

Laser Raman and infra-red spectra of biomolecule: 5-aminouracil

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Abstract. Laser Raman (200–4000 cm^{-1}) and IR (200–4000 cm^{-1}) spectra of 5-aminouracil were recorded in the region 200–4000 cm^{-1} . Assuming a planar geometry and C_s point group symmetry, it has been possible to assign all the 36 ($25a' + 11a''$) normal modes of vibration for the first time. The two NH bonds of the NH_2 group appear to be equivalent as the NH_2 stretching frequencies satisfy the empirical relation proposed for the two equivalent NH bonds of the NH_2 group. The two NH_2 stretching frequencies are distinctly separated from the CH/NH ring stretching frequencies. A strong and sharp IR band at 3360 cm^{-1} could be identified as the anti-symmetric NH_2 mode whereas the band at 3290 cm^{-1} with smaller density could be identified as the symmetric NH_2 stretching mode. All other bands have also been assigned different fundamentals/overtone/combinations.

Keywords. Infra-red spectrum; Raman spectrum; vibrational assignment.

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1. Introduction

Vibrational studies on nucleic acid bases and their derivatives are of considerable importance from biological point of view as these are constituents of genetic materials. Uracil derivatives are used in anti-carcinogenic drug synthesis against cancer and anti-HIV viruses. The earlier works of the paper are a continuation of works [1–4] on substituted biomolecules. These molecules do not occur freely in natural biological metabolism. The understanding of the vibrational spectra of free molecules might be helpful in understanding specific biological processes and in the analysis of relatively complex systems. Vibrational studies on uracil have been done by several authors [4–30] although there are still disagreement among various works for the assignment modes of uracil. I plan to perform a symmetric study of the vibrational spectra of 5-substituted uracil with substituent as 5- X -uracils ($X=\text{F}$, Cl, Br, I, NH_2 and CH_3). The present article is a part of vibrational spectroscopic study of 5- X -uracils and deals with the Raman and IR spectra and vibrational assignments for all the 36 normal modes of vibration for the first time.

2. Experimental

5-aminouracil was purchased from Aldrich Chemical Co. (USA) and was used as such for spectroscopic studies. All the spectra were recorded at room temperature. Infra-red spectrum of 5-aminouracil powder was recorded in the range 200–4000 cm^{-1} on a Perkin-Elmer-883 spectrophotometer using KBr pellet of optics. The Raman spectrum of the polycrystalline sample was recorded on a Spex-1877 Raman spectrophotometer in the range 200–4000 cm^{-1} using 4880 Å line from a $\text{C}_w \text{Ar}^+$ laser as the source of excitation, a 2 cm^{-1} spectral slit width, a constant scan speed of 0.1 cm^{-1}/s and a power less than 100 mW at sample to avoid decomposition of the samples. The accuracy of the measurement was within $\pm 3 \text{ cm}^{-1}$ and the resolution was better than 2 cm^{-1} for the IR and Raman spectra.

3. Results and vibrational assignments

The frequencies observed in the IR and Raman spectra along with their relative intensities and proposed vibrational assignment of the fundamental modes are given in table 1. When I compare the theoretically *ab initio* (quantum mechanical calculations) calculated frequencies of the parent molecule uracil as given in ref. [31] and the normal coordinate analysis of NH_2 group-substituted uracil of [32] they are certainly in ‘reasonably good agreement’ with the experimental IR and Raman spectra. Table 2 contains an assignment for the lattice modes, overtones and combination bands. To the best of my knowledge no structural data are available for 5-aminouracil in literatures. The parent molecule uracil is known to have a planar structure both from the theoretical [33] and experimental [34] studies in the solid phase. Therefore, to a first approximation, this molecule may be assumed to belong to the C_s point group symmetry, if the NH_2 group is taken to be coplanar with the uracil ring. Under the C_s point group, the distribution of the normal modes between the two species are given by $25a'+11a''$, of which 30 modes ($21a'+9a''$) correspond to the uracil moiety and 6 modes ($4a'+2a''$) to the NH_2 group which are given below:

