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Research article

Thermodynamic functions with other properties and vibrational spectra of pyrimidine ring of uracil for RNA and bio-molecule 5-aminouracil

J.S. Singh *

Department of Physics, Jamia Millia Islamia (Central University), New Delhi, 110025, India

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ABSTRACT

Vibrational spectra (Infra Red and Raman) of uracil and 5-aminouracil have been recorded as well as reproduced in solid phase for the pyrimidinal region (200-2000 cm^{-1}) and the internal modes were analyzed especially for pyrimidine ring of bio-molecules theoretically by using the density functional theory (DFT) calculations on the different basis sets for Restricted Hartree–Fock (RHF) by employing the Gaussian-03 program. These quantum chemical calculations have been employed to yield the Mulliken atomic charges, atomic polarizability tensor (APT) charges and thermodynamic functional properties of these bio-molecules. These DFT calculations have been computed for the some important internal ring modes especially to pyrimidine ring of uracil with a substituent amino-group (NH_2) at site of C_5 atom on pyrimidine ring.

1. Introduction

Pyrimidine is a heterocyclic shape and aromatic organic compound as well as the constituents of 5-methyluracil (thymine) of DNA and uracil of RNA. Similarly, the halogenated pyrimidines are acted as anti-tumor agents for the certain treatment of tumors. The transformation of pyrimidines or their derivatives significantly changes their spectroscopic properties, chemical behavior, vivo activity and bio-activity. Uracil derivatives, especially 5-substituted uracils, have been found to exhibit a significant role in pharmacological activities. Hence, in the medical community, 5-fluorouracil and some other substituted uracils are extensively used as an anti-cancer drug. Therefore, the experimental and theoretical studies on pyrimidine ring are more interesting due to the optical and biological properties [1, 2, 3] and these are commonly treated as the anti-carcinogenic drugs for the cancer and anti-HIV viruses [4, 5, 6, 7, 8]. Anti-carcinogenic drug, 5-FU is well-known as fluorinated based pyrimidine for the antimetabolite that is usually used in the treatment of solid tumors and colorectal carcinoma [4, 5]. Moreover, the replacements of hydrogen on site of C_5 atom by halogen atoms for all these derivatives are now tested as the drugs for HIV and anti-tumor [6, 8]. Hence, this present text is a comparative study for the vibrational modes of bio-molecules on the effect of mass and electro-negativity of the substituted amino-group (NH_2) on the C_5 atom of pyrimidine ring. The vibrational studies of 5-substituted-uracils [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24] have been made by several authors, that are still required more study on the C_5 atom on pyrimidine ring. Therefore, these bio-molecular property is not fully decided and is required a further study.

2. Material and methods

2.1. Experiment

Uracil and 5-aminouracil crystalline white powder of spectral grade were obtained from the Aldrich chem. Co. (USA). Their spectra (IR and Raman spectra) were recorded without any further purification for the spectroscopic analysis in solid phase at room temperature. As reproduced Raman spectra frequencies are collected in Tables 4a, 4b and 5a, 5b of these titled compounds were recorded in the region 200-2000 cm^{-1} on the Raman spectrophotometer (Model-Spex-1877) using an C_w Ar^+ laser with the 4880 A^0 wavelength as the excitation source with the resolution ~1 cm^{-1} and laser spot size 1 μm, and it was better than other recording of as the ref. [15] only in the pyrimidinal region. As reproduced IR spectrum of uracil is collected in Tables 4a and 5a, was recorded at room temperature in the region 400-2000 cm^{-1} on a FT-IR spectrophotometer (Model-5300) and reproduced Infra-red spectrum of 5-aminouracil is collected in Tables 4b and 5b, was recorded in the region 200-2000 cm^{-1} on a spectrophotometer (Perkin-Elmer-883). This resolution was more

* Corresponding author.
E-mail addresses: jssaec@rediffmail.com, jssaec@gmail.com.

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than 2 cm^{-1} for Infra-red and Raman spectra as well as within the accuracy of $\pm 2\ cm^{-1}$, which was better than other recording of the ref. [15] only for a good precision in the pyrimidinal region as above.

2.2. Theoretical

The density functional theory calculations were computed for the vibrational frequencies of uracil and 5-aminouracil bio-molecules. Initially, *ab initio* calculation at basic set RHF/6-31+G* has been computed for the optimization of parameters. This optimized geometrical parameter has been used for DFT calculations by implementing the Gaussian-03 software [25] and lastly, the optimized geometrical parameter at the level DFT/B3LYP/6-311++G** has been applied for this calculation by minimizing the energies with respect to all parameters. In the optimization, the calculated spectra have been traced for the vibrational frequencies with the Raman scattering activities as in Figure 1a, b and IR intensities as in Figure 2a, b of these bio-molecules. The DFT calculations have been employed to yield thermodynamic functions and related properties of these bio-molecules as shown in Figure 3a, b.

