

Vibrational Spectroscopic Studies of Thymine

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Abstract:- The molecular vibrations of thymine was investigated by FT-IR and FT-Raman spectroscopies. Normal coordinate calculations of thymine have been carried out using Wilson's FG matrix mechanism on the basis of General valence Force field (GVFF) for both in-plane and out-of-plane vibrations. The potential energy constants obtained in the study are refined using numerical methods.

Key words : FT-IR, FT-Raman, thymine, normal coordinate analysis, potential energy distribution.

I. INTRODUCTION

Thymine is one of the five bases that form nucleic acids, along with adenine, guanine, cytosine and uracil. Thymine is always paired up with adenine through two hydrogen bonds only in DNA to stabilize the nucleic acid structure. Uses of thymine include cancer treatment, where it serves as a target for actions of 5-fluorouracil. Substitution of this compound to thymine (in DNA) and uracil (in RNA) allows inhibition of DNA synthesis in actively-dividing cells.

In 2015, NASA scientists reported that evidence of thymine had been formed in a laboratory under conditions that stimulated outer space.

In the present paper, an effort has been made to record spectra and to assign the observed fundamental modes of vibrations. The evaluation of potential energy constant has been made on the basis of General valence force field (GVFF) by applying Wilson's FG matrix mechanism[1].

II. EXPERIMENTAL METHODS

Pure chemical of thymine is obtained from Lancaster chemical company and used as such without any further purification.

The FT-IR spectrum of the title compound was recorded in the region 4000-400cm⁻¹ using KBr pellet. The Bruker IFS 66V model FT-IR spectrometer was used for the spectral measurements. The globar and mercury are sources, KBr beam splitters are used while recording FT-IR spectrum of the title compound.

The FT-Raman spectrum was recorded on a Bruker IFS 66V model interferometer equipped with an FRA-106 FT-Raman accessory. The spectrum was recorded in the stoke's region (4000-100cm⁻¹) using the 1064nm line of a Nd: YAG laser for excitation operating at 200mW of power.

III. Results and Discussion

A. Structure and symmetry

The molecular structure of thymine is shown in Fig 1. From the structural point of view the molecule is assumed to have C_s point group symmetry. The 39 fundamental modes of vibrations arising for this molecule are distributed into 26A' and 13A'' species. The A' and A'' species represent the in-plane and out-of-plane vibrations.

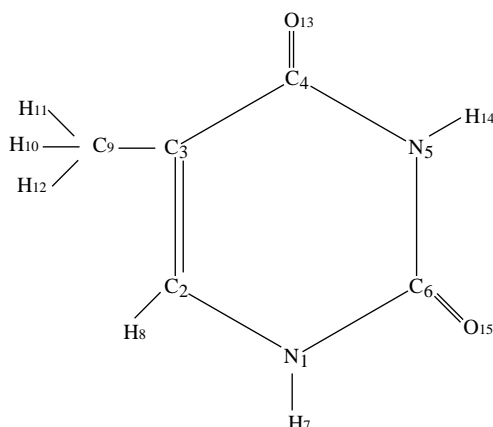


Fig 1: Molecular structure of Thymine

B. Normal Coordinate Analysis

The evaluation of potential energy constants are made on the basis of GVFF by applying Wilson's FG matrix mechanism. The structural parameters were taken from the Sutton's table[2]. The vibrational secular determinants have been solved using the computer programmes with the SIMPLEX optimization procedure[3]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature[4]. All the force constants have been refined via a non-linear square fit analysis between the calculated and observed frequencies. The refinement converged smoothly in three cycles.

C. Symmetry Coordinates

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 52 standard internal valence coordinates (containing 13 redundancies) were defined in Table 1. From these a non-redundant set of local internal coordinates were constructed (Table 2) much like the natural internal coordinates recommended by IUPAC [5,6]. Theoretically calculated force fields were transformed to the latter set of vibrational coordinates and used in all subsequent calculations.

