

Density Functional Theory Calculations of The Vibrational Spectra of Deoxy 5'-Monophosphate Nucleotides Using FHI-aims code

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Abstract

We calculated vibrational frequencies, infrared intensities and total free energies of the most stable conformers of the four nucleotides: Deoxyadenosine 5'-monophosphate, deoxycytidine 5'-monophosphate, deoxyguanosine 5' monophosphate and deoxythymidine 5'-monophosphate. The infrared spectra of these nucleotides have been observed from about 3700 to about 50 cm^{-1} and are presented. The spectra were interpreted with the aid of IRPal 2.0 software. The vibrational frequencies calculated were compared favorably with those reported in the literature. Some of the vibrations observed in the ir-spectra are the stretching vibration of C-O group which give rise to strong band in the region 1320-1000 cm^{-1} , bending vibration of P-H group which give rise to weak band in the region 1250-950 cm^{-1} , stretching vibration of C=O group which give rise to strong band in the region 1690-1720 cm^{-1} , out of plane vibration of C-H group which produces medium intensity in the region 865-810 cm^{-1} , in plane bending vibration of the NH_2 group produces strong intensity in the region 1640-1500 cm^{-1} , stretching vibration of O-H group produces variable intensity in the region 3600-3400 cm^{-1} and stretching vibration of C=C group produces weak intensity in the region 1616-1550 cm^{-1} . Total free energy for each nucleotide was also calculated with variation of temperature from 25K to 400K in the interval of 25. We have observed that an increase in temperature leads to a decrease in total free energy. This feature is observed in all the nucleotides. Principal moment of inertia as well as the zero point energy for the five nucleotides were also calculated. The results of the zero point energy were also compared favorably with those reported in the literature. Generalized gradient approximation, [GGA-Perdew-Burke-Ernzerhof (pbe)] exchange-correlation functional of the Density functional theory was employed throughout the work.

1.0 Introduction

Nucleic acids are vital molecules which carry the genetic code and are responsible for its expression by protein synthesis. The nucleic acids, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), may be studied by using infrared spectroscopy [1]. Infrared (IR) spectroscopy is one of the most important techniques available to scientists. One of the great advantages of IR spectroscopy is that any sample in virtually any state may be studied. The infrared region starts immediately after the visible region at 700 nm. The infrared region extends from 2,500 to 50,000 nm. This spectral region encompasses three subdivisions: the far-infrared (FIR: 400–10 cm^{-1} or 26–1,000 μm), mid-infrared (MIR: 4,000–400 cm^{-1} or 2.6–26 μm), and near-infrared (NIR: 13,000–4,000 cm^{-1} or 0.76–2.6 μm), named in relation to the visible region. Infrared spectroscopists often use wavenumbers to describe the infrared spectral region. The mid-IR is the most commonly used region for analysis as all molecules possess characteristic absorbance frequencies and primary molecular vibrations in this range. Mid-infrared spectroscopy methods are based on studying the interaction of infrared radiation with samples. As IR radiation is passed through a sample, specific wavelengths are absorbed causing the chemical bonds in the material to undergo vibrations such as stretching, contracting, and bending. Functional groups present in a molecule tend to absorb IR radiation in the same wavenumber range regardless of other structures in the molecule, and spectral peaks are derived from the absorption of bond vibrational energy changes in the IR region [2].

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Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule .

Spectrum interpretation is simplified by the fact that the bands that appear can usually be assigned to particular parts of a molecule, producing what are known as group frequencies[3]. Infrared radiation is that part of the electromagnetic spectrum between the visible and microwave regions. Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration, either stretching or bending. Different types of bonds, and thus different functional groups, absorb infrared radiation of different wavelengths. An IR spectrum is a plot of wavenumber (X-axis) versus intensity (Y-axis)[4].

Principle features of experimental RNA and DNA spectra have been described in numerous studies previously and we recapitulate them only briefly. The C=O stretching region of the bases (1600-1700 cm⁻¹) gives rise to a strong absorption, while relatively minor distinct features can be found in the mid-IR region of 1150-1500 cm⁻¹, additionally perturbed by D₂O absorption (around 1220 cm⁻¹). Another strong absorption given by vibrations of the polar sugar and phosphate residues appears approximately at 900-1150 cm⁻¹[5]. Vibrational IR spectra in the region 750-1200cm⁻¹ of various DNA bases: cytosine; thymine; adenine; and guanine along with 2' deoxyadenosine 5'-monophosphate (dAMP); 2' deoxyguanosine 5'-monophosphate (dGMP); 2' deoxycytidine 5'-monophosphate (dCMP); 2' deoxythymidine 5'-monophosphate (dTMP) using HF/6-31G (d) and B3LYP approximation have been studied and reported in [6]. The vibrational IR and Raman spectra of nucleic acids and the general assignment of resonances have been known and have been used to structurally characterize single-stranded, double-stranded DNA and various RNA structural elements[7,8]