a' species	a'' species
Symmetric stretching – $\nu_s(\text{NH}_2)$	NH_2 wagging – $\omega(\text{NH}_2)$
Anti-symmetric stretching – $\nu_{as}(\text{NH}_2)$	NH_2 torsion or twist – $\tau(\text{NH}_2)$
Symmetric deformation – $\beta(\text{NH}_2)$	
Anti-symmetric deformations or rocking – $\rho(\text{NH}_2)$	

All the modes are allowed to appear both in the Raman and IR spectra.

The complexity of the spectra of the nucleic acid bases makes vibrational assignments rather difficult. Susi *et al* [11,12,35] have observed that skeletal mode of uracil appears to be surprisingly close and therefore, one might expect a similar pattern for the skeletal modes of 5-aminouracil. In the assignment of 5-aminouracil modes, assistance has also been taken from studies on uracil [1–27,31], NH_2 -containing

benzene derivatives [36] and substituted uracil [1,32,37]. The assignment of the normal modes of 5-aminouracil may be discussed in the forthcoming sections.

3.1 NH_2 modes

The NH_2 group gives rise to six internal modes, namely, symmetric stretching – $\nu_s(NH_2)$, anti-symmetric stretching – $\nu_{as}(NH_2)$, scissoring or symmetric deformation or simply deformation – $\beta(NH_2)$, anti-symmetric deformations or rocking – $\rho(NH_2)$, wagging – $\omega(NH_2)$ and torsion or twist – $\tau(NH_2)$ modes. For aniline and its derivatives the ν_s, ν_{as}, τ and ω modes are usually localized and are pure group modes whereas the β and ρ modes mix up with the other ring modes. However, due to the presence of intermolecular hydrogen bonding between the hydrogen atom of amino group of one molecule and the two oxygen atoms of the two different molecules, the remaining NH_2 group modes may interact with the other modes in pyrimidine derivatives. In the case of two NH bonds of the NH_2 group being identical, the ν_s and ν_{as} modes satisfy the relationship $\nu_s = 345.5 + 0.876 \nu_{as}$ as proposed empirically by Bellamy and Williams [38]. For 5-aminouracil, the two NH_2 stretching modes appear at 3290 and 3360 cm^{-1} in the infra-red spectra of each one as given in ref. [32]. The lower frequency is assigned to the symmetric (ν_s) mode and the higher one to the anti-symmetric (ν_{as}) mode. Using the relation of Bellamy and Williams and taking ν_{as} to be 3360 cm^{-1} , ν_s comes out to be 3289 cm^{-1} which is only 1 cm^{-1} lower than the observed frequency (3290 cm^{-1}). In the case of two NH bonds of the NH_2 group being equivalent to the calculated value, ν_s agrees with the observed values within $\pm 2 \text{ cm}^{-1}$. It appears that the two NH bonds of NH_2 group are equivalent due to their involvement in the hydrogen bonding.

The scissoring mode (β) of the NH_2 group gives rise to its characteristic frequencies in the region 1600–1700 cm^{-1} which contains a broad and strong IR band with peak at 1670 cm^{-1} for 5-aminouracil. The rocking $\rho(NH_2)$ mode usually appears in the region 900–1150 cm^{-1} for nucleic acid bases [39,40]. In the present case the IR band at 1100 cm^{-1} is associated with this mode. For 2-thiocytosine the $\omega(NH_2)$ and $\tau(NH_2)$ modes have been assigned at 540 and 527 cm^{-1} by Beetz and Ascarelli [15]. In fact, $\omega(NH_2)$ and $\tau(NH_2)$ modes arise due to the out-of-phase and the in-phase coupling of the two NH out-of-plane bending motions of the NH_2 group. In the assignment [41], the $\omega(NH_2)$ and $\tau(NH_2)$ modes have been assigned at 650 and 315 cm^{-1} and also in the assignments [42,43], the modes have been assigned at ~ 750 and 400 cm^{-1} . But 2-thiocytosine has been assigned the $\omega(NH_2)$ and $\tau(NH_2)$ modes at 804 and 527 cm^{-1} [2]. For removal of the complexity in $\omega(NH_2)$ and $\tau(NH_2)$ modes, I have done the parallel studies of substituted uracils (5- X -uracil, $X=F, Cl, Br, I, NH_2$ and CH_3) making with a comparison of $\omega(NH_2)$ and $\tau(NH_2)$ modes [32] which are clearly expected at 485 and 430 cm^{-1} respectively.

