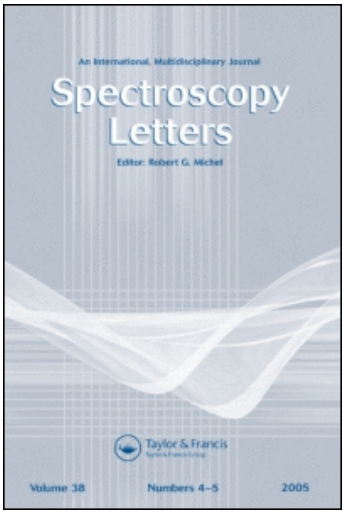

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Infrared and Raman Spectra for Amino Group and C=O Stretching Modes in Biomolecule 5-Aminouracil

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ABSTRACT Assuming planar geometry of 5-aminouracil and C_s point group symmetry, it has been possible to assign all the 36 ($25a' + 11a''$) normal modes of vibration. The two NH bonds of the NH_2 group appear to be non-equivalent as the NH_2 stretching frequencies and do not satisfy the empirical relation proposed for the two equivalent NH bonds of the NH_2 group due to their involvement and interaction with one hydrogen bond and the other adjacent oxygen atom of the parent molecule. The planar and nonplanar bending modes due to the C_4═O_8 bond are expected with have lower magnitude compared with those due to the C_2═O_7 bond.

KEYWORDS infrared spectrum, Raman spectrum, stretching mode

INTRODUCTION

Vibrational studies on nucleic acid bases and their derivatives are of considerable importance from a biological point of view as these are constituents of genetic material. Uracil derivatives are used in anticarcinogenic drugs synthesis for drugs used against cancer and HIV. This paper is a continuation of prior work[1–4] on substituted metabolism. These molecules do not occur naturally in biological metabolism. The understanding of the vibrational spectra of the free molecules might be helpful in understanding specific biological processes and in the analysis of relatively complex systems. Vibrational studies on uracil and its derivatives have been made by several authors[4–34] although there is still disagreement amongst various researchers for the assignment of the modes of uracil. It is planned to perform a parallel study of the vibrational spectra of 5-substituted uracil with substituents as 5-X-uracils (X = F, Cl, Br, I, NH_2, and CH_3). The present article is a vibrational spectroscopic study of 5-X-uracils and deals with Raman and IR spectra and vibrational assignments for all the 36 normal modes vibration.

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MATERIALS AND METHODS

The compound 5-Aminouracil was purchased from the Aldrich Chemical Co., WI, USA and was used as such for spectroscopic measurements. All the spectra

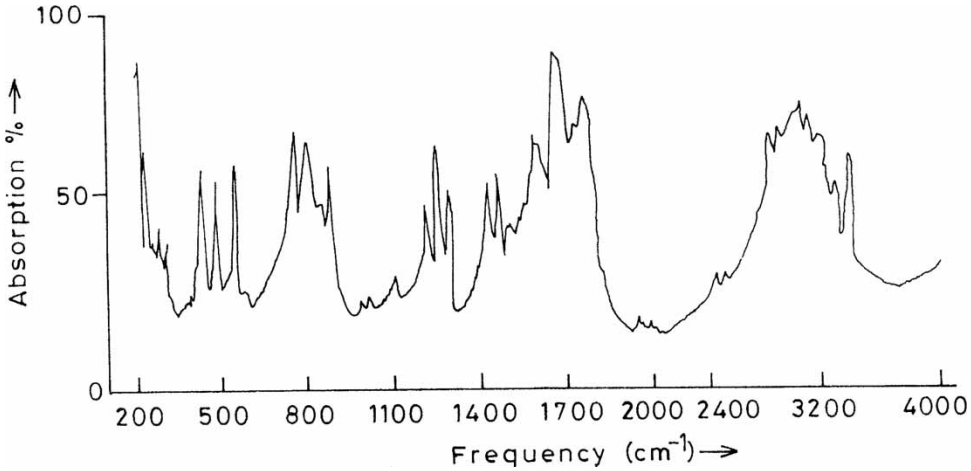

FIGURE 1 Infrared Spectrum of 5-AminoUracil.

