) + 6γ(C-NH ₂) + 5γ(C ₆ O)		37φ(ring) + 18φ(ring) + 12φ(ring) + 7γ(C ₆ O) + 7φ(ring) + 6γ(N ₁ H)	
V ₁₅	23β(C ₆ O) + 21β(C-NH ₂) + 20α(ring) + 5ν(ring) + 4ρ(NH ₂) + 4φ(ring) + 4α(ring)		23β(C ₆ O) + 23β(C-NH ₂) + 20α(ring) + 8α(ring) + 5ν(ring) + 6ρ(NH ₂)		24β(C ₆ O) + 23β(C-NH ₂) + 21α(ring) + 7ν(ring) + 5ρ(NH ₂) + 4α(ring)	
V ₁₆	36φ(ring) + 23γ(C-NH₂) + 9γ(C ₆ O) + 9φ(ring) + 6φ(ring) + 6φ(ring) + 5γ(N ₁ H)		60γ(C-NH₂) + 17φ(ring) + 9φ(ring) + 5φ(ring) + 5γ(C ₆ O)		29φ(ring) + 23γ(C-NH₂) + 19γ(C ₆ O) + 14φ(ring) + 7φ(ring) + 5γ(N ₁ H)	
V ₁₇	38γ(C₆O) + 30γ(C-NH ₂) + 18φ(ring) + 4φ(ring)		30φ(ring) + 28γ(C₆O) + 19γ(N ₁ H) + 13φ(ring)		38γ(C-NH ₂) + 31γ(C₆O) + 14φ(ring) + 4ω(NH ₂)	
V ₁₈	33φ(ring) + 31φ(ring) + 14γ(C ₆ O) + 9φ(ring) + 6γ(C-NH ₂)		32φ(ring) + 27φ(ring) + 18γ(C ₆ O) + 10φ(ring) + 6γ(C-NH ₂)		45φ(ring) + 31φ(ring) + 11γ(C ₆ O) + 7γ(C-NH ₂)	
V ₁₉	33α(ring) + 20α(ring) + 11ν(ring) + 10ν(ring) + 5ν(C-NH ₂) + 5α(ring)		42α(ring) + 18α(ring) + 9ν(ring) + 7ν(ring) + 5ν(ring)		37α(ring) + 20α(ring) + 11ν(ring) + 9ν(ring) + 5α(ring) + 5ν(C-NH ₂)	
V ₂₀	75γ(C₈H) + 17φ(ring) + 6φ(ring)		76γ(C₈H) + 17φ(ring) + 6φ(ring)		76γ(C₈H) + 16φ(ring) + 6φ(ring)	
V ₂₁	46α(ring) + 31α(ring) + 10ν(ring)		42α(ring) + 30α(ring) + 18ν(ring)		46α(ring) + 29α(ring) + 8ν(ring)	
V ₂₂	43ν(ring) + 13ρ(NH ₂) + 7ν(ring) + 7α(ring) + 7β(N ₁ H) + 6ν(C-NH ₂) + 4β(C ₆ O)		34ν(ring) + 28ρ(NH ₂) + 7β(N ₁ H) + 7β(C ₆ O) + 9ν(ring)		35ν(ring) + 15ρ(NH ₂) + 10ν(ring) + 10α(ring) + 7β(C ₆ O) + 5β(N ₁ H) + 4ν(C-NH ₂) + 4β(N ₇ H)	
V ₂₃	24ν(ring) + 16ρ(NH ₂) + 12β(N ₇ H) + 9α(ring) + 6ν(ring) + 5β(C ₆ O) + 5β(C ₈ H) + 5α(ring) + 4β(C ₆ O)		34ν(ring) + 20ν(ring) + 10ν(ring) + 9β(C ₆ O) + 8ρ(NH ₂)		28ν(ring) + 21ν(ring) + 18ρ(NH ₂) + 7β(C ₆ O) + 6β(N ₇ H) + 4ν(ring1)	
V ₂₄	31ν(ring) + 29β(N₇H) + 14ν(ring) + 8ρ(NH ₂) + 6β(C ₈ H) + 4β(C ₆ O)		47ν(ring) + 32β(N₇H) + 5α(ring ₂) + 4ν(ring ₂)		27ν(ring) + 23β(N₇H) + 18ν(ring) + 7β(C ₈ H) + 4α(ring)	