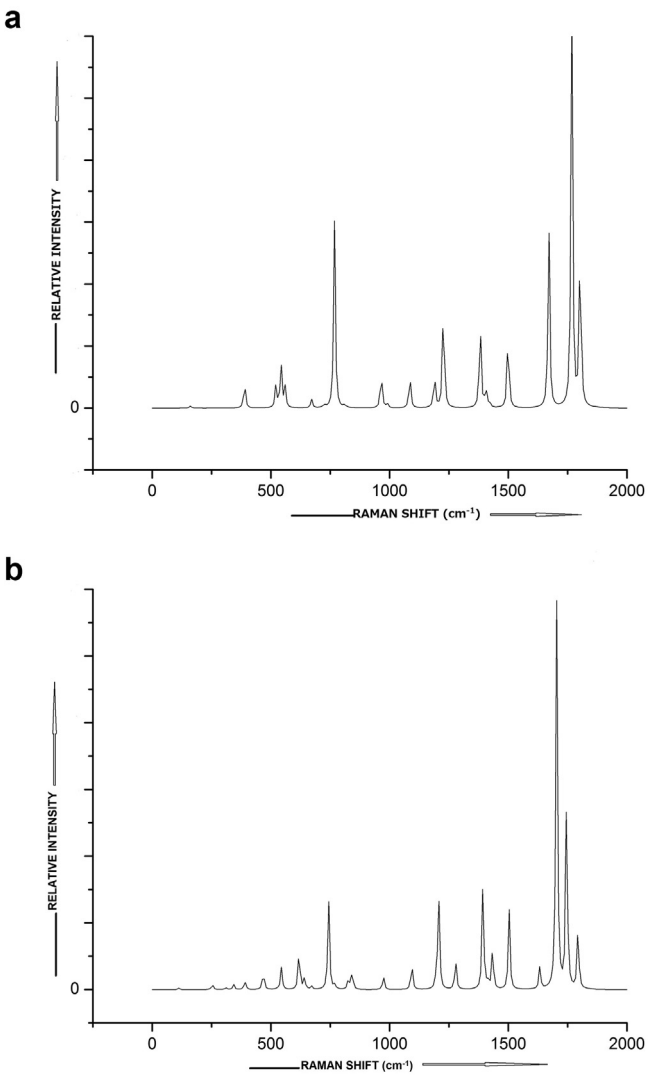

Figure 1. Raman spectrum of (a) uracil (Cal.) (b) 5-aminouracil (cal.).

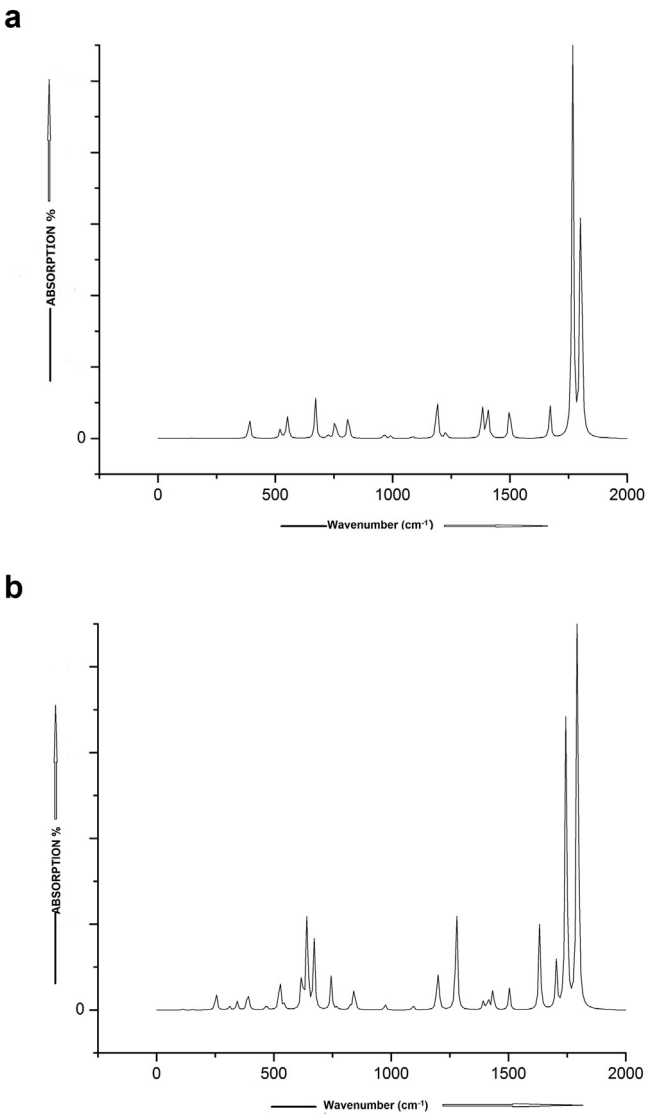

Figure 2. IR spectrum of (a) uracil (Cal.) (b) 5-aminouracil (cal.).

