

Vibrational Assignments of FT-IR and FT-Raman Spectra of Adenine

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ABSTRACT

Normal coordinate calculations of Adenine 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 this study are refined using numerical methods. A satisfactory vibrational band assignment has been made by using FT-IR and FT-Raman spectra of the title compound.

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1. Introduction

Adenine is a nucleobase with an amine group attached to the carbon at position 6. Adenine is the precursor for adenosine and deoxyadenosine nucleotides. Its derivatives have a variety of roles in biochemistry. It also has functions in protein synthesis and as a chemical component of DNA and RNA.

Adenine is one of the two purine nucleobases (the other being guanine) used in forming nucleotides of the nucleic acids. In DNA adenine binds to thymine via two hydrogen bonds to assist in stabilizing the nucleic acid structures. In RNA which is used for protein synthesis, adenine binds to Uracil.

Adenine can be found in tea, vitamin B12 and several other coenzymes.

In the present paper, an effort has been made to record spectra and to assign the observed fundamental modes of vibrations.

2. Experimental methods

Pure chemical of Adenine 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 $4000-400\text{cm}^{-1}$ using KBr pellet. The Bruker IFS 66V model FT-IR spectrometer was used for the spectral measurements. The globar and mercury arc 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 ($4000-100\text{cm}^{-1}$) using the 1064nm line of a Nd:YAG laser for excitation operating at 200 mW of power.

3. Results and Discussion

3.1. Structure and symmetry

The molecular structure of Adenine is shown in Fig. 1. From the structure 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 $27A'$ and $12A''$ species. The A' and A'' species represent the in-plane and out-of-plane vibrations.

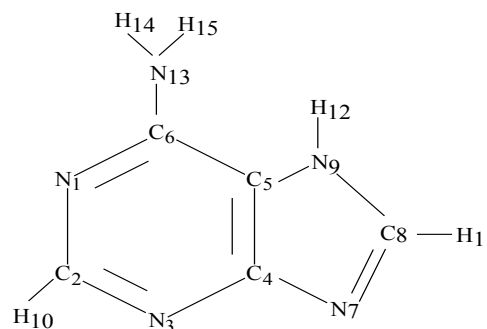


Fig 1. Molecular structure of Adenine

3.2. 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 [1]. The vibrational determinants have been solved using the computer programmes with the SIMPLEX optimization procedure [2]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature [3]. 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.

3.3. Symmetry Coordinates

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 56 standard internal valence coordinates (containing 17 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 [4,5]. Theoretically calculated force fields was transformed to the latter set of vibrational coordinates and used in all subsequent calculations.

Table 1. Definition of internal coordinates of Adenine.

| No (i) | Symbol | Type | Definition |
|-----------------------------|------------|--------------------------|--|
| Stretching | | | |
| 1-2 | r_i | C-C | C4-C5, C5-C6 |
| 3-11 | R_i | C-N | C2-N1, C6-N1, C2-N3, C4-N3, C4-N7, C8-N7, C5-N9, C8-N9, C6-N13 |
| 12-13 | q_i | C-H | C2-H10, C8-H11 |
| 14-16 | Q_i | N-H | N9-H12, N13-H14, N13-H15 |
| In-Plane bending | | | |
| 17 | α_i | C-C-N | C5-C6-N13 |
| 18 | α_i | N-C-N | N1-C6-N13 |
| 19-22 | α_i | N-C-H | N1-C2-H10, N3-C2-H10, N7-C8-H11, N9-C8-H11 |
| 23-24 | α_i | C-N-H | C5-N9-H12, C8-N9-H12 |
| 25-26 | σ_i | C-N-H | C6-N13-H14, C6-N13-H15 |
| 27 | σ_i | H-N-H | H14-N13-H15 |
| 28-33 | β_i | Ring1 | N1-C6-C5, C6-C5-C4, C5-C4-N3, C4-N3-C2, N3-C2-N1, C2-N1-C6 |
| 34-38 | β_i | Ring2 | N9-C8-N7, C8-N7-C4, N7-C4-C5, C4-C5-N9, C5-N9-C8 |
| Out-of-plane bending | | | |
| 39 | ω_i | C-N | N13-N1-C6-C5 |
| 40-41 | π_i | C-H | H11-C8-N7-N9, H10-C2-N1-N3 |
| 42 | ψ_i | N-H | H12-N9-C8-C5 |
| 43-48 | t_i | τ Ring1 | N1-C6-C5-C4, C6-C5-C4-N3, C5-C4-N3-C2, C4-N3-C2-N1, N3-C2-N1-C6, C2-N1-C6-C5 |
| 49-53 | t_i | τ Ring2 | C8-N7-C4-C5, N7-C4-C5-N9, C4-C5-N9-C8, C5-N9-C8-N7, N9-C8-N7-C4 |
| 54 | t_i | τ C-NH ₂ | C6-N13-H14-H15 |
| 55-56 | t_i | Butterfly | N7-C4-C5-C6, N3-C4-C5-N9 |