Table 4 continued

Modes	Guanine	
	Gua ⁺ PED	Gua ⁻ PED
V ₂₅	27 ρ (NH ₂) + 19v(ring) + 11v(C-NH ₂) + 9v(ring) + 7v(ring) + 5 α (ring) + 4 α (ring) + 4 β (N ₁ H) + 4 β (C ₈ H)	31 ρ (NH ₂) + 17v(ring) + 16v(ring) + 10v(C-NH ₂) + 9v(ring) + 4 α (ring)
V ₂₆	20 v(ring) + 16v(ring) + 14 α (ring) + 11 β (C ₈ H) + 7v(ring) + 8 β (C ₈ H) + 5 ρ (NH ₂) + 5v(C-NH ₂) + 4 β (C ₆ O)	24 v(ring) + 15 β (C ₈ H) + 15v(ring) + 15 α (ring) + 8v(ring) + 4 α (ring)
V ₂₇	27 β (C ₈ H) + 23v(ring) + 15v(ring) + 10v(ring) + 10v(ring) + 5 β (N ₇ H)	24v(ring) + 21 β (C ₈ H) + 18v(ring) + 17v(ring) + 5v(ring)
V ₂₈	36 β (N ₁ H) + 24v(C-NH ₂) + 8 ρ (NH ₂) + 6v(C ₆ O) + 8 α (ring) + 4v(ring)	25 β (N ₁ H) + 15v(ring) + 10 α (ring) + 12v(ring) + 11v(ring) + 6 β (C ₂ H) + 6v(C-NH ₂) + 9 α (ring)
V ₂₉	28 v(ring) + 21v(ring) + 15v(ring) + 11v(ring) + 7 β (C ₈ H) + 4 α (ring)	39 v(ring) + 27v(ring) + 11 β (C ₈ H) + 5v(ring) + 4v(ring)
V ₃₀	12 β (N ₇ H) + 12 v(ring) + 12v(ring) + 12v(ring) + 11 α (ring) + 10v(ring) + 8v(ring) + 8v(ring) + 4v(ring)	18v(C-NH ₂) + 15 v(ring) + 8 β (N ₁ H) + 8 β (N ₇ H) + 8 α (ring) + 7 ρ (NH ₂) + 7 α (ring) + 7v(ring)
V ₃₁	22 v(ring) + 16 β (N ₇ H) + 12v(ring) + 8 β (C ₈ H) + 7v(ring) + 11v(ring) + 9 α (ring) + 4 β (N ₁ H)	24 v(ring) + 19 β (N ₇ H) + 12v(ring) + 11v(ring) + 6 β (N ₁ H) + 6v(ring)
V ₃₂	24 v(ring) + 15v(ring) + 12v(ring) + 12v(ring) + 11 β (N ₁ H) + 5v(ring) + 4v(C ₆ O) + 4v(C-NH ₂)	30 v(ring) + 18 β (C ₈ H) + 13v(ring) + 7v(ring) + 5v(C ₆ O) + 5 α (ring) + 5 β (N ₁ H)
V ₃₃	22 v(ring) + 13v(ring) + 12v(ring) + 9 α (ring) + 11 α (ring) + 6v(ring) + 5 β (C ₈ H)	25 v(ring) + 11 α (ring) + 11 β (N ₁ H) + 9 β (N ₇ H) + 8 β (C ₈ H) + 8v(C-NH ₂) + 10v(ring) + 5v(ring) + 4v(C ₆ O)
V ₃₄	29 v(ring) + 13v(ring) + 8v(C ₆ O) + 7v(ring) + 7 β (N ₇ H) + 6v(ring) + 6 β (N ₁ H) + 5 α (ring) + 4 σ (NH ₂)	33 v(ring) + 30v(ring) + 11 α (ring) + 8 α (ring) + 6v(ring)
V ₃₅	42 σ (NH ₂) + 25v(ring) + 4 α (ring) + 4 β (N ₁ H)	36v(ring) + 22 σ (NH ₂) + 5v(ring) + 4 ρ (NH ₂)
V ₃₆	41 σ (NH ₂) + 24v(ring) + 16 v(C-NH ₂) + 5 β (N ₁ H) + 4 α (ring)	59 σ (NH ₂) + 15 v(C-NH ₂) + 14v(ring)
V ₃₇	59 v(C ₆ O) + 19v(ring) + 5 α (ring)	62 v(C ₆ O) + 12v(ring) + 9 β (N ₁ H) + 5v(ring)
V ₃₈	99 v(C ₈ H)	99 v(C ₈ H)
V ₃₉	52 v(N ₁₀ -H ₁₆) + 47 v(N ₁₀ -H ₁₅)	91 v(N ₁₀ -H ₁₆) + 8 v(N ₁₀ -H ₁₅)
V ₄₀	99 v(N ₁ H)	99 v(N ₁ H)
V ₄₁	99 v(N ₇ H)	99 v(N ₇ H)
V ₄₂	52 v(N ₁₀ -H ₁₆) + 48 v(N ₁₀ -H ₁₅)	92 v(N ₁₀ -H ₁₅) + 8 v(N ₁₀ -H ₁₆)
Modes	Thioguanine	TGua ⁻ PED
	TGua ⁺ PED	
V ₁	39 ϕ (ring) + 23 ϕ (ring) + 16 γ (N ₁ H) + 8 ϕ (ring) + 4 γ (C-NH ₂)	78 ϕ (ring) + 7 γ (N ₁ H) + 5 γ (C ₈ H)
V ₂	25 ϕ (ring) + 31 ϕ (ring) + 25 ϕ (ring) + 10 γ (N ₁ H) + 4 γ (C ₆ S) + 10 γ (N ₇ H) + 8 γ (N ₁ H) + 18 ϕ (ring) + 10 γ (N ₇ H) + 8 γ (N ₁ H) + 5 ϕ (ring)	57 γ (C ₈ H) + 37 ϕ (ring) + 8 γ (N ₁ H) + 8 ϕ (ring) + 4 γ (C-NH ₂) 50 γ (C ₈ H) + 38 ϕ (ring) + 12 ϕ (ring)