3. Results and discussion

3.1. ATP charges

The APT charges are represented the total sum of charge flux tensor and sum of charge tensor, which are supporting to the charge-charge flux model. In optimized structure and atomic labeling schemes for these bio-molecules are shown in Figure 3a, b. The APT atomic charges at various atomic site of uracil and 5-aminouracil bio-molecules have been computed by using the Gaussian-03 program at level DFT/B3LYP/6-311++G** [25] and are comparatively collected in a Table 1 from Ref. [15] for more discussion. From the perusal of Table 1, the respective electro-negativities of atoms are compared with other accumulated negative charge on the atomic sites. The APT charges of 5-aminouracil molecule have been expressed in comparison to the uracil molecule. Here, except the C_5 atom bears the ATP charge -0.4258 a.u., and all of the remaining three carbon atoms of the pyrimidine ring C_2, C_4 and C_6 possess the positive charges as 1.3180, 1.1871 and 0.5019 a.u. respectively only for uracil and due to more negative charge of the C_5 atom of the pyrimidine ring bears reactant property than other carbon atoms of ring. From Table 1, one can notice that all of the C atoms of pyrimidine ring of 5-aminouracil molecule, C_2, C_4, C_5 and C_6 possess positive APT charges with different magnitudes 1.3167, 1.1163, 0.1629 and 0.2685

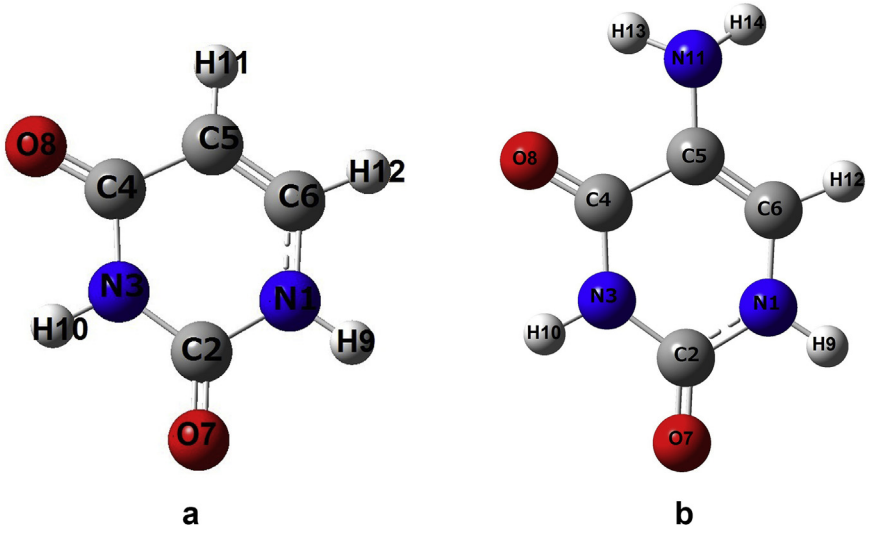

Figure 3. (a) Uracil and (b) 5-Aminouracil.

Table 1. Calculated ATP charges[$] of uracil and 5-aminouracil molecules.

S. N.	Atoms[#]	Uracil[a]	5-Aminouracil[a]
1	N_1	-0.7178	-0.6788
2	C_2	1.3180	1.3167
3	N_3	-0.7409	-0.6711
4	C_4	1.1871	1.1163
5	C_5	-0.4258	0.1629
6	C_6	0.5019	0.2685
7	O_7	-0.8894	-0.9523
8	O_8	-0.8522	-0.8569
9	H_9	0.2495	0.2453
10	H_{10}	0.2227	0.2263
11	H_{11}/N_{11}	0.0837	-0.6638
12	H_{12}	0.0634	0.0578
13	H_{13}		0.2357
14	H_{14}		0.1934

[#] the numbering of atoms, as shown in Figure 3a, b.
[$] the atomic charge in unit of e.
[a] from Ref. [15].

a.u. respectively only in it. The two atoms, O_7 and O_8 have the negative APT charges as -0.8894 and -0.8522 a.u. for uracil, -0.9523 and -0.8569 a. u. for 5-amino-uracil at site of respective atoms. Similar as, the two atoms, N_1 and N_3 have the negative APT charges as -0.7178 and -0.7409 for uracil, -0.6788 and -0.6711 a.u. for 5-aminouracil at site of respective atoms. Due to the high electro-negativity, all the O and N atoms have the negative APT charges. The 4 hydrogen atoms (H_9, H_{10}, H_{11}, H_{12}) of uracil have the positive APT charges as 0.2495, 0.2227, 0.0837 and 0.0634 a.u. respectively and all 5 hydrogen atoms (H_9, H_{10}, H_{12}, H_{13}, H_{14} of 5-amino-uracil have the positive APT charges as 0.2453, 0.2263, 0.0578, 0.2357 and 0.1934 a.u. respectively, except N_{11} atom bears high electro-negativity with the negative APT charge -0.6638 a.u. at site of atom. One can notice that all H atoms of both molecules are directly attached to O atoms and hold the positive APT charges.

3.2. Mulliken atomic charges

These charges have had the important application role in the DFT calculations for optimized molecular geometry; molecular & electronic structure, the charges affect polarizability, dipole moment and some other properties of the molecular systems. These Mulliken atomic charges of the pyrimidine ring of uracil and 5-aminouracil have been calculated by using the Gaussian-03 program at level DFT/B3LYP/6-311++G** [25]. These calculated values are collected in Table 2. Here, one can notice that two carbon atoms C_2 and C_4 bear the positive charges with values 0.3318 and 0.0452 a.u. respectively for uracil, except other two C_5 and C_6 hold the negative charges as -0.0418 and -0.0138 a.u. respectively. For 5-aminouracil, all of three carbon atoms C_2, C_4 and C_6 possess positive charges as 0.3089, 0.2185 and 0.1361 a.u. respectively, except the C_5 bears negative Mulliken atomic charge (-0.1989 a.u.) due to the high electro-negativity of substituted N atom at site C_5 atom. In both, the atoms O_7 and O_8 hold the negative Mulliken atomic charges as -0.3415 and -0.3185 a.u. for uracil, -0.3540 and -0.3421 a.u. for 5-aminouracil at site of respective atoms. Similar as, the two atoms, N_1 and N_3 possess negative Mulliken atomic charges as -0.3534 and -0.3942 a.u. for uracil, -0.3744 and -0.4114 a.u. for 5-aminouracil. All of the O and N atoms hold the high electro-negativity. These 4 hydrogen atoms (H_9, H_{10}, H_{11}, H_{12}) of uracil possess positive Mulliken atomic charges with as 0.3428, 0.3578, 0.2105 and 0.1753 a.u. respectively and the 5 hydrogen atoms (H_9, H_{10}, H_{12}, H_{13}, H_{14} of 5-aminouracil hold the positive charges as 0.3385, 0.3615, 0.1738, 0.2701 and 0.2364 a.u. respectively which bear