Vibrational spectroscopy is an alternative structural approach for the study of nucleic acids and their complexes, particularly for investigating the aqueous solution structures and the interactions of large oligonucleotides, native nucleic acids and their biological assemblies, like chromosomes and viruses. The high information content of vibrational spectra is reflected in the many new insights that have been obtained into the conformation, composition, interaction and functioning of DNA molecules. Because the IR spectrum of each molecule is unique, it can serve as a signature or *fingerpr*int to identify the molecule. Areas in which IR spectroscopy is used extensively include pharmaceutical analysis, quality control in industrial processes, environmental chemistry, geology and astronomy[9].

It is the purpose of this work to study the vibrational spectra, vibrational frequencies, infrared intensities, total free energy and principal moment of inertia of the following nucleotides: Deoxyadenosine '5 -monophosphate, deoxycytidine 5' -monophosphate, deoxyguanosine 5' monophosphate and deoxythymidine 5' -monophosp by theoretical means. FHI-aims (“Fritz Haber Institute *ab initio* molecular simulations”) code was used throughout the work.

THEORETICAL BACKGROUND

Density Functional Theory (DFT)

Density Functional Theory (DFT) is a computational tool that derives properties of molecules base on a determination of their electron density[10]. DFT methods have become the most widely-spread *ab-initio* methods in Computational Material Science (CMS) and Solid state Physics, due to their high computational efficiency and very good accuracy for the structure of molecules, crystals, surfaces and their interactions[11]. In DFT methods, the energy of the molecule is a functional of the electron density [12,13]. The basis of DFT is given by two theorems formulated by Hohenberg and Kohn[14] .

In terms of Quantum Mechanics, a system comprising N electrons and M nuclei is described by a Hamiltonian H as[15] .

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N \sum_{I=1}^M \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} - \frac{1}{2} \sum_{I=1}^M \nabla_I^2 + \sum_{I<J}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad , \quad (1)$$

where

Z denotes the nuclear charge,

$\mathbf{r}_i - \mathbf{r}_j$ is the distance between electron number i and electron number j ,

$\mathbf{r}_i - \mathbf{R}_I$ is the distance between electron number i and nucleus number I ,

$\mathbf{R}_I - \mathbf{R}_J$ is the distance between nucleus number I and nucleus number J ,

∇_i is the kinetic energy term of the electrons, and

∇_I is the kinetic energy term of the nucleus

Solving exactly a Schrodinger equation with such many-body Hamiltonian is only possible in principle. For any practical system, one has to resort to approximations. First of all, by the Born-Openheimer (or adiabatic) approximation one drops the last two terms in the Hamiltonian above and treats the nuclei separately. The grounds for this treatment are that the nuclei are much heavier; hence move much slower than the electrons. In this approximation, the kinetic energy of the nuclei is neglected and the interaction between the nuclei is handled classically. Thus, the original problem in Eq (1) is reduced to one regarding a system of interacting electrons moving in an external potential $V(\mathbf{r})$, formed by a frozen-in ionic configuration. For such an inhomogeneous system of interacting electrons, Hohenberg and Kohn[16] proved two theorems with regard to the electron density function $\rho(\mathbf{r})$:

Theorem(i). If the number of electrons in the system is conserved, the external potential $V(\mathbf{r})$ uniquely determines the electronic ground state density $\rho_0(\mathbf{r}_0)$.

Theorem(ii). There exists a universal energy functional of $\rho, E[\rho]$, which is minimized by the ground state density ρ_0 . These two theorems form the basis of DFT.

Kohn and Sham[17] carried this theory further and obtained a single-particle Schrodinger-like equation,

$$\left\{ -\frac{1}{2}\nabla^2 + \int \frac{\rho(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} + V(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2)$$

This is usually referred to as the Kohn-Sham equation. The KS equation maps a many-electron interacting system onto a single electron system within an effective potential formed by the nuclei and other electrons. The first term in the KS Hamiltonian accounts for the kinetic energy and the following three terms are the Coulomb (or Hartree), the exchange-correlation(xc) and the external potentials respectively. Comparing with the many-body Hamiltonian in Eq (1), solving the KS equation is much easier for a practical system.