Table 4 continued

Modes	Thioguanine		
	TGua PED	TGua ⁺ PED	TGua ⁻ PED
V ₃	71β(C₆S) + 10α(ring)	74β(C₆S) + 10α(ring)	66β(C₆S) + 10α(ring) + 4ν(ring) + 4γ(N ₁ H)
V ₄	44τ(NH ₂) + 18ω(NH₂) + 18β(C-NH ₂) + 4γ(N ₁ H) + 4ν(C-NH ₂)	61ω(NH ₂) + 28τ(NH₂) + 6γ(N ₁ H) + 4γ(CS)	41τ(NH₂) + 21γ(C ₈ H) + 19φ(ring) + 4ω(NH ₂) + 4φ(ring)
V ₅	37τ(NH ₂) + 21β(C-NH₂) + 13ω(NH ₂) + 5ν(ring) + 4α(ring)	57β(C-NH₂) + 16ν(ring) + 6α(ring) + 6ρ(NH ₂)	37γ(C ₈ H) + 34β(C-NH₂) + 10φ(ring) + 10β(C ₆ S)
V ₆	38φ(ring) + 16φ(ring) + 15φ(ring) + 13φ(ring) + 7γ(C-NH ₂)	66φ(ring) + 16φ(ring) + 15φ(ring)	38γ(C ₈ H) + 38φ(ring) + 11φ(ring) + 4γ(C-NH ₂)
V ₇	35α(ring) + 29α(ring) + 18ν(C ₆ S) + 5ν(ring) + 4β(C-NH ₂)	34α(ring) + 30α(ring) + 16ν(C ₆ S) + 5β(C ₆ S)	23α(ring) + 20α(ring) + 12ν(C ₆ S) + 12γ(C ₈ H) + 8α(ring) + 5γ(N ₁ H) + 4β(C ₆ S)
V ₈	62γ(N₇H) + 26φ(ring) + 9φ(ring)	39γ(C ₈ H) + 32γ(N₇H) + 12φ(ring) + 11φ(ring)	48φ(ring) + 42γ(N₇H)
V ₉	44α(ring) + 12β(C-NH ₂) + 9ν(C-NH ₂) + 10ν(ring) + 5β(C ₆ S)	42α(ring) + 12α(ring) + 12β(C ₆ S) + 5ν(C ₆ S) + 5β(C-NH ₂) + 4ν(ring)	33α(ring) + 12β(C ₆ S) + 10ν(ring) + 8ν(C-NH ₂) + 5ν(ring) + 5ν(N ₁ H) + 4γ(N ₇ H)
V ₁₀	39ω(NH₂) + 9ν(C-NH ₂) + 8φ(ring) + 12α(ring) + 7γ(N ₇ H)	38ω(NH₂) + 22γ(C-NH ₂) + 19τ(NH ₂) + 18φ(ring) + 10φ(ring) + 8γ(C ₈ H) + 8φ(ring)	49ω(NH₂) + 20γ(C ₆ S) + 11ν(C-NH ₂) + 10φ(ring)
V ₁₁	56γ(N₁H) + 9φ(ring) + 5γ(C ₆ S)	80γ(N₁H) + 9τ(NH ₂)	44γ(N₁H) + 14φ(ring) + 7φ(ring) + 6γ(C ₈ H) + 5α(ring) + 4ν(ring)
V ₁₂	30ω(NH ₂) + 26ν(ring) + 8α(ring) + 7ν(C ₆ S) + 5ν(ring)	20α(ring) + 20ν(ring) + 16α(ring) + 12ν(C ₆ S) + 12ν(ring) + 10ν(ring) + 5ν(C-NH ₂)	30α(ring) + 26ν(ring) + 12α(ring) + 11ν(C ₆ S) + 10ν(ring) + 5ν(C-NH ₂)
V ₁₃	40φ(ring) + 16φ(ring) + 13φ(ring) + 9γ(C ₆ S) + 8γ(N ₇ H) + 7φ(ring)	29γ(C ₈ H) + 28φ(ring) + 16φ(ring) + 13γ(C-NH ₂) + 9φ(ring)	57φ(ring) + 16φ(ring) + 9φ(ring) + 11φ(ring)
V ₁₄	32γ(N ₁ H) + 19α(ring) + 13β(C-NH ₂) + 8β(C ₆ S) + 7ν(ring) + 5α(ring)	21α(ring) + 20β(C ₆ S) + 12β(C-NH ₂) + 11ν(ring) + 10α(ring) + 8α(ring)	25γ(C ₆ S) + 24α(ring) + 7β(C ₆ S) + 9α(ring) + 7φ(ring) + 6φ(ring) + 6ω(NH ₂)
V ₁₅	47γ(C-NH₂) + 32φ(ring) + 12φ(ring)	45γ(C-NH₂) + 26φ(ring) + 14φ(ring) + 7φ(ring) + 4γ(N ₁ H)	25γ(C-NH₂) + 15φ(ring) + 8ω(NH ₂) + 12φ(ring) + 10α(ring) + 6β(C ₆ S) + 4γ(N ₁ H) + 4β(C-NH ₂)
V ₁₆	38φ(ring) + 31γ(C₆S) + 17γ(N ₇ H) + 7φ(ring)	26γ(C₆S) + 20τ(NH ₂) + 12φ(ring) + 12γ(C ₈ H) + 11φ(ring) + 10γ(N ₁ H) + 5ω(NH ₂)	27φ(ring) + 24γ(C₆S) + 17φ(ring) + 11γ(N ₁ H) + 10γ(C ₈ H) + 8γ(C-NH ₂) + 8τ(NH ₂)
V ₁₇	46φ(ring) + 37φ(ring) + 8γ(C-NH ₂)	36φ(ring) + 34φ(ring) + 11γ(C ₆ S) + 10φ(ring)	41φ(ring) + 24φ(ring) + 22φ(ring) + 5γ(C ₆ S) + 9φ(NH ₂)
V ₁₈	29α(ring) + 20α(ring) + 12ν(ring) + 11ν(ring) + 6α(ring) + 4ν(C-NH ₂)	40α(ring) + 18α(ring) + 11ν(ring) + 16ν(ring) + 6ν(ring)	32α(ring) + 15α(ring) + 13ν(ring) + 11ν(ring) + 9ω(NH ₂)
V ₁₉	78γ(C₈H) + 17φ(ring) + 4γ(N ₇ H)	75γ(C₈H) + 17φ(ring) + 7φ(ring)	52γ(N ₇ H) + 37γ(C₈H) + 11φ(ring)
V ₂₀	37α(ring) + 34α(ring) + 9ν(ring) + 4ν(C ₆ S)	37α(ring) + 27α(ring) + 13ν(C ₆ S) + 9ν(ring) + 4ν(ring)	39α(ring) + 17ν(ring) + 13ν(C ₆ S) + 10ν(ring) + 4β(C ₈ H)
V ₂₁	50ν(ring) + 14ν(C ₆ S) + 13β(N ₁ H) + 5α(ring) + 4ν(ring)	33ν(ring) + 31ρ(NH ₂) + 13ν(ring) + 5β(C-NH ₂) + 5α(ring)	25ν(ring) + 15ν(ring) + 10ρ(NH ₂) + 7β(C ₈ H) + 10α(ring) + 6α(ring) + 4β(C-NH ₂) + 4β(N ₇ H)
V ₂₂	20ρ(NH ₂) + 18ν(ring) + 13ν(ring) + 13α(ring) + 8ν(C ₆ S) + 6α(ring) + 4β(N ₇ H) + 4β(C ₆ S)	48ν(ring) + 8ν(C ₆ S) + 8ν(ring) + 6ν(ring) + 6β(N ₁ H) + 8α(ring)	46ν(ring) + 13ν(C ₆ S) + 6β(C ₈ H) + 5ν(ring) + 5β(N ₁ H) + 4α(ring)
V ₂₃	49ν(ring) + 30β(N₇H) + 7β(C ₈ H) + 4ρ(NH ₂)	45ν(ring) + 20β(C ₈ H) + 19β(N₇H) + 11α(ring)	51ν(ring) + 21β(N₇H) + 10β(C ₈ H) + 7ρ(NH ₂) + 6α(ring)
V ₂₄	41ρ(NH₂) + 16ν(ring) + 13ν(ring) + 11ν(C-NH ₂) + 5ν(C ₆ S)	35ρ(NH₂) + 27ν(ring) + 7ν(C ₆ S) + 10ν(ring) + 5α(ring) + 5ν(C-NH ₂)	36ρ(NH₂) + 26ν(ring) + 8ν(ring) + 7β(N ₁ H) + 6α(ring) + 4β(N ₇ H)