3.2 NH/CH modes

The NH and CH stretching modes usually appear in the region 3000–3200 cm^{-1} with the three N_1H, N_3H and one C_6H stretching modes on higher frequency sites

Table 1. Fundamental frequencies of 5-aminouracil.

Infra-red (IR) (cm ⁻¹)	Raman (cm ⁻¹)	Assignments
3360(s)	–	<i>a'</i> ν_{as} (NH ₂)
3290(m)	–	<i>a'</i> ν_s (NH ₂)
3180(sh)	3180(s)	<i>a'</i> ν (N ₁ H)
3125(mw)	3125(s)	<i>a'</i> ν (N ₃ H)
3070(sh)	3065(ms)	<i>a'</i> ν (C ₆ H)
1755(s)	1755(ms)	<i>a'</i> ν (C ₂ =O ₇)
1715(sh)	1715(w)	<i>a'</i> ν (C ₄ =O ₈)
1670(s)	1675(m)	<i>a'</i> β (NH ₂)
1650(s)	1645(m)	<i>a'</i> ν (C ₅ =C ₆) ring
1580(s)	1580(s)	<i>a'</i> β (N ₁ H)
1450(vs)	1465(m)	<i>a'</i> ν (ring)
1420(vs)	1420(s)	<i>a'</i> β (N ₃ H)
1365(w)	–	<i>a'</i> ν (C ₅ -NH ₂)
1298(vs)	1310(s)	<i>a'</i> ν (ring)
1240(vs)	–	<i>a'</i> ν (ring) Kekule
1205(s)	–	<i>a'</i> β (C ₆ H)
1100(ms)	1105(ms)	<i>a'</i> ρ (NH ₂)
1080(sh)	1075(ms)	<i>a'</i> ν (ring)
1010(m)	–	<i>a'</i> α (ring)
980(w)	975(ms)	<i>a''</i> γ (C ₆ H)
885(vs)	885(m)	<i>a''</i> γ (N ₃ H)
843(m)	840(ms)	<i>a''</i> γ (N ₁ H)
795(s)	785(ms)	<i>a''</i> γ (C ₂ =O ₇)
768(vs)	–	<i>a''</i> γ (C ₄ =O ₈)
740(sh)	–	<i>a''</i> ν (ring)-breathing
655(w)	655(s)	<i>a'</i> α (ring)
600(sh)	605(w)	<i>a''</i> δ (ring)
555(vs)	–	<i>a'</i> β (C ₂ =O ₇)
530(sh)	520(s)	<i>a'</i> β (C ₄ =O ₈)
485(vs)	–	<i>a''</i> ω (NH ₂)
430(vs)	430(ms)	<i>a''</i> τ (NH ₂)
410(sh)	–	<i>a'</i> α (ring)
380(ssh)	–	<i>a''</i> δ (ring)
280(s)	283(ms)	<i>a''</i> δ (ring)
230(vs)	–	<i>a'</i> β (C ₅ -NH ₂)
205(vs)	–	<i>a''</i> γ (C ₅ -NH ₂)

vw = very weak, w = weak, m = medium, mw = medium weak, ms = medium-strong, s = strong, vs = very strong, sh = shoulder, ssh = strong shoulder. ν : stretching, s: symmetric, as: anti-symmetric, α : angle bending, β : in-plane bending, γ = out-of-plane bending, τ = torsion/twist, ρ = rocking, ω = wagging, δ = out-of-plane ring deformation or ring torsion.