For numbering of atoms refer Fig. 1.

Table 2. Definition of local symmetry coordinates of Adenine.

| No. (i) | Type | Definition |
|---------|-----------------------|--|
| 1-2 | CC | r_1, r_2 |
| 3-11 | CN | $R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}$ |
| 12-13 | CH | q_{12}, q_{13} |
| 14-16 | NH | Q_{14}, Q_{15}, Q_{16} |
| 17 | bCN | $(\alpha_{17}-\alpha_{18})/\sqrt{2}$ |
| 18-19 | bCH | $(\alpha_{19}-\alpha_{20})/\sqrt{2}, (\alpha_{21}-\alpha_{22})/\sqrt{2}$ |
| 20 | bNH | $(\alpha_{23}-\alpha_{24})/\sqrt{2}$ |
| 21 | NH ₂ rock | $(\sigma_{25}-\sigma_{26})/\sqrt{2}$ |
| 22 | NH ₂ twist | $(\sigma_{25}+\sigma_{26})/\sqrt{2}$ |
| 23 | NH ₂ sciss | $(2\sigma_{27}-\sigma_{25}-\sigma_{26})/\sqrt{2}$ |
| 24 | Rtrigd | $(\beta_{28}-\beta_{29}+\beta_{30}-\beta_{31}+\beta_{32}-\beta_{33})/\sqrt{6}$ |
| 25 | Rsymd | $(-\beta_{28}-\beta_{29}+\beta_{30}-\beta_{31}-\beta_{32}+2\beta_{33})/\sqrt{6}$ |
| 26 | Rasymd | $(\beta_{28}-\beta_{29}+\beta_{30}-\beta_{31})/\sqrt{2}$ |
| 27 | R bend 1 | $\beta_{34}+a(\beta_{35}+\beta_{38})+b(\beta_{36}+\beta_{37})$ |
| 28 | R bend 2 | $(a-b)(\beta_{35}-\beta_{38})+(1-a)(\beta_{36}-\beta_{37})$ |
| 29 | ω CN | ω_{39} |
| 30-31 | π CH | π_{40}, π_{41} |
| 32 | ψ NH | ψ_{42} |
| 33 | t Rtrig | $(\tau_{43}-\tau_{44}+\tau_{45}-\tau_{46}+\tau_{47}-\tau_{48})/\sqrt{6}$ |
| 34 | t Rsym | $(\tau_{43}-\tau_{45}+\tau_{46}-\tau_{48})/\sqrt{2}$ |
| 35 | t Rasy | $(-\tau_{43}+2\tau_{44}-\tau_{45}-\tau_{46}+2\tau_{47}-\tau_{48})/\sqrt{12}$ |
| 36 | R torsion 1 | $\tau_{51}+b(\tau_{49}+\tau_{53})+a(\tau_{50}+\tau_{52})$ |
| 37 | R torsion 2 | $(a-b)(\tau_{52}-\tau_{50})+(1-a)(\tau_{53}-\tau_{49})$ |

| | | |
|----|---------------------|----------------------------------|
| 38 | NH ₂ waf | τ_{54} |
| 39 | Butterfly | $(\tau_{55}-\tau_{56})/\sqrt{2}$ |