Table 4 continued

Modes	Thioguanine		
	TGua PED	TGua ⁺ PED	TGua ⁻ PED
V ₂₅	22β(C ₈ H) + 17ν(ring) + 16α(ring) + 20ν(ring) + 6β(N ₇ H)	16β(N ₇ H) + 16ν(ring) + 15α(ring) + 14ν(ring) + 9ν(ring) + 14ν(ring) + 5ν(C-NH ₂)	26β(N ₇ H) + 20ν(ring) + 18α(ring) + 7ν(ring) + 7ν(NH ₂) + 9ν(ring) + 4β(C ₈ H)
V ₂₆	25ν(ring) + 20β(C ₈ H) + 14ν(ring) + 20ν(ring) + 6β(N ₁ H) + 5ν(C-NH)	28β(N ₇ H) + 26ν(ring) + 11β(C ₈ H) + 17ν(ring I) + 4β(N ₁ H)	32ν(C₈H) + 17(ring) + 12β(N ₇ H) + 7ν(C-NH ₂) + 5β(N ₁ H) + ν(ring)
V ₂₇	22ν(ring) + 16β(N ₁ H) + 10α(ring) + 10ν(C-NH ₂) + 14ν(ring) + 7ν(ring) + 6ν(NH ₂)	39β(N₁H) + 19ν(C-NH ₂) + 12α(ring) + 10ν(ring) + 5σ(NH ₂)	16β(N₁H) + 11β(C ₈ H) + 19ν(ring) + 14ν(ring 2) + 9α(ring) + 8ν(C-NH ₂) + 6α(ring)
V ₂₈	25ν(ring) + 16ν(ring) + 10α(ring) + 9β(N ₁ H) + 7ν(C-NH ₂) + 7α(ring) + 5ν(ring) + 5ν(ring)	35ν(ring) + 22ν(ring) + 9ν(ring) + 9α(ring) + 8α(ring) + 5α(ring)	25ν(ring) + 12ν(ring) + 11ν(ring) + 11ν(ring) + 5ν(ring) + 5β(N ₇ H) + 5α(ring) + 4β(C ₈ H)
V ₂₉	18ν(ring) + 13β(N ₇ H) + 20ν(ring) + 11ν(ring) + 6ν(ring) + 5α(ring)	37β(C ₈ H) + 25ν(ring) + 17β(N ₇ H) + 4α(ring)	24ν(ring) + 16β(C ₈ H) + 10β(N ₇ H) + 13ν(ring) + 9ν(ring) + 8ν(ring) + 4α(ring) + 4α(ring)
V ₃₀	21β(N ₇ H) + 19ν(ring) + 11ν(ring) + 12ν(ring) + 7ν(ring) + 7β(N ₁ H)	26ν(ring) + 24ν(ring) + 11ν(ring) + 10p(NH ₂) + 10β(C ₆ S) + 6β(C ₈ H)	23β(N ₁ H) + 21ν(ring) + 9β(N ₇ H) + 10ν(ring) + 7α(ring) + 5ν(ring)
V ₃₁	37ν(ring) + 21β(C ₈ H) + 10α(ring) + 15ν(ring) + 5ν(ring) + 4β(N ₁ H)	40ν(ring) + 23ν(ring) + 12α(ring) + 10β(N ₇ H)	23β(N ₁ H) + 22ν(ring) + 9β(N ₇ H) + 8ν(ring) + 7α(ring) + 5ν(ring)
V ₃₂	27ν(ring) + 16ν(ring) + 9α(ring) + 8ν(ring) + 6ν(ring) + 10α(ring) + 8ν(ring)	41ν(ring) + 17ν(ring) + 6ν(ring) + 6ν(ring) + 5β(C ₈ H) + 5ν(ring)	32ν(ring) + 17ν(ring) + 15ν(ring) + 10β(C ₈ H) + 9α(ring) + 7β(N ₇ H) + 4α(ring)
V ₃₃	33p(NH ₂) + 28ν(ring) + 8ν(ring) + 5α(ring)	32ν(ring) + 22ν(ring) + 9ν(ring) + 12α(ring) + 5σ(NH ₂) + 4β(N ₇ H)	37ν(ring) + 19ν(ring) + 8β(C ₈ H) + 12α(ring) + 4β(N ₁ H)
V ₃₄	28β(N ₁ H) + 21ν(ring I) + 12σ(NH₂) + 7ν(C-NH ₂) + 6ν(ring) + 12ν(ring) + 4α(ring)	31σ(NH₂) + 23β(N ₁ H) + 15ν(ring) + 8ν(C-NH ₂) + 8ν(ring)	48σ(NH₂) + 32ν(ring)
V ₃₅	38σ(NH ₂) + 29ν(ring) + 15ν(C-NH₂)	45σ(NH ₂) + 33ν(C-NH₂) + 5β(N ₁ H) + 8ν(ring) + 4α(ring)	40σ(NH ₂) + 35ν(ring) + 9ν(C-NH₂)
V ₃₆	35ν(ring) + 26ν(C₆S) + 11α(ring) + 9ν(C-NH ₂) + 4α(ring)	35ν(C₆S) + 13α(ring) + 11ν(ring) + 8ν(ring) + 12ν(ring) + 6α(ring)	34α(ring) + 23ν(C₆S) + 8α(ring) + 7α(ring) + 5ν(ring) + 4ν(ring)
V ₃₇	99ν(C₈H)	99ν(C₈H)	99ν(C₈H)
V ₃₈	39ν(N₁₀-H₁₆) + 37ν(N₁₀-H₁₅) + 24ν(N ₁ H)	57ν(N₁₀-H₁₆) + 37ν(N₁₀-H₁₅) + 5ν(N ₁ H)	77ν(N₁₀-H₁₆) + 22ν(N₁₀-H₁₅)
V ₃₉	75ν(N₁H) + 12ν(N ₁₀ -H ₁₆) + ν(N ₁₀ -H ₁₅)	95ν(N₁H)	99ν(N₁H)
V ₄₀	99ν(N₇H)	99ν(N₇H)	99ν(N₇H)
V ₄₁	51ν(N₁₀-H₁₅) + 49ν(N₁₀-H₁₆)	60ν(N₁₀-H₁₆) + 40ν(N₁₀-H₁₅)	77ν(N₁₀-H₁₆) + 22ν(N₁₀-H₁₅)
V ₄₂			

S_i same as in Table 3

Bold characters show the maximum possible vibrational modes of their species

to be 3648/3591 and 3632/3578 cm^{-1} for the Gua and TGua molecules respectively. The IR intensity and the Raman activity of the ν_{41} mode decrease while reverse is found for the mode ν_{40} in TGua as compared to Gua molecule. Delabar and Majoube [17] could not observe frequencies for the N–H stretching modes in Gua. These modes (ν_{41}/ν_{40}) are earlier assigned at 3460/3390 cm^{-1} with weak/medium intensity in IR spectrum for TGua [26]. The mode (ν_{28}) is calculated to have frequencies 1325/1382 cm^{-1} for the Gua/TGua molecules. The IR intensity and Raman activity are increased twofold for the TGua molecule. The depolarization ratio increases in TGua as compared to Gua. The ν_{28} mode arises due to strong coupling of the two N–H in-plane bending modes. The ν_{24} mode is calculated to be 1105/1106 cm^{-1} for Gua/TGua and Raman activity increases by a factor of ~ 2 only for TGua. This mode is a result of the coupling of the planar bending mode of the N_7H and C_8H bonds. The frequency 1118 cm^{-1} observed with medium IR intensity and earlier assigned as ν_{24} mode for Gua [17] and 1100/1112 cm^{-1} with strong and weak intensity in IR/Raman spectra are correlated to this mode for TGua [26]. The C–H out-of-plane bending mode (ν_{20}) is calculated to be 855/864 cm^{-1} for the Gua/TGua molecules. For the above mode the observed frequency is 850 cm^{-1} in the IR spectrum with strong intensity and 850 cm^{-1} as a weak Raman band for Gua molecule [17]. Both the N–H out-of-plane bending modes (ν_{12} and ν_9) are increased by 38 and 27 cm^{-1} with medium IR intensity in going from Gua to TGua. It could also be seen that the ν_{12} mode in the TGua molecule becomes polarized and the ν_9 mode becomes depolarized. The ν_{12} mode is assigned by Delabar and Majoube [17] at 557/568 cm^{-1} with medium intensities in IR/Raman bands and the ν_9 mode is correlated to 496 cm^{-1} with medium IR band for Gua. However, the ν_{12} mode is assigned at 600 cm^{-1} with medium intensity in IR spectrum and 490/486 cm^{-1} with weak intensity in IR and Raman spectra for the ν_9 mode respectively for TGua by Gunasekaran et al. [26].