Due to the fact that the potential and the charge density depend on each other, the KS equation has to be solved self-consistently. Starting from an assumed density $\rho(\mathbf{r})$, one first calculates the Coulomb and xc potentials, then solves Eq (2) for the KS orbitals $\psi_i(\mathbf{r})$. With these orbitals, a new density can be constructed by

$$\rho(r) = \sum |\psi_i(\mathbf{r})|^2, \quad (3)$$

where the index i goes over all occupied orbitals. The procedure is repeated until self-consistency i.e consistency between the output and input densities is achieved.

The five exchange functionals in DFT as given by J. Perdew in 2000 are as follows [11]

- First, the Local Density Approximation (LDA) which describes only the local density
- Second, the Generalized Gradient Approximation (GGA) in which further the dependence on the gradients of the density is added.
- Third, the Meta-GGA which include the dependence on the kinetic energy density
- Fourth, the Hybrid functional, in which is added further the dependence on the occupied orbitals, exact exchange.
- Fifth, the fully non-local functional, in which the dependence on the unoccupied orbitals is further added.

The simplest and most widely used DFT approximation for the exchange correlation energy, $E_{xc}[n(r)]$, is the so-called LDA given by

$$E_{xc}^{LDA} \equiv \int e_{xc}(n(r))n(r)dr, \quad (4)$$

where $e_{xc}(n)$ is the exchange-correlation energy of a uniform electron gas of density n . The exchange part is given in atomic units, by

$$e_x(n) \equiv -\frac{0.458}{r_s}, \quad (5)$$

where r_s is the radius of a sphere containing one electron and is given by $(\frac{4\pi}{3})r_s^3 = n^{-1}$. The correlation part was first estimated by E.P.Wigner [18] as

$$e_c(n) = -\frac{0.44}{r_s+7.8}. \quad (6)$$

and

$$V_{xc} = \frac{\delta e_{xc}(n)}{\delta n}$$

The next level of approximations beyond the LDA is a number of non-local approximations, with a spatial variation of density, and they usually termed as GGAs

$$E_{xc}^{GGA} = \int f(n(\mathbf{r}), |\nabla n(\mathbf{r})|)d\mathbf{r}, \quad (7)$$

in which $f(n, |\nabla n|)$ is a suitably chosen function of two variables.

By imposing the conditions for the correct exchange hole on the approximate hole given by the gradient expansion, Perdew [19] proposed a model which leaves only a 1% error in exchange energy. This model has also been further simplified to

$$E_x^{GGA}[n] = -C_1 \int dr n^{4/3} F(S), \quad \text{where} \quad (8)$$

$$S = \frac{|\nabla(r)|}{2K_F n}, \quad (9)$$

$$K_F = C_2 n^{1/3}, \quad (10)$$

$$F(S) = (1 + 1.29S^2 + 14S^4 + 0.2S^6)^{1/15}, \quad (11)$$

where C_1 and C_2 are constants.

Vibrational Frequency

A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. The frequency of the periodic motion is known as a vibration frequency[20]. The vibrational frequencies are calculated with the following equations [21].

$$V_{ij} = \frac{1}{\sqrt{m_i m_j}} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right) \tag{12}$$

where

V_{ij} is the Hessian matrix, m_i refers to the mass of atom i , and ∂_{q_i} refers to a displacement of atom i in the x-, y-, or z-direction,

$$VU = \lambda U \tag{13}$$

where U is a matrix of eigenvectors and λ is a vector of eigenvalues, and

$$\lambda_k = (2\pi\nu_k)^2 \tag{14}$$

where λ_k is the k^{th} eigenvalue and ν_k is the k^{th} vibrational frequency.

The infrared intensities is defined by the equation [21]

$$\frac{\partial E_{SCF}}{\partial f \partial a} = 2 \sum_i^{d.o} h_{ij}^{fa} + 4 \sum_i^{d.o} \sum_j^{all} U_{ji}^a h_{ij}^f, \tag{15}$$

where

$$h_{ij}^{fa} = \sum_{\mu\nu}^{AO} C_{\mu}^{i0} C_{\nu}^{j0} \left(\frac{\partial^2 h_{\mu\nu}}{\partial f \partial a} \right) \tag{16}$$

E_{SCF} is the self-consistent field energy, f is the electric field, a is a nuclear coordinate, $h_{\mu\nu}$ is the one electron atomic orbital integral, U^a is related to the derivative of the molecular orbital coefficients with respect to a by

$$\frac{\partial C_{\mu}^i}{\partial a} = \sum_m^{all} U_{mi}^a C_{\mu}^{m0} \tag{17}$$

The term ‘‘all’’ in the above summations refers to all occupied and virtual molecular orbitals and .d.o.. refers to doubly occupied orbitals such as those found in the ground state of a closed-shell system. Terms such as C_{μ}^{i0} refers to the coefficients of the atomic orbital m in the i th unperturbed molecular orbital.