were recorded at room temperature. The infrared spectrum (Fig. 1) of 5-aminouracil powder was recorded in the range 200–4000 cm^{-1} on a PerkinElmer 883 spectrophotometer using KBr pellets. The Raman spectrum (Fig. 2) of the polycrystalline sample was recorded on a Spex-1877 Raman spectrophotometer in the range 200–4000 cm^{-1} using the 4880 Å line from an C_w Ar^+ ion 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 the sample to avoid decomposition of the samples. The accuracy of the measurement was within ± 3 cm^{-1}, and the resolution was better than 2 cm^{-1} for the IR and Raman spectra.

RESULTS AND DISCUSSION

The frequencies observed in the IR and Raman spectra along with their relative intensities and the proposed vibrational assignment of the fundamental modes are given in Table 1. To the best of my information, no structural data are available for 5-aminouracil in the literature. The parent molecule uracil is known to have a planar structure both from the theoretical[35] and experimental[36] 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 a 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 with the uracil moiety and 6 modes ($4a' + 2a''$) with the NH_2 group, which are given Table 2.

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

The complexity of the spectra of the nucleic acid bases makes vibrational assignments rather difficult. Susi et al.[11,12,37] have observed that the skeletal mode of

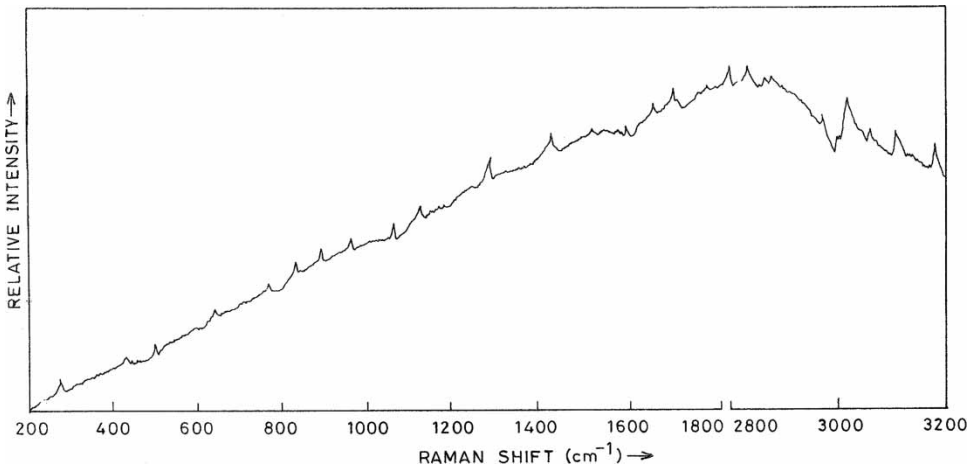

FIGURE 2 Raman Spectrum of 5-Aminouracil.