Table 2. Calculated Mulliken atomic charges[$] of uracil and 5-aminouracil molecules.

S. N.	Atoms[#]	Uracil	5-Aminouracil
1	N_1	-0.3534	-0.3744
2	C_2	0.3318	0.3089
3	N_3	-0.3942	-0.4114
4	C_4	0.0452	0.2185
5	C_5	-0.0418	-0.1989
6	C_6	-0.0138	0.1361
7	O_7	-0.3415	-0.3540
8	O_8	-0.3185	-0.3421
9	H_9	0.3428	0.3385
10	H_{10}	0.3578	0.3615
11	H_{11}/N_{11}	0.2105	-0.3628
12	H_{12}	0.1753	0.1738
13	H_{13}		0.2701
14	H_{14}		0.2364

[#] the numbering of atoms, as shown in Figure 3a, b.
[$] the atomic charge in unit of e.

the positive Mulliken charges as in case of APT charges, except N_{11} atom bears high electro-negativity with the negative Mulliken charge (-0.3628 a.u.) at site of atom.

3.3. Thermodynamical functions

The translational, rotational and vibrational contribute to thermodynamic functions (heat capacity, free energy, enthalpy and entropy). In density functional theory (DFT) calculations, the computed wavenumbers have been used to calculate the thermodynamic functional properties of these bio-molecules by using the Gaussian-03 software [25]. The thermodynamic functional properties of uracil and 5-aminouracil are collected in the Table 3. The theoretically calculated thermo-dynamical data are used to correct the experimental thermodynamical values at 0 K temp and the effect of zero-point vibrational energy. The calculated zero-point vibrational energy (ZPVE) and free energy are -414.8495 & -414.8900 a.u. for uracil and with higher magnitudes -470.2165 & -470.2486 a.u. for 5-aminouracil respectively. The calculated entropies of these bio-molecules are used to correct the experimental thermodynamical values at 0 K temp and these have been contributed to avoid the presented residual (orientation) entropy at 0 K temp in a crystal. Here, the translational, rotational and vibrational entropies are 40.057, 27.829, 11.383 calmol^{-1} K^{-1}for uracil and 40.431, 28.642, 16.664 calmol^{-1} K^{-1} for 5-aminouracil respectively. It is noticed that the translational and rotational are almost similar for both molecules, but the vibrational entropy of 5-aminouracil is higher than uracil, hence the total entropy of 5-aminouracil is higher than uracil. As well as, the dipole moment of uracil is higher than 5-amino-uracil.

All these calculated thermodynamic properties are useful information for the further study of uracil and 5-aminouracil. These calculated parameters are collected in Table 3. In thermo-chemical field, the thermodynamic energies and estimated chemical reactions are based on the relationships of thermodynamic functions. It is worth to mention that all of the thermodynamic calculations were computed in the gas phase, so that it could not be used in case of solution.

3.4. Vibrational assignments

In the spectroscopic investigation of 5-substituted-uracils, here, the vibrational spectra are made of for the substituent of amino (NH_2) group on C_5 atom of the uracil ring. This text is an extensive vibrational spectroscopic study of 5-aminouracil on the C_5 atom site of uracil ring due to the biological significance. Due to the mass of having order hydrogen < amino (NH_2) and electro-negativity of having order amino (NH_2) group > hydrogen, it deals the experimental and theoretical vibrational study of pyrimidine ring with respect to these above properties. The vibrational spectra of bio-molecules and their derivatives are very parallel analogy between the benzene ring with the pyrimidine ring [15]. This text has been made especially to the internal modes of the planarity and non-planarity of pyrimidine ring at the C_5 atom on uracil ring due to the substituent atom or group of atoms. Therefore, the splitting of frequencies could be raised due to the mass and electro-negativity effect of substituted groups at the site of C_5 atom on uracil ring. These symmetric studies of the vibrational spectra of pyrimidine ring modes for uracil and 5-aminouracil are given in Tables 4a, 4b and 5a, 5b compared to the uracil molecule as in following sections.

Table 3. Theoretically computed thermodynamic function of uracil and 5-aminouracil.