Total Free Energy

At zero temperature, the most stable structure is the conformer with the lowest energy E_0 . Increasing the temperature of the system, entropic effects start to play a role and the free energy F determines the stability of the system according to [22]

$$F = E_0 - k_B T \ln Z, \tag{18}$$

where Z is the partition function of the system defined as

$$Z = \sum_i e^{-\frac{E_i}{k_B T}}, \tag{19}$$

with i being the index running over all possible states of the system and E_i the corresponding energy of the system. For an atomic cluster system, assuming that rotations and vibrations can be decoupled, the partition function separates into

$$Z = Z_{trans} Z_{vib} Z_{rot}, \tag{20}$$

where Z_{trans} , Z_{vib} and Z_{rot} are the partition functions due to the translational, vibrational and rotational degrees of freedom. The free energy then adopts the form

$$F = E + F_{trans} + F_{vib} + F_{rot} . \quad (21)$$

The partition function Z_{trans} can be calculated in a straightforward manner and has the form

$$Z_{trans} = V \left(\frac{Mk_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}}, \quad (22)$$

V is the volume of the box in which the cluster is placed. Since the only system dependent parameter is the total mass M of the system, the translational degrees of freedom do not influence the energetic ordering of different isomers of the same system and can thus be neglected when addressing the energetic stability of free molecules.

The vibrational contribution to the free energy can be approximated using the vibrational frequencies obtained by the harmonic approximation. Using normal modes, the molecule i.e the system under consideration can be considered as being composed of $(3N-6)$ independent one-dimensional harmonic oscillators with the energies $E_{n,i} = \left(n + \frac{1}{2}\right)\hbar\omega_i$ where n is the principal quantum number of the vibrational state.

Thus the resulting vibrational contribution to the free energy is given by[22]

$$F_{vib} = E_{ZPE} + k_B T \sum_{i=1}^{3N-6} \ln \left(1 - e^{-\frac{\hbar\omega_i}{k_B T}} \right), \quad (23)$$

The first term corresponds to the zero-point energy since it contributes to the free energy already at zero temperature. It originates from the zero-point vibration of the molecules.

A good approximation to the rotational partition function based upon classical mechanics is[22]

$$Z_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{2k_B T}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{I_1 I_2 I_3}, \quad (24)$$

where I_1, I_2, I_3 are the principle moments of inertia, e.g the eigenvalues of the moment of inertia tensor. σ is the order of the rotational subgroup of the system, so the number of pure rotational symmetry operations.

METHODOLOGY

FHI-aims Code

FHI-aims (Fritz Haber Institute *ab initio* molecular simulations) is an efficient computer program package that is used to calculate physical and chemical properties of condensed matter and materials (such as molecules, clusters, solids, liquids) based on a first-principles description of the electronic structure based only on quantum-mechanical first principles. The primary production method is density functional theory (DFT). The package is also a flexible framework for advanced approaches to calculate ground-and excited-state properties, current developments including hybrid functionals, MP2, GW and QM/MM technique. FHI-aims uses numeric atom-centered orbitals as the quantum-mechanical basis set. This enables accurate all-electron/ full-potential calculations at a computational cost which is competitive with, for instance, plane wave methods, without invoking a priori approximations to the potential (such as pseudopotentials, frozen cores) [23]. The basic physical algorithms in FHI-aims concerning ground state DFT and applications are described in [24].

FHI-aims requires exactly two input files, located in the same directory where a calculation is started : control.in and geometry.in. The geometry.in contains only information directly related to the atomic structure for a given calculation. This obviously includes atomic positions, with a description of the particulars of each element (or *species*) expected in control.in. The species used in this case are H,O,C,N and P. The control.in contains all necessary computational information regarding the desired run. Typically, this file consists of a general part, where, again, the particular order of lines is unimportant. In addition, this file contains species subtags that are references by geometry.in. Within the description of a given species, the order of lines is again unimportant, but all information concerning the same species must follow the initial species tag in one block.

IRPal v.2.0

The program IRPal is a powerful tool for the interpretation of IR-spectra of organic compounds. It not only gives the user one or more functional groups that feature absorption band(s) for a selected wavenumber, but relates that information to the possible existence of other bands in the spectrum that could confirm these assignments [25].