Table 1: Definition of internal Coordinates of Thymine

No(i)	Symbol	Type	Definition
Stretching			
1-3	r_i	C-C	C2-C3, C3-C4, C3-C9
4-7	R_i	C-N	C4-N5, C6-N5, C6-N1, C2-N1
8	q_i	C-H	C2-H8
9-11	q_i	C-H (methyl)	C9-H10, C9-H11, C9-H12
12-13	Q_i	N-H	N1-H7, N5-H14
14-15	P_i	C-O	C4-O13, C6-O15
In-Plane bending			
16-17	α_i	C-C-H	C3-C2-H8, N1-C2-H8
18-19	α_i	C-C-C	C4-C3-C9, C2-C3-C9
20	θ_i	C-C-O	C3-C4-O13
21-23	θ_i	N-C-O	N5-C4-O13, N5-C6-O15, N1-C6-O15
24-27	σ_i	C-N-H	C4-N5-H14, C6-N5-H14, C2-N1-H7, C6-N1-H7
28-33	β_i	Ring	C4-C3-C2, C3-C2-N1, C2-N1-C6, N1-C6-N5, C6-N5-C4, N5-C4-C3
34-36	δ_i	C-C-H (methyl)	C3-C9-H10, C3-C9-H11, C3-C9-H12
37-39	σ_i	H-C-H	H10-C9-H11, H10-C9-H12, H12-C9-H11
Out-of-plane bending			
40	ω_i	C-H	H8-C2-N1-C3
41	π_i	C-C	C9-C3-C4-C2
42-43	ϕ_i	N-H	H7-N1-C2-C6, H14-N5-C6-C4
44-45	ψ_i	C-O	O13-C4-N5-C3, O15-C6-N1-N5
Torsion			
46-51	t_i	τ Ring	N1-C2-C3-C4, C2-C3-C4-N5, C3-C4-N5-C6 C4-N5-C6-N1, N5-C6-N1-C2, C6-N1-C2-C3
52	t_i	τ C-CH ₃	(C4, C2)-C3-C9-(H10, H11, H12)

For numbering of atoms refer Fig.1.

Table 2: Definition of local symmetry coordinates of Thymine

No.(i)	Type	Definition
1-3	CC	r_1, r_2, r_3
4-7	CN	R_4, R_5, R_6, R_7
8	CH	q_8
9	CH ₃ ss	$(q_9+q_{10}+q_{11})/\sqrt{3}$
10	CH ₃ ips	$(2q_9-q_{10}-q_{11})/\sqrt{6}$
11	CH ₃ ops	$(q_{10}-q_{11})/\sqrt{2}$
12-13	NH	Q_{12}, Q_{13}
14-15	CO	P_{14}, P_{15}
16	bCH	$(\alpha_{16}-\alpha_{17})/\sqrt{2}$
17	bCC	$(\alpha_{18}-\alpha_{19})/\sqrt{2}$
18-19	bCO	$(\theta_{20}-\theta_{21})/\sqrt{2}, (\theta_{22}-\theta_{23})/\sqrt{2}$
20-21	bNH	$(\sigma_{24}-\sigma_{25})/\sqrt{2}, (\sigma_{26}-\sigma_{27})/\sqrt{2}$
22	Rtrigd	$(\beta_{28}-\beta_{29}+\beta_{30}-\beta_{31}+\beta_{32}-\beta_{33})/\sqrt{6}$
23	Rsymd	$(-\beta_{28}-\beta_{29}+\beta_{30}-\beta_{31}-\beta_{32}+2\beta_{33})/\sqrt{6}$
24	Rasynd	$(\beta_{28}-\beta_{29}+\beta_{30}-\beta_{31})/\sqrt{2}$
25	CH ₃ sb	$(-\delta_{34}-\delta_{35}-\delta_{36}+\sigma_{37}+\sigma_{38}+\sigma_{39})/\sqrt{6}$
26	CH ₃ ipb	$(-\sigma_{37}-\sigma_{38}-2\sigma_{39})/\sqrt{6}$
27	CH ₃ opb	$(\sigma_{37}-\sigma_{38})/\sqrt{2}$
28	CH ₃ ipr	$(2\delta_{34}-\delta_{35}-\delta_{36})/\sqrt{6}$
29	CH ₃ opr	$(\delta_{35}-\delta_{36})/\sqrt{2}$
30	ω CH	ω_{40}
31	π CC	π_{41}
32-33	ϕ NH	ϕ_{42}, ϕ_{43}
34-35	ψ CO	ψ_{44}, ψ_{45}
36	tRtring	$(\tau_{46}-\tau_{47}+\tau_{48}-\tau_{49}+\tau_{50}-\tau_{51})/\sqrt{6}$
37	tRsym	$(\tau_{46}-\tau_{48}+\tau_{49}-\tau_{51})/\sqrt{2}$
38	tRasy	$(-\tau_{46}+2\tau_{47}-\tau_{48}-\tau_{49}+2\tau_{50}-\tau_{51})/\sqrt{12}$
39	tCH ₃	τ_{52}