S. No.	Parameters	Uracil	5-aminouracil
1.	Total energy + ZPE (AU)	-414.8495	-470.2165
2.	Gibb Free Energy (AU)	-414.8900	-470.2486
3.	Rotational Constants (GHz):	3.8859	3.2759
		2.0137	1.4135
		1.3264	0.9885
4.	Entropy; (Calmol^{-1} K^{-1}):		
	Total	79.268	85.737
	Translational	40.057	40.431
	Rotational	27.829	28.642
	Vibrational	11.383	16.664
5.	Dipole moments (Debyes)	4.5837	4.6246

3.4.1. In-plane modes

3.4.1.1. C– NH_2 (in-plane). Here, the stretching mode for C–NH_2 is usually expected to be appeared in the higher frequency region for pyrimidine derivatives than aromatic amines compound to the reported work [15]. Here, the spectral complexity has been solved out by the DFT calculation method. And the stretching mode for C–NH_2 is observed in the Raman and IR at 1280 cm^{-1}, as well as by theoretically, this mode is calculated to be at 1278 cm^{-1}, which is shifted up by ~ 2 cm^{-1} or wave numbers in experimental result. Here the C–NH_2 stretching mode frequency for C–NH_2 is found that it is expected not to be more affected from the aniline to bi-molecules. Now in plane, the bending deformation mode for C–NH_2 has been found in this region 400-500 cm^{-1}. Here for this mode, it has been assigned nearly below to the region 300 cm^{-1}, so that, the experimentally observed bending deformation (C–NH_2) mode is found in the IR and Raman at 286 and 290 cm^{-1}, as well as this theoretical mode is calculated to be at 310 cm^{-1}, the frequency is found to be shifted lower by ~ 22 cm^{-1} (wavenumbers) in experimental result. *In-plane* bending (C–NH_2) mode of 5-aminouracil is found to be a quite low frequency as below to 300 cm^{-1} that this is laying in lower regions with the complexities of mixing to the other modes i.e. vibration and rotational modes.

3.4.1.2. Pyrimidine ring modes (in-plane). The *twelve* normal vibrational modes of pyrimidine ring are found to be similar as the phenyl ring. In which, these *twelve modes* are distributed as *six* modes for ring stretching, *three* for ring deformation modes in-plane and *three* ring deformation modes for the out-of-plane. The pyrimidine ring stretching modes are the combinations of C=C, C–C and C–N bonds [15]. Moreover to a stretch (C=C) mode has arisen in region 1600–1800 cm^{-1} [15-24]. In which of

Table 4a. Pyrimidine ring modes frequencies of uracil (in-plane modes).

Exp. Obtained Infrared (FTIR) frequency (cm^{-1})	Exp. Obtained Raman frequency (cm^{-1})	Density Functional Theory Calculated^{+} at level DFT/B3LYP/6-311++G**	Characterizations$^{\$}$ of Pyrimidine Ring as Figure 3a
Uracil	Uracil	Uracil[a]	Uracil
1672	1670	1671	*in-plane;* ν ($C_5 = C_6$) ring mode
1404	1406	1406	*in-plane;* ν (ring) mode
1192	1190	1190	*in-plane;* ν (ring) mode
1086	1086	1086	*in-plane;* ν (ring)mode (Kekule)
994	992	990	*in-plane;* α (ring) mode (Trigonal bending)
960	970	965	*in-plane;* ν (ring) mode
770	770	769	*in-plane;* ν (ring) mode (breathing)
540	542	543	*in-plane;* α (ring) mode
518	520	521	*in-plane;* α (ring) mode

$^{+}$ {the calculated frequency (wave number)$\equiv\bar{\nu}$; in cm^{-1}}.
[a] from Ref. [15].
$^{\$}$ [ν = stretching, α = angle bending, β = in-plane bending, γ = out-of-plane bending, δ = out-of-plane ring deformation/ring torsion].

Table 4b. Pyrimidine ring modes frequencies of 5-aminouracil (in-plane modes).

Exp. Obtained Infrared (FTIR) frequency (cm^{-1})	Exp. Obtained Raman frequency (cm^{-1})	Density Functional Theory Calculated[+] at level DFT/B3LYP/ 6-311++G**	Characterizations[$] of Pyrimidine Ring as Figure 3b
5-Aminouracil	5-Aminouracil	5-Aminourail[a]	5-Aminourail
1708	1706	1704	*in-plane;* ν ($C_5 = C_6$) ring mode
1508	1510	1504	*in-plane;* ν (ring) mode
1435	1430	1434	*in-plane;* ν (ring) mode
1280	1280	1278	*in-plane;* ν(C_5 –NH_2) mode
1212	1210	1208	*in-plane;* ν(ring) mode (Kekule)
980	975	974	*in-plane;* ν (ring) mode
826	830	827	*in-plane;* α(ring) mode (Trigonal bending)
744	740	743	*in-plane;* ν(ring) mode (breathing)
545	540	544	*in-plane* α (ring) mode
475	470	468	*in-plane;* α (ring) mode
286	290	310	*in-plane;* β (C_5 –NH_2) mode

[+] {the calculated frequency (wave number)$\equiv\bar{\nu}$; in cm^{-1}}.
[a] from Ref. [15].
[$] [ν = stretching, α = angle bending, β = in-plane bending, γ = out-of-plane bending, δ = out-of-plane ring deformation/ring torsion].