TABLE 1 Fundamental Frequencies of 5-Aminouracil

Infrared (cm^{-1})	Raman (cm^{-1})	Assignments
3380(s)	—	a′ ν_{as} (NH_2)
3290(m)	—	a′ ν_s (NH_2)
3180(sh)	3180(s)	a′ ν (N_1H)
3125(mw)	3125(s)	a′ ν (N_3H)
3070(sh)	3065(ms)	a′ ν (C_6H)
1755(s)	1755 (ms)	a′ ν (C_2═O_7)
1715(sh)	1715(w)	a′ ν (C_4═O_8)
1670(s)	1675(m)	a′ β (NH_2)
1650(s)	1645(m)	a′ ν (C_5═C_6) ring
1580(s)	1580(s)	a′ β (N_1H)
1450(vs)	1465(m)	a′ ν (ring)
1420(vs)	1420(s)	a′ β (N_3H)
1365(w)	—	a′ ν (C_5–NH_2)
1298(vs)	1310(s)	a′ ν (ring)
1240(vs)	—	a′ ν (ring) Kekule
1205(s)	—	a′ β (C_6H)
1100(ms)	1105(ms)	a′ ρ (NH_2)
1080(sh)	1075(ms)	a′ ν (ring)
1010(m)	—	a′ α (ring)
980(w)	975(ms)	a″ γ (C_6H)
885(vs)	885(m)	a″ γ (N_3H)
843(m)	840(ms)	a″ γ (N_1H)
795(s)	785(ms)	a″ γ (C_2═O_7)
768(vs)	—	a″ γ (C_4═O_8)
740(sh)	—	a′ ν (ring) breathing
655(w)	655(s)	a′ α (ring)
600(sh)	605(w)	a″ δ (ring)
555(vs)	—	a′ β (C_2═O_7)
530 (sh)	520(s)	a′ β (C_4═O_8)
485(vs)	—	a″ ω (NH_2)
430(vs)	430(ms)	a″ τ (NH_2)
410(sh)	—	a′ α (ring)
380(ssh)	—	a″ δ (ring)
280(s)	283(ms)	a″ δ (ring)
230(vs)	—	a′ β (C_5–NH_2)
205(vs)	—	a″ 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, antisymmetric; 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.

TABLE 2 Amino Group Modes

a′ Species	a″ Species
Symmetric stretching, ν_s (NH_2)	NH_2 wagging, ω (NH_2)
Antisymmetric stretching, ν_{as} (NH_2)	NH_2 torsion or twist, τ (NH_2)
Symmetric deformation, β (NH_2)	
Antisymmetric deformations or rocking, ρ (NH_2)	

uracil appears to be surprisingly close, and therefore one might expect a similar pattern for the skeletal modes of the 5-aminoruacil. In the assignment of 5-aminouracil modes, assistance was also taken from studies on uracil,[1–27] NH_2-containing benzene derivatives,[40] and substituted uracil[1,38] with a comparison of theoretically calculated frequencies in reasonably good agreement with the experimental IR and Raman spectra for a pyrimidine bases- parent molecule uracil as given in Ref. [39] The assignment of the normal modes of 5-aminouracil are discussed under the following sections: NH_2 modes, C═O modes, NH/CH modes, C–NH_2 modes, and pyrimidine ring modes.

NH_2 Modes

The NH_2 group give rise to six internal modes, namely symmetric stretching, ν_s (NH_2) antisymmetric stretching, ν_{as} (NH_2); scissoring or symmetric deformation or simply deformation, β (NH_2) antisymmetric deformations or rocking, ρ (NH_2); wagging, ω (NH_2) and torsion or twist, τ (NH_2). 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 the 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 the two identical NH bonds of the NH_2 group, 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.[40] For 5-aminouracil, the two NH_2 stretching modes appear at 3290 and 3380 cm^{-1} in the infrared spectra of each one. The lower frequency is assigned to the symmetric (ν_s) mode and the higher one to the antisymmetric (ν_{as}) mode. Using the relation of Bellamy and Williams and taking ν_{as} to be 3380 cm^{-1}, the ν_s comes out to be 3306 cm^{-1}, which is 16 cm^{-1} above the observed frequency (3290 cm^{-1}). In the case of the two NH bonds of the NH_2 group that are not equivalent, the calculated value of ν_s disagrees with the observed values within the limit ± 2 cm^{-1}. It appears that the two NH bonds of the NH_2 group are not equivalent due to their involvement and interaction with one hydrogen bond and an adjacent oxygen atom of the parent molecule.