Optimization of some Key Parameters

The molecular geometry of the four nucleotides with lowest conformational energy were obtained using Conflex ver.7.A.0910 software and such structures can be found in [26]. Open babel 2.2.1 software was used to convert the geometries of the molecules from conflex acceptable format to FHI-aims acceptable format. The parameters : `sc_accuracy_rho` , `sc_accuracy_eev`, `sc_accuracy_etot`, `sc_accuracy_forces` , `n_max_pulay` , `charge_mix_param`, `occupation_type`, `final_forces_cleaned` and `relax_geometry` were first optimized to find the best set of values as shown in Table 1. Tier 1 basis set i.e the so called light species_ default was used throughout in order to ensure fast convergence of results.

Relaxation

The control.in was set up using the optimized parametrs while the geometry.in contained the molecular structure of a particular nucleotide. GGA(pbe) exchange functional was used and tier 1 basis set of light species_ default was also used to ensure fast convergence of results. The key word used for the relaxation was " `relax_geometry bfgs`". At the directory where the two input files were located, the command "`../..../bin/aims.081912.serial.x < /dev/null | tee run_relaxation.out`" was used to run the calculations. After each relaxation step, the convergence of the present geometry was checked by monitoring the maximum remaining force component on any atom in the structure and the updated geometry to be treated next appeared and that continued until the final (converged) geometry was found near the end in a format suitable for a follow-up run. This process was carried out for each of the nucleotide and in each case the calculation converged with a prompt "present geometry is converged. Have a nice day".

Vibration

The final atomic structures obtained from the converged results of relaxation calculations were used as initial geometry.in for the vibrational calculations. The control.in used for the vibration was the same as that used for the relaxation except that for the vibration, we used tier 2 basis set of tight species_defaults for the elements O,H,C,N and P. The tight settings prescribed denser integration grids than light settings and this lead to more accurate forces. The vibration was performed by computing the Hessian matrix and the force constants for all normal modes of each nucleotide. At the command line in the directory where the two input files were set for vibration calculations, the script "`../..../bin/aims.vibrations.081912.pl`" was used to run the calculations.

The Density Functional Theory (DFT) calculations were performed using FHI-aims code for the optimization, relaxation and vibrational analysis of the nucleotides. All results converged and produced the required data. We used IRPal v2.0 to interpret the spectra of the nucleotides. All graphs were plotted using Origin 50.

Characteristics Infrared bands

After all graphs were plotted, a particular vibrational frequency was chosen from the spectrum of a nucleotide using the data reader of origin 50 and the number was entered in the spin-edit input field of IRPal menu. The search database button was clicked and the output was displayed showing the assignment band, nature of the intensity and other information. This was repeated using different values of the vibrational frequencies of the spectra for other nucleotides.

RESULTS AND DISCUSSIONS
OPTIMIZED PARAMETERS

Table 1 shows the values of the optimized parameters. Each value was obtained after several trials of different values until the best ones suitable for the calculations were achieved.

Table 1. Optimized Parameters

PARAMETER	OPTIMIZED VALUE
<code>sc_accuracy_rho</code>	1E-6
<code>sc_accuracy_eev</code>	1E-6
<code>sc_accuracy_etot</code>	1E-6
<code>sc_accuracy_forces</code>	1E-3
<code>n_max_pulay</code>	10
<code>charge_mix_param</code>	0.3
<code>occupation_type</code>	gaussian 0.1
<code>final_forces_cleaned</code>	false.
<code>relax_geometry</code>	bfgs 1.e-2

4.2 Results of Relaxation Runs

From table 2 , it is clearly seen that 5'-dGMP is the most stable molecule because it has the lowest energy of - 0.417086638607448E+05 eV when compared with the other nucleotides. However, 5'-dGMP took more CPU time, more number of self consistency cycles and more relaxation steps to converge.

Table 2:Relaxation Runs

Nucleotide	No. of self consistency cycle	Relaxation step	Total Energy(eV)	CPU time (s)
5'-dAMP	603	36	- 0.396597579873105E+05	10629.092
5'-dCMP	1153	71	-0.376906795475705E+05	15234.976
5'-dGMP	1283	81	- 0.417086638607448E+05	20683.005
5'-dTMP	1082	66	- 0.393022497421742E+05	19061.563