3.2.1.3. C=O/S modes The C=O/C=S stretching mode (ν_{37}) has been calculated to be 1767/982 cm^{-1} for Gua/TGua. The IR intensity and Raman activity are found to decrease by factors of $\sim 1/16$ and $1/8$ and depolarization ratio increases in going from Gua to TGua. The IR intensity and Raman activity of the in-plane bending (ν_4) and out-of-plane bending (ν_{17}) modes are increased in TGua. Experimental frequencies for these modes ν_{37} , ν_{17} and ν_4 could be observed as 980, 564 and 233 cm^{-1} with medium intensity in the Raman spectrum for TGua by Gunasekaran et al. [26]. Delabar and Majoube [17] have observed the frequency 726 cm^{-1} for Gua and Gunasekaran et al. [26] observed the frequency 565 cm^{-1} for TGua with weak IR intensity corresponding to the mode ν_{17} .

3.2.1.4. C–NH₂ modes The identification of the C–NH₂ stretching frequency is very difficult task due to strong mixing of this mode with other modes but it could be assigned with the help of PED calculations. The mode ν_{36} has been observed as a strong IR band at 1675 cm^{-1} and a medium Raman band 1678 cm^{-1} for Gua [17]. For the TGua molecule 1666 cm^{-1} in the IR spectrum could be assigned as the ν_{36} mode by Kasende [24]. In the present calculation the in-plane bending mode (ν_6) is found to have frequency 336 cm^{-1} for Gua and 323 cm^{-1} for TGua while the IR intensity and depolarization ratio are increased in TGua than that of Gua. The mode ν_6 is observed at 348/343 cm^{-1} with medium intensity of IR/Raman bands for Gua [17] and at 320 cm^{-1} with weak intensity in Raman band for TGua by Gunasekaran et al. [26]. The calculated frequency 719 cm^{-1} is identified as the C–NH₂ out-of-plane bending mode (ν_{16}) for the both Gua and TGua molecules. However, it is noticed that calculated IR intensity is increased by a factor of ~ 2 in TGua. The experimental frequency could be found at 703 and 712 cm^{-1} with medium IR and weak Raman intensity for Gua by Delabar and Majoube [17] and at 693/719 cm^{-1} with medium intensity in IR/weak intensity in Raman spectra for TGua by Gunasekaran et al. [26].

3.2.1.5. NH₂ modes The frequencies for the NH₂ group appear in the frequency range 3500–3300 cm^{-1} for the stretching modes, 1700–1600 cm^{-1} for the scissoring mode and 1150–900 cm^{-1} for the rocking mode.

The 6-normal modes of the NH₂ group are: the antisymmetric (ν_{42}) and symmetric (ν_{39}) stretching, scissoring (ν_{35}), rocking (ν_{25}), wagging (ν_{11}) and torsion/twisting (ν_5). The modes ν_{42} and ν_{39} could be seen to be pure modes which are calculated to be 3673/3681 and 3346/3567 cm^{-1} for the Gua and TGua molecules. The IR frequencies for the above modes for TGua are observed at 3540 cm^{-1} with weak intensity by Gunasekaran et al. [26]. The mode ν_{35} is found to decrease by 22 cm^{-1} and IR intensity and Raman activity are increased by factors of ~ 6 and ~ 3 . This mode has been observed at 1638 and 1604 cm^{-1} for Gua [17] and at 1585 and 1590 cm^{-1} for TGua [26] with medium intensity in IR and Raman spectra. The above mode is also coupled with the in-plane bending mode of N_1H . The rocking mode (ν_{25}) is observed at 1150 (IR)/1161(R) cm^{-1} for Gua by Delabar and Majoube [17] and at 1143 (IR) cm^{-1} by Kasende et al. [23]. Twisting and wagging modes (ν_{11}/ν_5) are calculated to have frequencies 586/324 and 555/316 cm^{-1} for Gua/TGua. The wagging mode (ν_{11}) shifts downward by 31 cm^{-1} in going from the Gua to TGua molecules. The ν_{11} mode is observed at 568 cm^{-1} for Gua [17] and at 525 cm^{-1} for TGua [26] in the Raman spectra. In the present calculations, the IR

intensities are decreased while the Raman activities are increased for the modes ν_{11} and ν_5 .

3.2.2. Radical cations

Due to the conversion from the neutral molecules of Gua and TGua into cationic species, most of the vibrational characteristics of cationic species are found to be different as compared to their respective neutral molecules. In this section, only those vibrational modes have been discussed which are affected significantly in going from the neutral to the cationic radicals of the two molecules.

3.2.2.1. Ring modes The radicalization leads to decrease in the IR intensity for the ring stretching modes ν_{34} , ν_{30} , ν_{26} and ν_{13} by factors of $\sim 1/4$, $1/3$, $1/2$ and $1/4$ in going from Gua to Gua^+ and ν_{34} , ν_{33} , ν_{23} , ν_{22} and ν_{13} by factors of $\sim 1/8$, $1/2$, $1/5$, $1/64$ and $1/20$ in going from TGua to TGua^+ . In going from Gua to Gua^+ the frequency is decreased by 29 and 36 cm^{-1} with decrease in IR intensity by factors of $\sim 1/4$ and $\sim 1/2$ and increases in Raman activity by factors of ~ 5 and ~ 8 respectively for both the ν_{34} and ν_{26} modes. However, for TGua^+ the frequencies corresponding to the modes ν_{34}/ν_{26} do not change but IR intensities vary by factors of $\sim 1/8/\sim 3$ and Raman activities increase by factors of $\sim 25/\sim 2$ respectively corresponding to those of the neutral TGua molecule. The calculated frequencies for the ν_{33}/ν_{23} modes are increased by $87/33\text{ cm}^{-1}$ in going from Gua to Gua^+ . Due to the conversion from Gua to Gua^+ , the IR intensity and Raman activity increase by factors of ~ 17 and 3 respectively for the ν_{23} mode. For the above mode the frequency increases by 147 cm^{-1} with decreases in IR intensity by a factor of $\sim 1/5$ and increase in Raman activity by a factor of ~ 32 in going from TGua to TGua^+ . The mode ν_{22} is decreased in magnitude by 181 cm^{-1} with decrease in IR intensity for the cationic radical of TGua as compared to the neutral TGua molecule. It is to be noticed that the IR intensities for the modes ν_{32} , ν_{31} and ν_{29} are increased by factors of ~ 7 , 3, 3 in Gua^+ and ~ 3 , 10, 4 in TGua^+ compared to those of neutral molecules. The Raman activity increases by a factor of ~ 10 for the mode ν_{32} but decreases by a factor of $\sim 1/15$ for the ν_{30} mode in going from Gua to Gua^+ . The lowest ring stretching mode ν_{13} assigned at the 623 and 569 cm^{-1} with decrease in IR intensity by a factor of $\sim 1/4$ and $1/20$ for Gua^+ and TGua^+ as compared to those of the neutral molecules.