the *six* ring stretching modes of 5-aminouracil, the one of double (C=C) bond stretching mode has been observed in the IR and Raman spectra at 1708 and 1706 cm^{-1}, this calculated mode is found to be at 1704 cm^{-1}. But for uracil, it has been observed in the IR and Raman spectra at 1672 and 1670 cm^{-1}, this mode is calculated to be at 1671 cm^{-1}, which is found to be shifted up by ~ 34 cm^{-1} or increasing up to ~2 % with the substitution of amino (NH_2) group on the C_5 atom of uracil ring. Theoretically calculated modes are closed to the experimental results as well as nearly to the ref [21]. Here, it is found here a modification for the reported earlier works [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. The *second* one popular ring stretching mode, the Kekule ring stretching mode has been observed in the IR and Raman at 1212 and 1210 cm^{-1} as well as this mode is calculated to be at 1208 cm^{-1} for 5-aminouracil, but this mode for uracil has been observed in IR and Raman at 1086 cm^{-1}, this mode is calculated to be at 1086 cm^{-1}, which is found to be shifted up by ~ 120 cm^{-1} or increasing up to ~11 % due to

Table 5a. Pyrimidine ring modes frequencies of uracil (out-of-plane modes).

Exp. Obtained Infrared (FTIR) frequency (cm^{-1})	Exp. Obtained Raman frequency (cm^{-1})	Density Functional Theory Calculated[+] at level DFT/ B3LYP/6-311++G**	Characterizations[$] of Pyrimidine Ring as Figure 3a
Uracil	Uracil	Uracil[a]	Uracil
410	410	391	*out-of-plane;* δ (ring) or ring torsion
	260	161	*out-of-plane;* δ (ring) or ring torsion
	230	142	*out-of-plane;* δ (ring) or ring torsion

[+] {the calculated frequency (wave number)$\equiv\bar{\nu}$; in cm^{-1}}.
[a] from Ref. [15].
[$] [ν = stretching, α = angle bending, β = in-plane bending, γ = out-of-plane bending, δ = out-of-plane ring deformation/ring torsion].

Table 5b. Pyrimidine ring modes frequencies of 5-aminouracil (out-of-plane modes).

Exp. Obtained Infrared (FTIR) frequency (cm^{-1})	Exp. Obtained Raman frequency (cm^{-1})	Density Functional Theory Calculated[+] at level DFT/B3LYP/ 6-311++G**	Characterizations[$] of Pyrimidine Ring as Figure 3b
5-Aminouracil	5-Aminouracil	5-Aminourail[a]	5-Aminourail
402	410	386	*out-of-plane;* δ (ring) or ring torsion
330	340	342	*out-of-plane;* δ (ring) or ring torsion
230	230	154	*out-of-plane;* δ (ring) or ring torsion
205	210	111	*out-of-plane;* γ (C_5 –NH_2) mode

[+] {the calculated frequency (wave number)$\equiv\bar{\nu}$; in cm^{-1}}.
[a] from Ref. [15].
[$] [ν = stretching, α = angle bending, β = in-plane bending, γ = out-of-plane bending, δ = out-of-plane ring deformation/ring torsion].

the substituted amino (NH_2) groups on uracil pyrimidine ring. These calculated Kekule modes of both bio-molecules are very similar to the observed results and also a guide line to the refs [10, 15]. Here the assigned Kekule ring stretching mode of 5-aminouracil is observed to be comparatively in high frequency region than the uracil mode and it is found to have the involvement of hydrogen bonding of amino group as well as due to the mass and electro-negativity of having order amino (NH_2) group > hydrogen. The *third* most popular stretching mode as ring breathing has been found in IR and Raman at 744 and 740 cm^{-1} and this mode is calculated to be at 743 cm^{-1} for 5-aminouracil, but this mode for uracil has been observed in the IR and Raman at 770 cm^{-1} and this mode is calculated to be at 769 cm^{-1}, which is found to be shifted below up to ~25 cm^{-1} or lowered by ~3.4 % for a substitution of amino group on C_5 atom of uracil ring. These calculated ring breathing-stretching modes are much closed to these experimental results and also to this earlier ref [15]. Hence, the difficulty is found to assign the Kekule stretching mode and ring breathing due to the mixing with the stretching of pyrimidine ring and other modes of the outer bond ring modes i.e. with hydrogen bond, substituted amino (NH_2) groups or some other modes of vibration. Here, it is noticeable that the Kekule mode and ring breathing are to be lowered in frequencies compared to the phenyl rings. Therefore, these proposed assignments for uracil and its derivatives are as the wide spectra and modifications under a guide line for the reported works [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. Now, the above results are compared as the Kekule type (ν_{14}) of benzene to the frequency of uracil at ~1085 cm^{-1} and for 5-aminouracil at ~1208 cm^{-1} which appears to be higher magnitude by ~ 11% than uracil molecule due to the amino group. Whereas, the frequency ~744 cm^{-1} of the 5-amino-uracil is lowered in the frequency by ~3.4 % than the frequency ~770 cm^{-1} of uracil molecule due to the mass of amino group atoms, as well as the above respective frequencies of both molecule are identified as the ring breathing of pyrimidine rings showing the similar to the ν_1 mode of benzene and nearly similar to refs [12, 15] with a guide line to these works [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. Now in the rest of three stretching, the one of *first* mode is observed in the IR and Raman spectra at 1508 and 1510 cm^{-1} and this mode is theoretically computed to be at 1504 cm^{-1} for 5-aminouracil, but this mode for uracil has been observed in the IR and Raman at 1404 and 1406 cm^{-1} and this mode is calculated to be at 1406 cm^{-1}, which is found to be shifted up by ~100 cm^{-1} or higher up to ~7 % for the substitution of amino group on the C_5 atom of uracil ring and the hydrogen bonding of the group. Now *second*, it has been found in the IR and Raman at 1435 and 1430 cm^{-1}, and this mode is calculated to be at 1434 cm^{-1} for 5-aminouracil, but this mode for uracil has been observed in the IR and Raman at 1192 and 1190