Infrared Spectra

The vibrations results contain basic information regarding vibrational frequencies, free energies,zero point energy,principal moment of inertia and infrared (IR) intensities. IR spectra of the nucleotides were plotted and the results are shown in Figures 1-4. These spectra were interpreted using **IRPal v.2.0** software. In Figure 1, the IR spectrum of d'AMP in the region 50 to 3692 cm⁻¹ is displayed. A strong peak was observed at 3054cm⁻¹. In Figure 2, the IR spectrum of d'CMP in the region 45 to 3677 cm⁻¹ was recorded. The most intense peak was observed at 1691cm⁻¹. Similarly, in Figure 3, the IR spectrum for d'GMP in the region 60 to 3694cm⁻¹ was recorded and the most intense peak was observed at 2677cm⁻¹. In Figure 4, the IR spectrum for d'TMP in the region 30 to 3740cm⁻¹ was recorded and the most intense peak was observed at 1702cm⁻¹. Different modes of vibrations were observed. Some of the vibrations observed in the ir-spectra are the stretching vibration of C-O group which give rise to strong band in the region 1320-1000cm⁻¹, bending vibration of P-H group which give rise to weak band in the region 1250-950cm⁻¹, stretching vibration of C=O group which give rise to strong band in the region 1690-1720cm⁻¹, out of plane vibration of C-H group which produces medium intensity in the region 865-810cm⁻¹, in plane bending vibration of the NH₂ group produces strong intensity in the region 1640-1500cm⁻¹, stretching vibration of O-H group produces variable intensity in the region 3600-3400cm⁻¹ and stretching vibration of C=C group produces weak intensity in the region 1616-1550cm⁻¹. Table 3 shows some of the characteristics infrared bands of the nucleotides obtained using the **IRPal v.2.0** software. Some band assignments and nature of the intensities of the highest peaks and some other peaks were obtained.