The scissoring modes (β) of the NH_2 group give rise to its characteristic frequencies in the region 1600–1700 cm^{-1}, which contain a broad and strong IR band with peak at 1670 cm^{-1} and a medium, strong Raman peak at 1675 cm^{-1} for 5-aminouracil. The rocking ρ (NH_2) mode usually appears in the region 900–1150 cm^{-1} for nucleic acid bases.[41,42] In the current case, the IR band at 1100 cm^{-1} and Raman band at 1100 cm^{-1} are associated with this mode. For 2-thiocytosine, the ω (NH_2) and τ (NH_2) modes have been assigned at 540 and 527 cm^{-1} by Beetz and Ascarelli.[15] In fact, the ω (NH_2) and τ (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 assignments for substituted uracil,[43] the ω (NH_2) and τ (NH_2) modes have been assigned at 650 and 315 cm^{-1} and also in the assignment of benzene derivatives[44,45] assigned near 750 and 400 cm^{-1}. But the assignment[2] of 2-thiocytosine has been assigned to the ω (NH_2) and τ (NH_2) modes at 804 and 527 cm^{-1}. In order to remove the complexity in the ω (NH_2) and τ (NH_2) modes, parallel studies for substituted uracil (5-X-uracil: X = F, Cl, Br I, NH_2, and CH_3) with a comparison of ω (NH_2) and τ (NH_2) modes are clearly expected at 485 and 430 cm^{-1}.

C=O Modes

The most interesting modes of 5-aminouracil, out of the six C=O modes, the two C=O stretching modes are easily identified as strong and IR and Raman band peaks both at 1715 and 1755 cm^{-1}, which have also been assigned by other authors.[1,4,15,20,21] Out of the two ν (C=O) modes, the mode due to ν ($C_4 = O_8$) is assigned a lower magnitude as the oxygen atom attached to the C_4 atom participates in the hydrogen bonding due to intermolecular forces that weaken the C_4=O_8 band thereby reducing the magnitude of the ν (C_4=O_8) mode. The two C=O deformation modes have some controversies in the assignment, but are expected in the region 300–900 cm^{-1}. These two modes β (C_2=O_7) and β (C_4=O_8) in-plane bending modes are observed in the IR with strong band peaks at 555, 530 cm^{-1} and in the Raman for β (C_4=O_8) at 520 cm^{-1} with strong band peak. However, the two C=O in-plane bending modes, have made assignments near ~390 and ~625 cm^{-1}[15,18,37,46] for uracil and its derivatives. These bands which have similar characteristics are also observed in both the IR and Raman spectra of 5-X-uracils (X = F, Cl, Br, I, CH_3, and NH_2). The γ (C=O) modes have been proposed near 430 cm^{-1} by some workers,[15,18] whereas some other workers[24,30,39,47] have proposed the region 680–820 cm^{-1} for these modes, with which this author agrees. For 5-aminouracil, these bands are observed with very strong peaks at 795 and 768 cm^{-1} and have been correlated with the two γ (C_2=O_7) and γ (C_4=O_8) modes. The participation of the O_8 atom in intermolecular hydrogen bonding is expected to the make the planar as well as the nonplanar C_4=O_8 motion more difficult compared with the corresponding modes due to the nonbonded one (C_2=O_7 motion). Hence, the planar and nonplanar bending modes due to the C_4=O_8 bond are expected to have lower magnitude compared with that due to the C_2=O_7 bond in accordance with Ref. [4] and also making a comparison with Ref. [39].

NH/CH Modes

The NH and CH stretching modes usually appear in the region 3000–3200 cm^{-1} with the N_1H, N_3H, while the C_6H stretching modes at the higher frequencies are in accordance with the reported works.[1,4,24,47–49] The Raman band spectrum shows two strong band peaks at 3180 and 3125 cm^{-1} for N_1H and N_3H stretching modes, also one C_6H stretching mode appears with medium strong peak band at 3065 cm^{-1} (Table 1). The N_1H, N_3H, and C_6H in-plane bending deformations are observed at 1580, 1420, and 1205 cm^{-1} in accordance with Refs. [1, 2, 47] and are given in Table 1.