cm^{-1}, and this mode is calculated to be at 1190 cm^{-1}, which is found to be shifted up by ~245 cm^{-1} or higher up to ~20 % due to the substituted amino (NH_2) groups on uracil ring and also for the hydrogen bonding of amino group. Therefore, it is also found to be appeared higher value by ~ 20% than uracil molecule for involving the hydrogen bonding of amino group substitution like as the above mode of 5-aminouracil. So that, with this discussion, it is assigned that the second stretching mode in the rest *three* modes of 5-aminouracil is raised to be compared higher frequency value by ~245 cm^{-1} (~20%) than the uracil having the involvement of hydrogen bond of amino group like as the above mode of 5-aminouracil. And now the last *third,* it has been found in the IR and Raman at 980 and 975 cm^{-1}, and this mode is calculated to be at 974 cm^{-1} for 5-aminouracil, but this mode for uracil has been reported here in the IR and Raman frequencies 960 and 970 cm^{-1} respectively and this mode is calculated to be at the frequency 965 cm^{-1}, which is found to be shifted up by ~10 cm^{-1} or higher up to ~1 % due to the substitution. Therefore, it is found to be increased only magnitude by ~ 1% than the uracil due to the few involvement of hydrogen bond of the amino group substitution. So far, in the last assigned ring stretching mode, it has been observed the more complexities having mixed up with the hydrogen bond and other modes. Now for the pyrimidine ring and its derivatives, the ring deformation mode in-plane has been discussed as similar to the benzene ring and its derivatives. Here *in-plane* ring deformation, the out of *three* angle bending modes, in which of the *first* trigonal angle ring bending mode is the most interesting and widely discussed mode as like Kekule ring mode and ring breathing mode. The trigonal angle ring bending mode is comparatively reduced with the strong mixing to other modes. Here in this observation, it has been observed in the IR and Raman at 826 and 830 cm^{-1}, and this mode is calculated to be at 827 cm^{-1} for 5-aminouracil, but this mode for uracil has been found in the IR and Raman at 994 and 992 cm^{-1}, and this mode is calculated to be at 990 cm^{-1}, which is found to be shifted below up to ~160 cm^{-1} or lowered by ~ 16 % due to the substituted amino (NH_2) groups on uracil ring and also with involving the hydrogen bond of amino group, and these calculated modes are closed to the observed results and also to the reported authors [3, 10, 12, 15]. Now, the *second* angle ring bending mode has been found in the IR and Raman at 545 and 540 cm^{-1}, and this mode is calculated to be the frequency 544 cm^{-1} for 5-aminouracil, but this mode for uracil has been found in the IR and Raman at 540 and 542 cm^{-1}, and this is calculated to be at the frequency 543 cm^{-1}, which is found to be almost unaffected with substitution of amino (NH_2) group and these calculated modes are more closed to the observed results and also nearly similar to the reported refs [3, 10, 12, 15]. And that is a guide-line for the other works and to the earlier refs [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. The last *third* angle ring bending mode has been found in the IR and Raman frequencies at 475 and 470 cm^{-1} and this mode is calculated to be at the frequency 468 cm^{-1} for 5-aminouracil, but this mode for uracil has been found in the IR and Raman at 518 and 520 cm^{-1} and the calculated mode is to be at 521 cm^{-1}, which is found to be shifted below up to ~55 cm^{-1} or lowered by ~ 10 % for the substitution of amino (NH_2) group on the C_5 atom of uracil ring and also to the involvement of hydrogen bond of the amino. For lower region, the rest two plane ring deformation modes are assigned as a guide-line and modification for the reported workers [9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. In the above results, the trigonal angle ring bending is found for uracil at ~ 990 cm^{-1} and for the 5-aminouracil at ~ 825 cm^{-1}, this is represented as the vibration mode (ν_{12}) of benzene ring, which is to be lowered in the frequency by ~160 cm^{-1} (~16 %) than the uracil molecule for the mass substitution of amino group. Therefore, these have the similar effect as like the Kekule and ring breathing modes. By the above results, all of these three ring torsional modes are found to be lying in the lower regions with the complexities. As well as in lower region, it is predicted that the all modes are mixing with other modes and rotational modes. Hence the most probably, the discrepancies are arisen by the packing effects in solid phase and hydrogen bonding, Here due to theoretical defects, it is required to the considering a more successful theoretical model for the all other phase.

3.4.2. Out-of-plane

3.4.2.1. C–NH_2(out-of-plane). The out-of-plane bending (C–NH_2) mode of 5-aminouracil has been found to be a quite low frequency as below to the 300 cm^{-1} that is lying with more complexities in the lower region for the rotational vibration and intermolecular/lattice modes. For out-of-plane bending (C–NH_2) mode, it has been found in the IR and Raman at 205 and 210 cm^{-1}, and this mode is calculated to be at the frequency 111 cm^{-1}, the frequency is found to be shifted up to ~100 cm^{-1} (wavenumbers) in experimental result due to the isolated in Ar matrix for calculation. Here, it is found that this is the sensitive for the matrix environment. In the solid phase, the effect is related to the intermolecular hydrogen bonding. Obviously, the above complexity has been solved the problem by the DFT calculation for a correct assignment of the vibrational modes.