are in accordance with the reported works [1,4,24,44–46]. The Raman band spectrum shows two strong band peaks at 3180 and 3125 cm⁻¹ for N₁H and N₃H stretching modes. Also one C₆H stretching mode which appears with medium strong peak band at 3065 cm⁻¹ is given table 1. The N₁H, N₃H and C₆H in plane bending deformations are observed at 1580, 1420 and 1205 cm⁻¹ in accordance with [1,2,31,45] and are given in table 1.

Table 2. Lattice modes, overtones and combination frequencies of 5-aminouracil.

IR (cm ⁻¹)	Raman (cm ⁻¹)	Assignments
		1420+1580
	2985(mw)	1310+1675
2880(ms)	2880(w)	1420+1460
	2840(mw)	2 × 1420
2820(ms)		1240+1580
2450(w)		1450+1010
2020(m)		2 × 1010
1980(w)		1420+555
1950(w)		1420+530
1500(m)	1500(m)	1080+410, 2× ring stretching
380(w)		Intermolecular/lattice
300(s)		Intermolecular/lattice

Abbreviations are similar to those defined in table 1.

In uracil, the out-of-plane NH bending has been assigned in the region 800–860 cm⁻¹ [18,37,45] and we assign the frequencies 840 and 885 cm⁻¹ to the $\gamma(\text{N}_1\text{H})$ and $\gamma(\text{N}_3\text{H})$ modes respectively. One out-of-plane C₆H bending is assigned at 975 cm⁻¹ and similar to [31] and to the 2-thiouracil [1].

3.3 C-NH₂ modes

According to the crystallographic studies of Furberg and Jensen [47], the C-NH₂ bond in 2-thiocytosine (1.333 Å) is close enough to the C=N bond in the ring (1.334 Å) and is considerably shorter than the corresponding band in aniline (1.42 Å) (Bowen *et al* [48]). The C-NH₂ stretching mode is, therefore, expected to appear at markedly higher frequencies than in aromatic amines. For 5-aminouracil I assign the frequency 1365 cm⁻¹ to this mode in agreement with the assignment of [36] and [35]. The $\beta(\text{C-NH}_2)$ and $\gamma(\text{C-NH}_2)$ modes for 5-aminouracil are observed with strong band peaks at 230 and 205 cm⁻¹ which are closely agreed with the assignment of [36] and also nearly associated with the in-plane bending and out-of-plane bending frequencies for 2-thiocytosine [2] at very strong IR band peaks.

3.4 C=O modes

The most interesting modes of 5-aminouracil has out of the six C=O modes, the two C=O stretching modes easily identified as strong and IR band peaks at 1715 and 1755 cm⁻¹. Obviously it has also been assigned by authors [1,4,15,20,21] and also theoretically by [31]. Out of the two $\nu(\text{C=O})$ modes, the mode due to $\nu(\text{C}_4=\text{O}_8)$ is assigned at lower magnitude as the oxygen atom attached to the C₄ atom participates in the hydrogen bonding due to intermolecular forces which weaken the