3.2.2.2. N-H/C-H modes The frequencies of the two stretching N-H modes (ν_{41} and ν_{40}) shift downwards. The ν_{41} mode is decreased by 68 and 38 cm^{-1} with slight increase in IR intensity and Raman activity in going from the neutral to cationic radicals of Gua and TGua

respectively while the mode ν_{40} for $\text{Gua}^+/\text{TGua}^+$ is found to decrease by $34/26\text{ cm}^{-1}$ with increased IR intensity. The IR intensity and Raman activity for the ν_{40} mode increases by factors of ~ 7 and ~ 2 in Gua^+ while the IR intensity increases slightly and Raman activity decreases by a factor of $\sim 1/5$ in TGua^+ compared to that of neutral TGua molecule. For the C-H stretching mode (ν_{38}) the IR intensity is found to increase by factors of $\sim 7/\sim 4$ in $\text{Gua}^+/\text{TGua}^+$. The ν_{28} mode is shifted downward by frequencies $53/38\text{ cm}^{-1}$ in going from neutral Gua/TGua to their respective cationic species. It is to be noted that for this mode the IR intensities are decreased by factors of $\sim 1/38$ and $1/7$ for Gua^+ and TGua^+ respectively while Raman activity increases by a factor of ~ 7 for Gua^+ and decreases by a factor of $\sim 1/3$ for TGua^+ . The frequencies for other N-H in-plane bending mode ν_{24} is decreased by 92 cm^{-1} in going from the Gua to Gua^+ while in going from TGua to TGua^+ the ν_{24} mode is decreased by 55 cm^{-1} . The C-H bending mode ν_{27} has been assigned at 1282 cm^{-1} with increases Raman activity by a factor of ~ 5 for Gua^+ and 1289 cm^{-1} with increase Raman activity by a factor of ~ 4 for TGua^+ .

In going from TGua to TGua^+ the mode ν_{12} changes from polarized to depolarized. The mode ν_9 shifts upward by $157/107\text{ cm}^{-1}$ for $\text{Gua}^+/\text{TGua}^+$ while the mode ν_{20} is increased by 62 cm^{-1} for TGua^+ . For all these modes smaller changes are noted in the IR intensity and Raman activities for both cations due to conversion of neutral Gua and TGua to the cationic species.

3.2.2.3. C=O/S modes Due to removal of the electronic change from S atom it becomes positive in TGua^+ as compared to the TGua molecule. The stretching frequency of C=S (ν_{37}) is decreased by 42 cm^{-1} due to increase in bond length of C=S in going from TGua to TGua^+ and the IR intensities for $\text{Gua}^+/\text{TGua}^+$ are increased by factors of ~ 2 and Raman activity decreased by factors of $\sim 5/10$. The out-of-plane bending mode (ν_{17}) is found to decrease by the same magnitude 45 cm^{-1} and the Raman band becomes depolarized in Gua^+ and TGua^+ . The in-plane bending mode ν_4 for Gua^+ and TGua^+ radicals is identified at lower frequency 307 and 207 cm^{-1} . The IR intensity of this mode is increased by a factor of ~ 6 for the Gua^+ and by factor ~ 2 increases the Raman activity for TGua^+ and it is also noticed that the depolarization ratios increase for both the cations.

3.2.2.4. C-NH₂ modes The C-NH₂ stretching mode (ν_{36}) for the cationic species Gua/TGua has been found at 1679 and 1678 cm^{-1} . The IR intensity and Raman activity increase by equal factors of ~ 2 for the mode ν_{36} in going from TGua to TGua^+ . The frequencies $347/329\text{ cm}^{-1}$ are assigned to the mode ν_6 (in-plane

bending mode of C–NH₂) for Gua⁺/TGua⁺ with smaller change of IR intensity and Raman activity. It is very difficult task to assign the out-of-plane bending mode of C–NH₂ which is coupled with the non-planar ring deformation. This mode ν_{16} could be assigned at the calculated frequency 723 and 719 cm⁻¹ with decreased in IR intensity for Gua⁺ and TGua⁺.

3.2.2.5. NH₂ modes Changes in the vibrational characteristics of the NH₂ group accompanying the radicalization have been noticed. The mode ν_{42} has been assigned at the frequencies 3677 and 3694 cm⁻¹ with increased IR intensity by equal factor of ~ 3 for Gua⁺ and TGua⁺ respectively. The mode ν_{39} is found to be 3548/3571 cm⁻¹ with increase in IR intensity by factors of $\sim 4/8$ for Gua⁺ and TGua⁺ while the Raman activity decreases by a factor of 1/3 in Gua⁺ and increases by a factor of ~ 3 in the TGua⁺ radical. The frequency for the σ (NH₂) mode ν_{35} is decreased by 34 cm⁻¹ in going from the Gua to Gua⁺. The rocking mode (ν_{25}) is decreased by 89/41 cm⁻¹ for Gua⁺/TGua⁺ as compared to their respective neutral molecules. However, the wagging mode (ν_{11}) is found to be decreased only for TGua⁺ by 46 cm⁻¹ with decrease in IR intensity by a factor of 1/4. The frequency for the twisting mode (ν_5) shifts upward by 37/65 cm⁻¹ in Gua⁺/TGua⁺ as a result of conversion from neutral to cationic species. The IR intensity of the above mode is decreased by a factor of $\sim 1/2$ for Gua⁺ while it is increased threefold and becomes depolarized for TGua⁺.

3.2.3. Radical anions

The conversion of the neutral Gua and TGua molecules into the corresponding radical anions leads to the significant change in the vibrational characteristics of all the vibrational modes. It could also be noticed that the IR intensity and Raman activities of anionic species undergo unusual increase which cannot be compared with the neutral molecules.