3.4.2.2. Pyrimidine ring modes (out-of-plane). In the out-of-plane for the *three* ring torsional modes/deformation modes in lower region, the one of *first* ring torsional mode has been found in the IR and Raman at 402 and 410 cm^{-1}, and this mode is calculated to be at the frequency 386 cm^{-1} for 5-aminouracil, but this mode for uracil has been found in the IR and Raman at the frequency 410 cm^{-1} and this is calculated to be at 391 cm^{-1}, which is found to be shifted below up to ~5 cm^{-1} or lowered by ~ 1 %, which is found to be almost unaffected on the substitution of the amino (NH_2) group and these calculated modes are closed to the observed results and also to the authors [3, 15]. The *second* mode for ring torsional has been found in the IR and Raman at 330 and 340 cm^{-1}, and this mode is calculated to be at the frequency 342 cm^{-1} for 5-aminouracil, but this mode for uracil has been observed in the Raman frequency at 260 cm^{-1} and it is calculated to be at 161 cm^{-1}, which is found to be shifted up to ~180 cm^{-1} or increased drastically up to ~112 % for the substitution of amino group on the C_5 atom of uracil ring and also involving the hydrogen bond of substitution of amino group, and this above facts shows that this mode is more affected in the lower region than rest of the other modes. And lastly, the *third* ring torsional mode has been found in the IR and Raman at 230 cm^{-1} and this mode is calculated to be at the frequency 154 cm^{-1} for 5-aminouracil, but this mode for uracil has been observed in Raman at 230 cm^{-1} and it is calculated to be at 142 cm^{-1}, which is found to be shifted up by ~12 cm^{-1} or higher up to ~8 % due to the substituted amino (NH_2) groups and also to the involvement of hydrogen bonding of amino group. These above facts show that all these three ring torsional modes are found to be in the lower regions due to the mixing with other modes i.e. rotational and vibration modes. In overall view, it is required a more adequate theoretical model to overcome the packing effects in solid phase as well as in all other phase.

4. Conclusions

The carbon atom in both molecules, the C_2 atom is directly associated with the oxygen atom and it bears highest APT charge. And the H atom, H_{10} is directly associated with the nitrogen atom and it bears highest Mulliken atomic charge. The translational, rotational and vibrational contribute to thermodynamic functions which are as the parts of these entropies constants. In the DFT calculations, the calculated frequencies have been employed to produce the thermodynamic functional properties of these bio-molecules. These theoretically calculated thermodynamical data have been employed to correct the experimental thermo-dynamical information at 0 K temp. It is noticed that the translational and rotational are almost similar for both molecules, but the vibrational entropy of 5-aminouracil is higher than uracil, hence the total entropy of 5-aminouracil is higher than uracil. As well as, the dipole moment of uracil is higher than 5-aminouracil.

In the *twelve* normal modes of pyrimidine ring of the uracil and 5-aminouracil molecules, the C=C double bond stretching mode has been

reported to both molecules in a good agreement with experimentally observed and theoretically calculated frequencies within the region 1710–1650 cm^{-1}. In this case, the Kekule modes and ring breathing are also lowered in frequencies and these are compared to the modes of phenyl rings. Kekule ring mode has been reported in both results for the frequency of uracil at ~ 1085 cm^{-1} and for 5-aminouracil at ~ 1208 cm^{-1}, and it could be represented as the Kekule type (ν_{14}) of benzene mode and which appears to be shifted up to ~120 cm^{-1} or to be high frequency by ~ 11% than the uracil molecule with involving the hydrogen bond of substituted amino group. And the ring breathing has been assigned in all results for the frequency of uracil at ~ 770 cm^{-1} and for 5-aminouracil at ~ 744 cm^{-1} which is to be lowered in the frequency by ~ 3.4 % (shifted below up to ~25 cm^{-1}) than the uracil molecule with the substituted mass of amino group, is showing as similar to the ν_1 mode of benzene, and it is reported as the ring breathing mode of pyrimidine ring. The last important trigonal angle ring bending is reported at the frequency of uracil at ~ 990 cm^{-1} and for 5-aminouracil at ~ 825 cm^{-1}, and this is represented as trigonal angle bending as similar to the vibration mode (ν_{12}) of benzene which appears to be lower in the frequency by ~ 16% cm^{-1} (shifted below up to ~160 cm^{-1}) than the uracil molecule with the mass of substituted amino group, whereas the similar effect is found in the Kekule ring mode and ring breathing. The one of plane deformation or ring torsional mode is found to be increased drastically up to ~112 % (shifted up to ~180 cm^{-1}) with the substituted amino group on the C_5 atom of uracil ring. It is believed that this will provide extremely valuable information about the vibrational spectra and some other properties of the bio-molecules i.e. the complexity of nucleic acid bases as well as their derivatives for development of the anti-carcinogenic drugs for the anti-HIV viruses, cancers and in the DNA repairing.

Declarations

Author contribution statement

J. S. SINGH: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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