$$a = \cos 144^\circ \text{ and } b = \cos 72^\circ$$

3.4. Vibrational Band Assignments

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

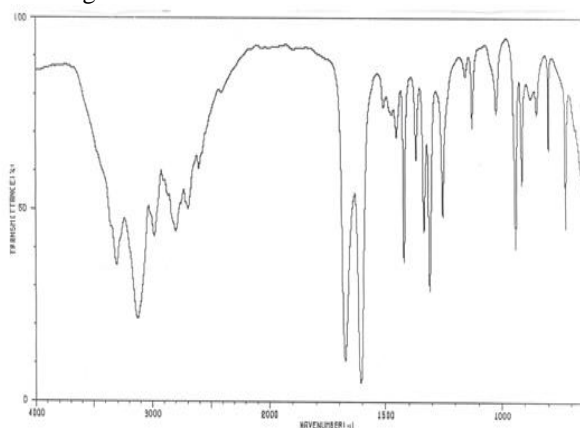


Fig 2. FT-IR spectrum of Adenine.

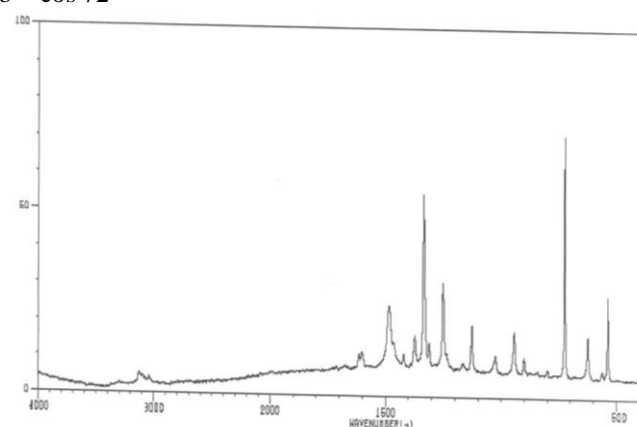


Fig 3. FT-Raman spectrum of Adenine.

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 adenine.

| S. No. | Species | Observed Frequency (cm ⁻¹) | | Calculated Frequency (cm ⁻¹) | Assignment (% PED) |
|--------|---------|--|----------|--|--|
| | | FT-IR | FT-Raman | | |
| 1 | A' | 3303 | - | 3294 | N-H Stretching (95) |
| 2 | A' | 3123 | - | 3115 | N-H Stretching (94) |
| 3 | A' | - | 3093 | 3083 | N-H Stretching (96) |
| 4 | A' | - | 3031 | 3020 | C-H Stretching (99) |
| 5 | A' | 3003 | - | 2995 | C-H Stretching (98) |
| 6 | A' | 1673 | - | 1664 | NH ₂ Sciss (84) |
| 7 | A' | - | 1616 | 1605 | C-C Stretching (70) |
| 8 | A' | 1605 | - | 1594 | C-C Stretching (71) |
| 9 | A' | 1508 | - | 1499 | C-N Stretching (76) |
| 10 | A' | - | 1486 | 1474 | C-N Stretching (75) |
| 11 | A' | 1471 | - | 1462 | C-N Stretching (71) |
| 12 | A' | 1463 | - | 1453 | C-N Stretching (75) |
| 13 | A' | 1451 | - | 1440 | C-N Stretching (71) |
| 14 | A' | - | 1424 | 1412 | C-N Stretching (76) |
| 15 | A' | 1417 | - | 1408 | C-N Stretching (71) |
| 16 | A' | - | 1374 | 1383 | C-N Stretching (75) |
| 17 | A' | 1368 | - | 1376 | C-N Stretching (76) |
| 18 | A' | - | 1252 | 1263 | N-H in-plane bending (73) |
| 19 | A' | 1156 | - | 1168 | Ring deformation in-plane bending (53) |
| 20 | A' | - | 1129 | 1138 | NH ₂ rock (68) |
| 21 | A' | 1122 | - | 1113 | C-H in-plane bending (71) |
| 22 | A' | - | 1029 | 1018 | C-H in-plane bending (72) |
| 23 | A'' | - | 946 | 937 | C-H out-of-plane bending (65) |
| 24 | A'' | 938 | - | 929 | C-H out-of-plane bending (64) |
| 25 | A' | 913 | - | 901 | Ring deformation in-plane bending (51) |
| 26 | A' | - | 902 | 891 | R bend 1 (74) |
| 27 | A'' | 875 | - | 884 | N-H out-of-plane bending (48) |
| 28 | A' | 849 | - | 857 | R bend 2 (85) |
| 29 | A' | 792 | - | 803 | C-N in-plane bending (66) |