$C_4=O_8$ band and thereby reduces the magnitude of the $\nu(C_4=O_8)$ mode. The two C=O deformation modes with some controversies in the assignments are expected in the region 300–900 cm^{-1} . These two modes, $\beta(C_2=O_7)$ and $\beta(C_4=O_8)$ in-plane banding modes, are observed in IR strong band peaks at 555, 530 cm^{-1} and in Raman for $\beta(C_4=O_8)$ at 520 cm^{-1} with strong band peak which are closely agreed with the theoretical assignment of [31]. However, these two C=O in-plane bending modes have been assigned at ~ 390 and ~ 625 cm^{-1} by [15,18,35,49] for uracil and its derivatives. These bands having similar characteristic are also observed in both IR and Raman spectra of 5-*X*-uracils ($X=\text{F}$, Cl, Br, I, CH_3 and NH_2). The $\gamma(\text{C}=\text{O})$ modes have been proposed near 430 cm^{-1} by some workers [15,18], whereas some other workers [24,30,45] and also theoretically by [31] have proposed in the region 680–820 cm^{-1} for these modes and I agree with the assignments of the latter group of workers. For 5-aminouracil these bands are observed with very strong peaks at 795 and 768 cm^{-1} and have been correlated to the two $\gamma(C_2=O_7)$ and $\gamma(C_4=O_8)$ modes [31]. The participation of the O_8 atom in intermolecular hydrogen bonding is expected to make the planar as well as the non-planar $C_4=O_8$ motion a more difficult comparison to the corresponding modes due to the non-bonded one ($C_2=O_7$ motion). Hence, the planar and non-planar bending modes due to the $C_4=O_8$ bond are expected to have lower magnitude compared to that due to the $C_2=O_7$ bond.

3.5 Pyrimidine ring modes

The pyrimidine ring similar to the phenyl ring has 12 normal modes of vibration, six of which correspond to the ring stretching, three to the ring in-plane deformation (α) and three to the ring out-of-plane deformation (δ) modes. The stretching modes of pyrimidine ring are complicated combinations of the stretching of the C–N, C=N, C–C and C=C bonds of the ring. The ring stretching modes have been observed and correlated to the frequencies 1650, 1450, 1298, 1240, 1075 and 740 cm^{-1} as given in ref. [31]. These assignments are in good agreement with those proposed for uracil [30] and its derivatives [1,2,4,37]. The frequency 1240 cm^{-1} with strong peak could be correlated to the Kekule-type vibration mode (ν_{14}) of benzene whereas frequency 740 cm^{-1} , similar to that of ν_1 of benzene with a weak IR band peak, is identified as the ring breathing vibration of the pyrimidine ring.

Similar to benzene and its derivatives, out of the three in-plane ring deformation or angle bending modes, the mode due to trigonal angle ring bending is one of the most interesting and most widely discussed mode similar to the ring breathing and Kekule ring modes. The frequency of this mode is substantially reduced due to its strong mixing with other modes. The planar ring deformations are assigned at 982, 559/536 and 516 cm^{-1} by Harsanyi *et al* [30], at 802, 548 and 480 cm^{-1} by Colombo and Kirin [45], at 785, 556 and 482 cm^{-1} by Susi and Ard [12], at 995, 732 and 480 cm^{-1} by Szczesniak *et al* [23] and for 5-trifluoromethyluracil at 1009, 637 and 446 cm^{-1} [4]. In the present case the frequencies 1010, 655 and 410 cm^{-1} are assigned to the plane ring deformation which is in good agreement with [4,8,23,30]. The three ring torsional or out-of-plane deformation modes, in 1-methyluracil [45] of these modes proposed at 525, 445 and 268 cm^{-1} and for 5-trifluoromethyluracil at 602, 418 and 208 cm^{-1} by Shankar *et al* [4] are in good agreement with 5-aminouracil of the ring torsional mode frequencies at 600, 380 and 280/283 cm^{-1} in table 1.

4. Conclusions

For the first time, all the 36 normal fundamental modes of 5-aminouracil could be assigned. The ring breathing, Kekule and trigonal angle bending modes are observed to have closely same magnitudes as 5-trifluoromethyluracil. However, all the C=O modes are observed at nearly same frequencies compared to 5-trifluoromethyluracil. Symmetry and anti-symmetry NH stretching modes of the NH₂ group show the validity of the empirical relationship of Bellamy and Williams [38].

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