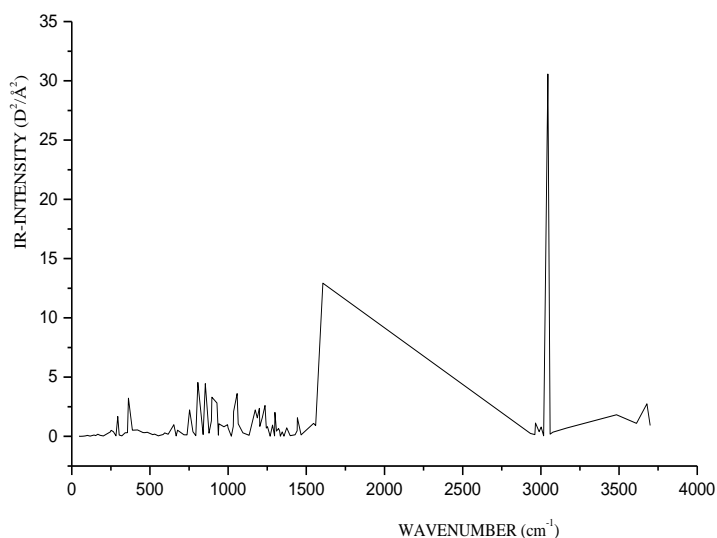


Figure 1. IR-Spectrum of Deoxyadenosine 5'-Monophosphate

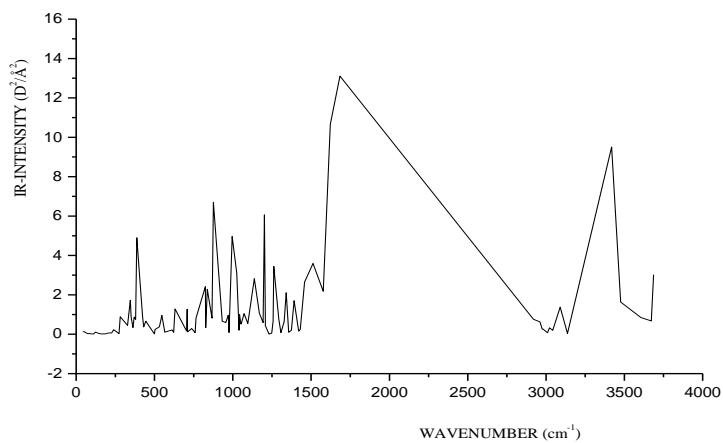


Figure 2. IR-Spectrum of Deoxycytidine 5'-Monophosphate

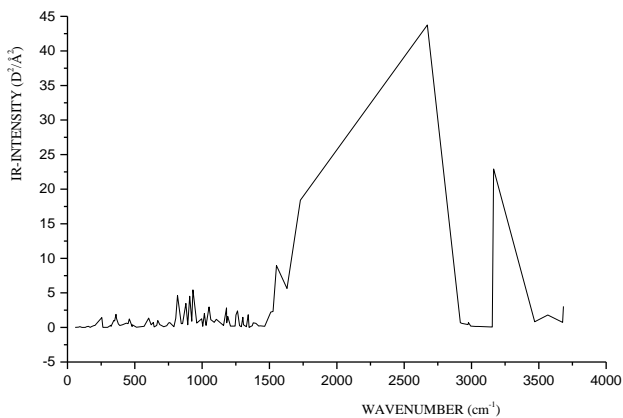


Figure 3. IR-Spectrum of Deoxyguanosine 5'-Monophosphate

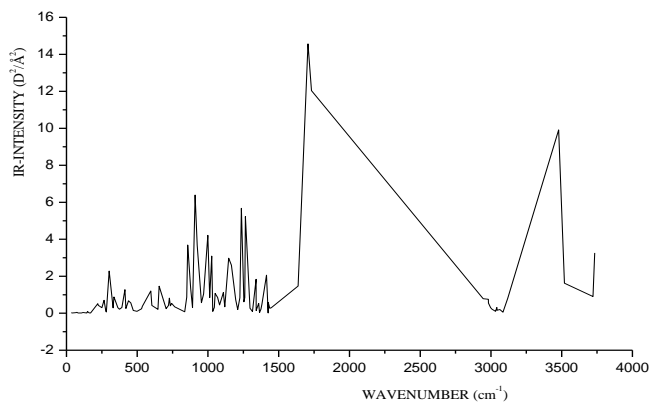


Figure 4. IR-Spectrum of Deoxythymidine 5'-Monophosphate

Table 3: Characteristics Infrared bands of the Nucleotides

Nucleotides	Region [Wavenumber (cm ⁻¹)] * Highest peak	Some approximate band assignment (nature of vibration)	Intensity (strong,medium,weak)
5'-dAMP	*3054 (3140-3040) (3100-3000) (3400-2800) 1611 (1616-1606) (1640-1600) (1640-1500) 1060 (1230-1030) (1250-950) (1320-1000)	=C-H stretch Ar-H stretch Dimer OH C=C stretch NH out of plane NH ₂ in plane bend C-N stretch P-H bending C-O stretch	m s s m s s m w s
5'-dCMP	*1690 (1690-1680) 3087 (3140-3040) (3100-3000) 830 (840-790) (840-820)	C=O stretch =C-H stretch Ar-stretch =CH out of plane C-H out of plane	s m s s m
5'-dGMP	*2679 (2700-2550) 1563 (1571-1561) (1610-1550) (1640-1560) 3170 (3400-2800) 823 (865-810)	(O=)PO-H phosphonic acid C=C stretch C-O stretch Dimer OH C-H out of plane	s w m s s m
5'-dTMP	*1712 (1720-1710) 3489 (3600-3400) 1236 (1260-1220) (1250-950) (1260-1230)	C=O stretch O-H stretch C-O stretch P-H bending P=O phosphonate	s v s w s

Total Free Energy

Total free energy was observed at the temperature ranging from 25K to 400K in steps of 25. The relations between the total free energy and temperature for all the nucleotides using both pw-lda and pbe exchange correlations are shown in Figures 5-8. All the graphs have a common feature that the total free energy increases with decrease in temperature.

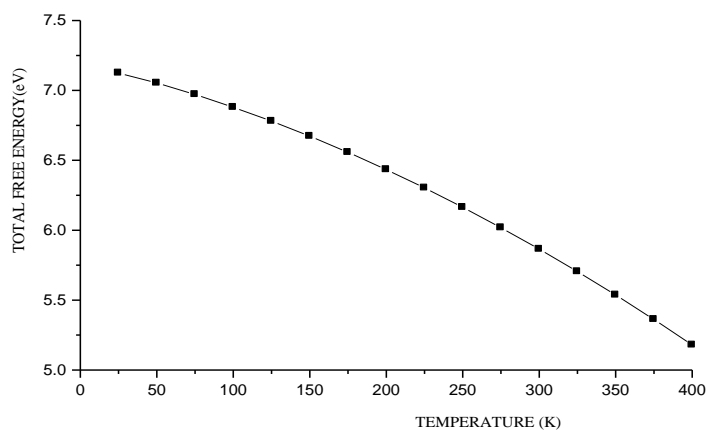


Figure 5. A Graph of Total free Energy Versus Temperature for Deoxyadenosine 5'-Monophosphate