D. . Vibrational Band Assignments

The FT-IR and FT-Raman spectra of the title compound are shown in Figs. 2-3.

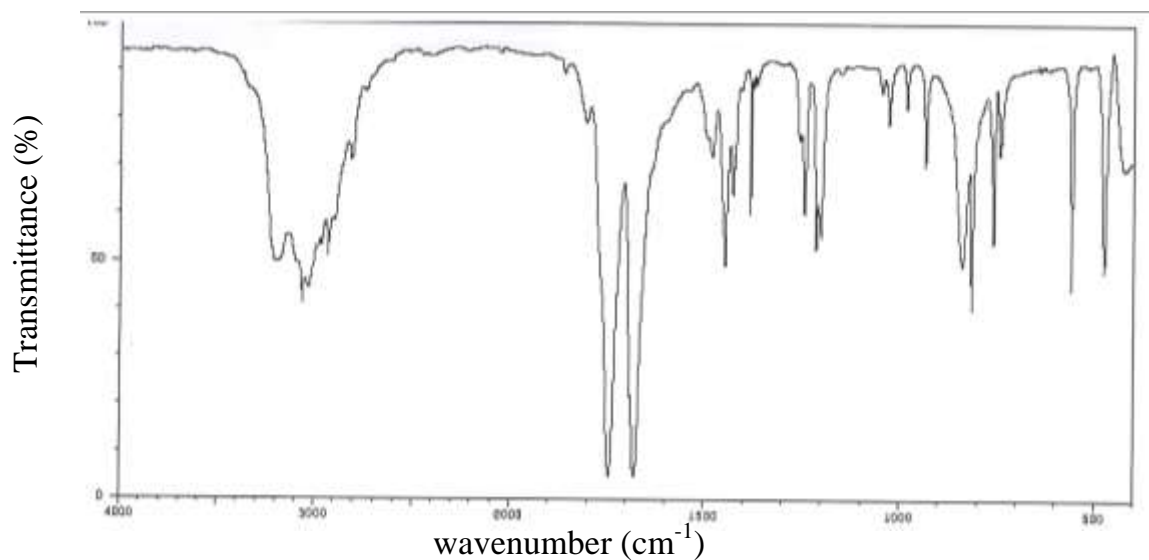


Fig 2: FT-IR spectrum of Thymine

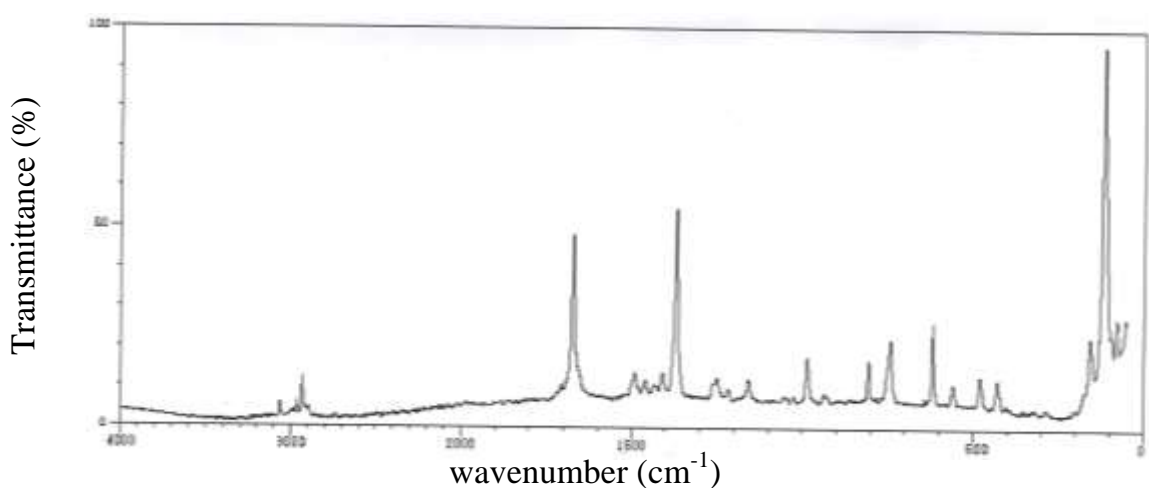


Fig 2: FT-Raman spectrum of Thymine

The observed frequencies of the title compound together with probable assignment, calculated frequencies and PEDS are presented in Table 3.

Table 3: Vibrational frequencies and assignments of Thymine

S. No.	Species	Observed frequency (cm ⁻¹)		Calculated Frequency (cm ⁻¹)	Assignment (% PED)
		FT-IR	FT-Raman		
1	A'	3201	-	3190	N-H Stretching (98)
2	A'	3191	-	3182	N-H Stretching (97)
3	A'	3065	-	3055	C-H Stretching (99)
4	A'	3030	-	3022	CH ₃ ips (98)
5	A'	2952	-	2943	CH ₃ ss (98)

6	A''	2914	-	2903	CH ₃ ops (89)
7	A'	1805	-	1795	C-O Stretching (83)
8	A'	1743	-	1735	C-O Stretching (81)
9	A'	1492	-	1482	C-C Stretching (87)
10	A'	1483	-	1474	CH ₃ ipb (84)
11	A'	1448	-	1437	C-C Stretching (72)
12	A'	1428	-	1420	C-N Stretching (76)
13	A'	-	1411	1400	C-C Stretching (71)
14	A'	1383	-	1374	C-N Stretching (75)
15	A'	1377	-	1367	CH ₃ sb (88)