3.2.3.1. Ring modes From the present computations for the radical anions it is observed that the most of the ring stretching frequencies are shifted a little downward. Due to radicalization the frequencies for the ν_{34}/ν_{30} modes are increased by 32/72 cm⁻¹ in Gua⁻ and 70/28 cm⁻¹ in TGua⁻. All the calculated vibrational frequencies for the Gua⁻ radical for the ring stretching modes are unchanged while only two ν_{34}/ν_{30} modes shift downward by 32/62 cm⁻¹ due to conversion from the neutral to the anionic species. However, the changes of magnitudes of calculated frequencies of ring stretching modes are noted for the TGua⁻ radical. The modes ν_{33} , ν_{29} , ν_{26} , ν_{22} and ν_{13} are decreased by wavenumbers 117, 43, 25, 181 and

26 cm⁻¹ while the mode ν_{23} is increased by 68 cm⁻¹ in going from TGua to TGua⁻ and the other modes are found to have similar frequencies in TGua⁻ and TGua. The Raman band becomes depolarized for the lowest ring stretching mode ν_{13} for Gua⁻ and depolarization ratio of the ν_{14} mode increases for Gua⁻ while reverse is found in case of TGua⁻.

In case of in-plane deformation mode ν_{21} depolarization ratio is increased but for modes ν_{15} and ν_8 it is found to decrease in going from neutral to anions of Gua and TGua. For the mode ν_{10} the depolarized band becomes polarized in going from Gua to Gua⁻ and it slight increases for TGua⁻. No changes are found in the calculated frequency for out-of-plane deformation modes for Gua⁻ while the modes ν_{18} , ν_{14} and ν_7 are found to decrease by 62, 49 and 59 cm⁻¹ in going from TGua to TGua⁻. For the butterfly mode, the depolarization ratio is decreased considerably in both the radical anions of Gua and TGua compared to their respective neutral molecules. Depolarization ratios for all the out-of-plane ring deformation modes decrease for Gua⁻ and TGua⁻ while it is increased only for the ν_{14} mode in going from Gua to Gua⁻.

3.2.3.2. N–H/C–H modes The modes ν_{41} and ν_{40} are decreased by 107 and 128 cm⁻¹ in Gua⁻ than those in Gua. The depolarization ratios for all the stretching modes are increased for both the radical anions of Gua and TGua. It could be concluded that due to radicalization the frequencies of in-plane bending modes ν_{27} and ν_{24} are decreased. The frequency of the mode ν_{24} is decreased by 58 cm⁻¹ for Gua⁻ and TGua⁻ with increased depolarization ratio. The frequency for the mode ν_{28} is decreased by 71 cm⁻¹ with increases/decrease in depolarization ratio for the Gua⁻/TGua⁻. For the C–H in-plane bending mode (ν_{27}) in going from TGua to TGua⁻ the frequency decreases by 48 cm⁻¹. The depolarization ratio is decreased for the ν_{27} mode in anions of Gua and TGua as compared to the neutral molecules. It could be noticed that the out-of-plane bending mode of C–H (ν_{20}) has frequency 511 cm⁻¹ with increase in IR intensity by a factor of ~ 5 and Raman band changes polarization from depolarized to polarized for TGua⁻. The vibrational frequency of the mode ν_{12} decreases by 192 cm⁻¹ for TGua⁻ and band becomes polarized only for Gua⁻ as compared to Gua. The frequency for the mode ν_9 shifts downward by 48/130 cm⁻¹ for Gua⁻/TGua⁻ and the Raman band becomes polarized only for TGua⁻ compared to that of TGua.

3.2.3.3. C=O/S modes The stretching modes of C=O/S vibrations are also sensitive to the conversion from the neutral molecules to radical anions. The mode ν_{37} is decreased by 99/64 cm⁻¹ for the Gua⁻/TGua⁻ species. The calculated frequency for the in-plane bending mode

(ν_4) for Gua^- and TGua^- are calculated to be 301 and 186 cm^{-1} . The out-of-plane bending mode of $\text{C}=\text{S}$ (ν_{17}) for the TGua^- is decreased by the 226 cm^{-1} than that of neutral TGua molecule. It could be seen clearly that the depolarization ratios for this mode section are decreased in radical anion of Gua^- and TGua^- compared to those of neutral molecules.

3.2.3.4. C-NH₂ modes The changes in the vibrational characteristics of all the normal modes of C-NH₂ accompanying the conversion of neutral Gua/TGua into the radical anion have been found. The mode ν_{36} is found to decrease by 57 cm^{-1} with increased depolarization ratio for the Gua^- species as compared to the neutral Gua molecule. The frequency of ν_{16} decreases by 72 cm^{-1} and polarization ratio decreases in going from the TGua to TGua^- . However, depolarization ratio decreases for ν_{16} while increases for ν_{28} and ν_6 in Gua^- due to the radicalization process.

3.2.3.5. NH₂ modes The radicalization leads to changes in the vibrational characteristics of the NH₂ group. The anti symmetric mode ν_{42} decreases by $113/69\text{ cm}^{-1}$ for the $\text{Gua}^-/\text{TGua}^-$ and the depolarization ratio decreases for Gua while bands become polarized in going from TGua to TGua^- . The symmetric stretching mode ν_{39} decreases by $221/78\text{ cm}^{-1}$ for $\text{Gua}^-/\text{TGua}^-$. The $\sigma(\text{NH}_2)$ mode decreases by 52 cm^{-1} in going from Gua to Gua^- and depolarization ratio is increased in both the anions of Gua and TGua as compared to the neutral molecules. The depolarization ratio increases for the rocking mode ν_{25} in going from the neutral to radical anions of Gua/TGua . For the wagging mode ν_{11} , the frequency shifts downward by 107 cm^{-1} with decreased depolarization ratio for Gua^- and shifts upward by 247 cm^{-1} with increased depolarization ratio for the TGua^- as result of radicalizations. The effect of the radicalization could be seen on the vibrational frequency of the twisting mode (ν_5) which upshifts by 32 cm^{-1} and enhances IR intensity by a factor of ~ 3 in going from Gua to Gua^- .