| | | | | | |
|-----|-----|-----|-----|-----|--|
| 30 | A' | - | 729 | 741 | Ring deformation in-plane bending (52) |
| 31. | A'' | 720 | - | 730 | C-N out-of-plane bending (59) |
| 32 | A'' | 643 | - | 634 | NH ₂ wag (61) |
| 33 | A'' | - | 628 | 617 | R torsion 1 (86) |
| 34 | A'' | 620 | - | 609 | R torsion 2 (96) |
| 35 | A'' | - | 564 | 555 | Ring deformation out-of-plane bending (59) |
| 36 | A'' | 541 | - | 530 | Ring deformation out-of-plane bending (57) |
| 37 | A'' | - | 533 | 521 | Ring deformation out-of-plane bending (58) |
| 38 | A'' | - | 334 | 324 | NH ₂ twist (69) |
| 39 | A'' | - | 249 | 241 | Butterfly (57) |

3.4.1. N-H Vibrations

In all the heterocyclic compounds, the N-H stretching vibrations [6], Occur in the region 3500-3000cm⁻¹. Hence the FT-IR band observed at 3303 and 3123cm⁻¹ and FT-Raman at 3093cm⁻¹ in adenine have been designated to N-H stretching modes of vibrations.

3.4.2. C-H Vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region 3100-3000cm⁻¹ which is the characteristic region for the ready identification of C-H stretching vibrations [7,8]. In the present investigation, the C-H vibrations have been found at 3031cm⁻¹ in Raman and 3003cm⁻¹ in IR.

3.4.3. C-C vibrations

The bands between 1400 and 1650cm⁻¹ in benzene derivatives are due to C-C stretching vibrations [9]. Therefore, the C-C vibrations of the title compound are observed at 1616cm⁻¹ in Raman and 1605cm⁻¹ in IR.

3.4.4. 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 band observed at 1508, 1471, 1463, 1451, 1417, 1368cm⁻¹ and the FT-Raman at 1486, 1424, 1374cm⁻¹ are assigned to C-N stretching modes of vibration. These assignment is made in accordance with the assignments proposed by Krishnakumar et al. [10].

3.4.5. Amino Group Vibrations

According to socrates [11] the frequencies of the amino group appear around 1700-1600cm⁻¹ for NH₂ scissoring and 1150-900cm⁻¹ for rocking deformations. The band appeared at 1673cm⁻¹ in infrared is assigned unambiguously to the scissoring mode of the NH₂ group. The NH₂ rocking mode has been assigned to 1129cm⁻¹ in Raman for the title compound. The IR and Raman bands for wagging and twisting NH₂ modes of Adenine are identified at 643 and 334cm⁻¹ respectively.

4. Conclusion

Based on the normal coordinate analysis a complete vibrational analysis was performed for Adenine. A systematic set of symmetry 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.

References

1. L.E. Sutton, "The inter atomic bond distance and bond analysis in molecules and ions" (Chemical society, London), 1958.
2. J.A. Nelder and R. Mead, *Comput. J.*, **7**, 308, 1965.
3. V. Suryanarayan, Pavankumar and G. Ramanarao, *Spectrochim. Acta A*, **48**, 1481, 1992.
4. IUPAC commission on molecular structure on spectroscopy, *pure & Appl. Chem*, **50**, 1707, 1978.
5. P. Pulay, G. Fogarasi, F. Prog and J.E. Boggs, *J. Am. Chem. soc.*, **101**, 2550, 1979.
6. V. Krishnakumar and R. Ramasamy, *spectrochim. Acta A*, **69**, 8-17, 2008.
7. H.G. Silver, J.L. Woods, *Trans faraday Soc.*, **60**, 5, 1964.
8. V. Krishnakumar and R. Ramasamy, *Indian J. Pure & App. Phys.*, **41**, 258-261, 2003.
9. R. Ramasamy, *Journal of Applied spectroscopy*, **80**, 506-512, 2013.
10. V. Krishnakumar and R. Ramasamy, *Indian J. Pure & Appl. Phys.*, **40**, 252-255, 2002.
11. G. Socrates, *Infrared and Raman characteristic Group frequencies, Tables and charts*, 3rd Edn., John wiley & sons, chi chester, 2001.