16	A'	-	1371	1362	C-N Stretching (86)
17	A'	1366	-	1356	N-H in-plane bending (75)
18	A'	-	1261	1272	C-N Stretching (84)
19	A'	1246	-	1255	N-H in-plane bending (73)
20	A'	1216	-	1224	Ring deformation in-plane bending (52)
21	A'	1203	-	1213	C-H in-plane bending (71)
22	A''	-	1159	1150	CH ₃ opb (87)
23	A'	1047	-	1037	Ring deformation in-plane bending (53)
24	A'	1039	-	1028	Ring deformation in-plane bending (51)
25	A'	1030	-	1019	CH ₃ ipr (78)
26	A''	-	987	997	CH ₃ opr (76)
27	A'	840	-	849	C-C in-plane bending (65)
28	A'	760	-	771	C-O in plane bending (64)
29	A''	748	-	756	N-H out-of-plane bending (48)
30	A'	-	740	730	C-O in-plane bending (63)
31	A''	-	619	610	N-H out-of-plane bending (47)
32	A''	-	569	561	Ring deformation out of-plane bending (57)
33	A''	560	-	549	C-H out-of-plane bending (60)
34	A''	-	540	531	Ring deformation out-of-plane bending (58)
35	A''	476	-	467	Ring deformation out-of-plane bending (59)
36	A''	-	462	452	C-C out-of-plane bending (54)
37	A''	-	431	420	CH ₃ torsion (55)
38	A''	158	-	167	C-O out-of-plane bending (56)
39	A''	120	-	131	C-O out-of-plane bending (55)