3.2.4. HOMO-LUMO analysis

The most important orbitals in a molecule that determine the way the molecule interacts with the other species are, the frontier molecular orbitals (FMOs), called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). They are the main orbitals that take part in chemical stability [50]. They are the key parameters in determining molecular properties and molecular electrical transport properties [51, 52]. The eigen value of HOMO characterizes the ability of donating electron and the eigen value of LUMO characterizes the

ability of accepting electrons. The energy gap between HOMO and LUMO reflects the chemical stability and they are responsible for chemical and spectroscopic properties of the molecule [53, 54]. The orbitals HOMO-LUMO and their properties such as their energy are very useful for physicists and chemists. This is also used by the frontier electron density for predicting the most reactive position in π -electron system and also explains several type of reaction in conjugated system [55]. In conjugated molecules there is a small separation between HOMO and LUMO which is the result of a significant degree of intermolecular charge transfer from the end-capping electron donor groups to the efficient electron acceptor groups through π -conjugated path [56]. Energy difference between the HOMO and LUMO orbitals is called energy gap which is important for stability of structures [57]. An electronic system with larger HOMO-LUMO gap is less reactive than one having smaller gap [58]. If energy gap is larger, kinetic stability will be greater and chemical reactivity will be lower because it is energetically unfavourable to add electrons to a high lying HOMO and to remove electrons from a low lying LUMO and hence, to form an activated complex of any potential reaction [59]. The sketch of the atomic orbital compositions of the frontier MOs are shown in Fig. 6. The green and red solid regions in Fig. 6 represent the MOs with completely opposite phases. The present calculations predict that the energies of HOMO/LUMO orbitals of the Cyt and TCyt are $-1.3665/-6.6628\text{ eV}$ and $-1.6538/-6.6600\text{ eV}$, respectively. The energy gap (ΔE), i.e. the transition energy from HOMO to LUMO of the Gua and TGua is 5.0547 and 4.0743 eV respectively.

3.2.5. Molecular electrostatic potential and electrostatic potential

Molecular electrostatic potential (MEP) and electrostatic potential are correlated with the dipole moment, electronegativity, partial charges and site of chemical reactivity of the molecule. It provides a visual method to understand the relative polarity of a molecule. While the negative electrostatic potential corresponds to an attraction of the proton by the concentrated electron density in the molecule (and is colored in shades of red on the ESP surface), the positive electrostatic potential corresponds to repulsion of the proton by atomic nuclei in regions where low electron density exists and the nuclear charge is incompletely shielded (and is colored in shades of blue). By definition, electron density iso-surface is a surface on which molecule's electron density has a particular value and that encloses a specified fraction of the molecule's electron probability density. The electrostatic potential at different points on the electron density iso-surface is

Fig. 6 HOMO–LUMO energy gap for Gua and TGua

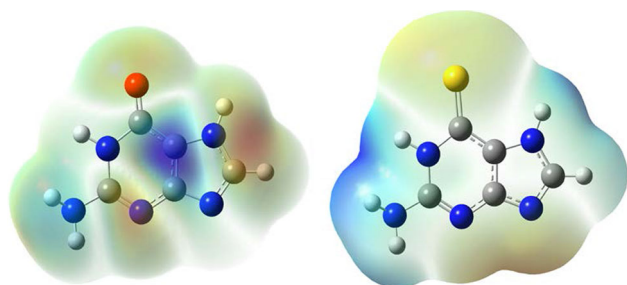
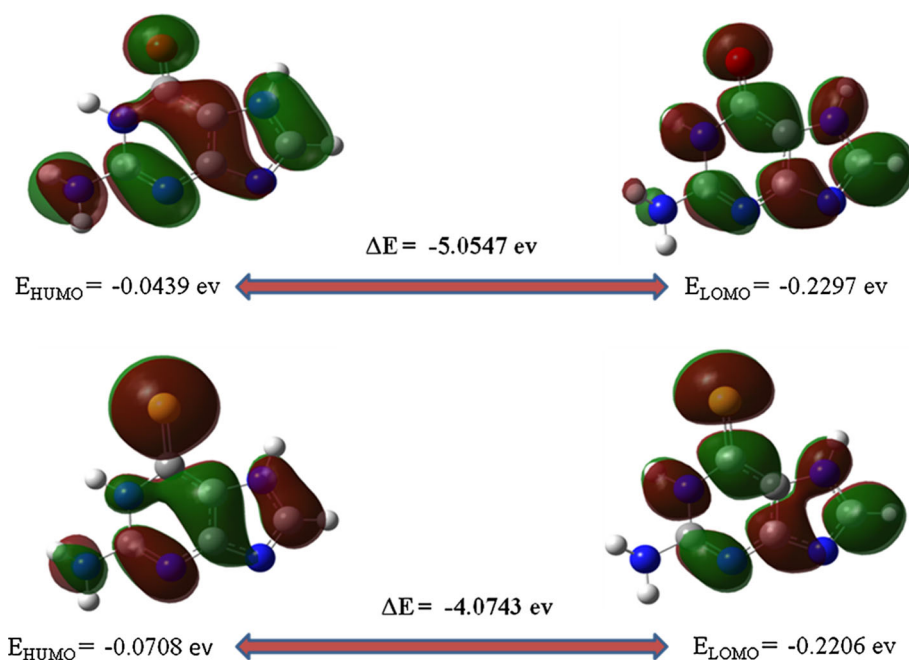


Fig. 7 Molecular electrostatic potential surface of Gua and TGua

shown by coloring the iso-surface with contours. The graphical representation of the molecular electrostatic potential surface, as described by Politzer and Truhlar [60] is a series of values representing the evaluation of the interaction energy between a positively charged (proton) probe and points on a solvent accessible surface as defined by Connolly [61–64]. The electron density isosurface onto which the electrostatic potential surface has been mapped is shown in Fig. 7. Such surfaces depict the size, shape, charge density and site of chemical reactivity of the molecules. The different values of the electrostatic potential at the surface are represented by different colors; red represents regions of most negative electrostatic potential, blue represents regions of most positive electrostatic potential and green represents regions of zero potential. Potential increases in the order red < orange < yellow < green < blue. From the MEP surface (Fig. 7), it is clear that the site close to sulfur shows region of most negative electrostatic potential.

4. Conclusions

The complete vibrational assignments of wavenumbers are made on the basis of PEDs. Reasonably good agreement of the calculated scaled frequencies and observed vibrational spectra suggests the advantages of higher basis set for quantum chemical calculations. The neutral and anions of Gua and TGua possess non-planar structures with C_1 point group symmetry and Cations of Gua and TGua show planar structures and belong to C_s point group symmetry and the character table for C_s point group. Computations have been carried out for molecular structures, APT charges and vibrational spectra of Gua, TGua and their ions. In the cationic radicalization, the electron is removed mainly from the N_3 , C_5 and O/S atoms in Gua/TGua molecule. Due to attaching an electron on Gua the electronic charge is attached mainly on all C and all H sites and in TGua the electronic charge is attached mainly on all C except C_5 , S and all H sites. Due to the attaching of an electron to the TGua, there is large intensity difference in the frequency region for the TGua⁻ and TGua⁺. The frequency of $\tau(\text{NH}_2)$ mode is increased in cations of Gua and TGua. The frequency of $\omega(\text{NH}_2)$ and $\gamma(\text{CO/S})$ modes are decreased in all ionic species while only in TGua⁻ it is increased drastically. The frequency of $\nu(\text{CO/S})$ mode is decreased for all the ionic species of Gua and TGua. The MEP surfaces together with complete analysis of the vibrational spectra, both IR and Raman, help us to identify the structural properties of the studies species. The MEP surface suggests that the site close to the sulfur the region of most negative electrostatic potential.

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