In uracil, the out-of-plane NH bending has been assigned in the region 800–860 cm^{-1}[18,38,47] contrary to the assignment of modes in the region 550–665 cm^{-1} in Ref. [30] and others. The assignments of Ref. [18] are based on N-deuteration and hence are more reliable. Here, the frequencies 840 and 885 cm^{-1} were assigned to the γ (N_1H) and γ (N_3H) modes, respectively. One out-of-plane C_6H bending is assigned at 975 cm^{-1} similar to 2-thiouracil.[1]

C–NH_2 Modes

According to crystallography studies of Furberg and Jensen,[50] the C–NH_2 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).[51] The C–NH_2 stretching mode is, therefore, expected to appear at markedly higher frequencies than in aromatic amines. For 5-aminouracil, the frequency 1365 cm^{-1} was assigned here in agreement with the assignment of trifluoromethyl anilines[52] and cytosine.[37] The β (C–NH_2) and γ (C-NH_2) modes for 5-aminouracil are observed with strong band peaks at 230 and 205 cm^{-1}, which closely agrees with the assignment in Ref. [52] and is nearly associated with the in-plane bending and out-of-plane bending frequencies for 2-thiocytosine[2] at very strong IR band peaks.

Pyrimidine Ring Modes

The pyrimidine ring, similar to the phenyl ring, has 12 normal modes of which six correspond to the ring stretching, three with the ring in-plane deformation/angle bending (α), and three with 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 with the frequencies 1650/1645, 1450/1465, 1298/1310, 1240, 1080/1075, and 740 cm^{-1}. These assignments are in good agreement with those proposed for uracil[30] and its derivatives.[1,2,4,38,39] The frequency 1240 cm^{-1} with strong peak could be correlated with the Kekule-type vibration mode (ν_{14}) of benzene, whereas type frequency 740 cm^{-1}, is similar to the that of ν_1 of benzene with a weak IR band peak, identified as the ring breathing vibration of the pyrimidine ring.

Similar to benzene and its derivatives,[44,53] of the three in-plane ring deformation or angle bending modes, the mode due to trigonal angle ring bending is one of the must interesting and most widely discussed modes 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 deformation are assigned at 982, 559/536, and 516 cm^{-1} by has Harsanyi et al.,[30] at 802, 548, and 480 cm^{-1} by Colombo and Kirin,[47] 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-trifluoromethyl uracil at 1009, 637, and 446 cm^{-1}.[4] In the current case, the frequencies 1010, 655, and 410 cm^{-1} are assigned to the plane ring deformation with a good agreement with the reported workers.[4,8,23,30] The three ring torsional or out-of-plane deformation modes, in 1-methyluracil[47] of these modes have been proposed at 525, 445, and 268 cm^{-1} and for 5-trifluoromethyl uracil at 602, 418, and 208 cm^{-1} by Yadav et al.[4] are in good agreement with 5-aminouracil of the ring torsional modes frequencies at 600, 380, and 280/283 cm^{-1} (Table 1).

CONCLUSIONS

All the 36 normal fundamental modes of 5-aminouracil could be assigned in the current case. The ring breathing, Kekule, and trigonal angle bending modes are observed to have closely the same magnitudes for 5-trifluoromethyl uracil. The symmetrical and antisymmetrical NH stretching modes of the NH_2 group show the invalidity of the empirical relationship of Bellamy and Williams[40] for the two nonequivalent NH bonds of the NH_2 group due to their involvement and interaction with one hydrogen bond and the other adjacent oxygen atom of the parent molecule. The participation of the O_8 atom in intermolecular hydrogen bonding is expected to make the planar as well as the nonplanar C_4═O_8 motion is comparable to the corresponding modes due to the nonbonded one (C_2═O_7 motion). Hence, the planar and nonplanar bending modes due to the C_4═O_8 bond are expected to have lower magnitude compared to, those due to the C_2═O_7 bond.

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