Abbreviations used : *ss* – symmetric stretching, *ips*-in-plane stretching, *ops*-out-of-plane stretching, *sb*-symmetric bending, *ipb*-in-plane bending, *opb* out-of-plane bending, *ipr*-in-plane rocking, *opr*-out-of-plane rocking.

1) N-H vibrations

In all the heterocyclic compounds, the N-H stretching vibration[7] occur in the region 3500-3000 cm^{-1} . Hence the FT-IR bands at 3201 and 3191 cm^{-1} have been designated to N-H stretching modes of vibrations.

2) C-H vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region 3000-3100 cm^{-1} , which is the characteristic region for the ready identification of C-H stretching vibrations[8]. In this region the bands are not effected appreciably by the nature of the substituents. Hence, in the present investigation, C-H vibration has found at 3065 cm^{-1} in FT-IR.

3) C-C vibrations

The bands between 1400 and 1650 cm^{-1} in benzene derivatives are due to C-C stretching vibrations[9]. Therefore, the C-C stretching vibrations of the title compound are observed at 1492, 1448 cm^{-1} in IR and 1411 cm^{-1} in Raman.

4) C-N vibrations

The identification of C-N stretching frequency is very difficult task, since the mixing bands are possible in this region. Hence the FT-IR bands observed at 1428, 1383 cm^{-1} in IR and 1371, 1261 cm^{-1} in Raman of the title compound are assigned to C-N stretching modes of vibration. These assignments are made in accordance with the assignments proposed by krishnkumar etal. [10].

5) C-O vibrations

If a compound contains a carbonyl group, the absorption caused by the C-O stretching is generally strongest [11]. Consideration of these factors lead to assign the very strong FT-IR band observed at 1805 and 1743 cm^{-1} to C-O stretching vibration for the title compound.

6) Methyl Group vibrations

The methyl group substituted at the third position of the title compound give raise to asymmetric and symmetric stretching vibrations.

The CH_3 ss frequency is established at 2952 cm^{-1} in IR and CH_3 ips at 3030 cm^{-1} in IR for the title compound.

The two in-plane methyl hydrogen deformation modes are also well established. We have observed the symmetrical methyl deformation mode CH_3 sb at 1377 cm^{-1} in the infrared and in-plane bending methyl deformation mode CH_3 ipb at 1483 cm^{-1} in the infrared. The bands at 2914 cm^{-1} in IR and 1159 cm^{-1} in Raman are attributed to CH_3 ops and CH_3 opb respectively in the A'' species. The methyl deformation modes mainly coupled with the in-plane bending vibrations.

The bands obtained at 1030 cm^{-1} in IR and 987 cm^{-1} in Raman are assigned to CH_3 in-plane and out-of-plane rocking modes. The assignment of the band at 431 cm^{-1} in Raman is attributed to methyl twisting mode. These assignments are also supported by the literature[12].

IV. CONCLUSION

Based on the normal coordinate analysis a complete vibrational analysis was performed on thymine. A systematic set of symmetric coordinates have been constructed. The closer agreement obtained between the calculated and the observed frequencies and the PED calculations are also supporting the assignments made for various functional groups present in the molecule. A complete vibrational band assignment of thymine has been carried out using FT-IR and FT-Raman spectra on the basis of C_s point group symmetry.

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