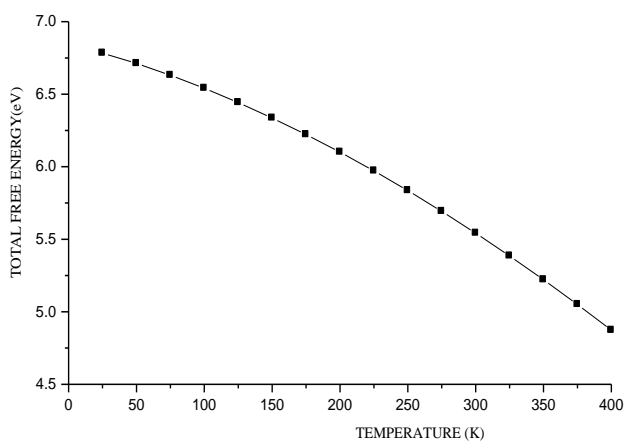


Figure 6. A Graph of Total free Energy Versus Temperature for Deoxycytidine 5'-Monophosphate

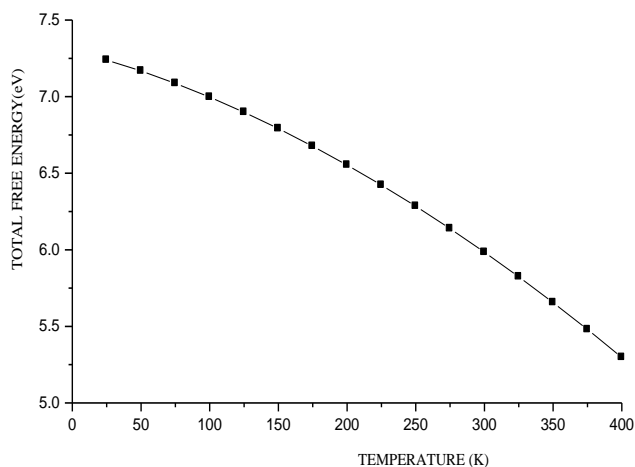


Figure 7. A Graph of Total free Energy Versus Temperature for Deoxyguanosine 5'-Monophosphate

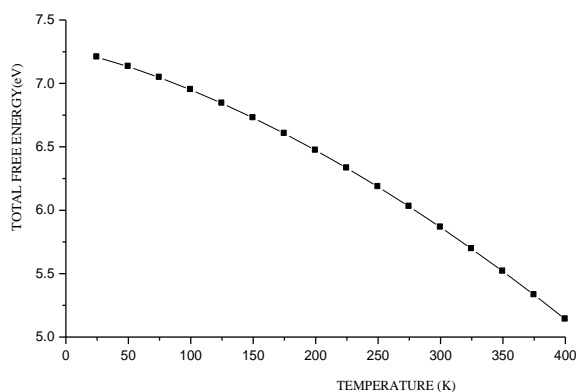


Figure 8. A Graph of Total free Energy Versus Temperature for Deoxythymidine 5'-Monophosphate

Vibrational Frequencies

Tables 4-7 show the results of the calculated vibrational frequencies of the nucleotides for both pw-lda and pbe . The results obtained were compared well with those of reference [27].

Table 4: Calculated vibrational frequencies (cm⁻¹) of 5'-dAMP

mode	This work	Ref. [27]	mode	This work	Ref. [27]
1	3698.68	3708.8	21	1035.23	1084.36
2	3166.31	3050.28	22	1033.17	1078.89
3	3044.69	2895.25	23	1000.18	1020.6
4	2988.92	2859.26	24	996.29	1001.03
5	2965.59	2850.94	25	972.72	993.8
6	2961.86	2849.74	26	937.81	964.67
7	1422.65	1421.3	27	928.24	951.2
8	1299.17	1357.14	28	853.80	856.35
9	1283.58	1309.4	29	840.42	852.18
10	1268.28	1254.31	30	806.15	826.6
11	1243.64	1226.66	31	717.39	696.53
12	1235.86	1205.23	32	676.20	652.88
13	1218.63	1204.88	33	616.44	601.45
14	1202.47	1204.46	34	594.55	590.34
15	1199.13	1196.09	35	584.10	559.34
16	1186.33	1177.74	36	372.82	336.49
17	1134.16	1140.39	37	85.70	95.25
18	1094.37	1122.61	38	71.55	61.52
19	1064.35	1120.79	39	55.23	59.56
20	1057.33	1104.08	40	45.77	49.09

Table 5 : Calculated vibrational frequencies (cm^{-1}) of 5'-dCMP

mode	This work	Ref. [27]
1	3022.044	2850.76
2	3009.34	2848.61
3	1684.32	1638.23
4	1622.703	1608.69
5	1576.921	1562.99
6	1512.263	1557.11
7	1457.888	1547.21
8	1430.447	1527.73
9	1420.897	1416.75
10	1391.483	1381.13
11	1373.817	1360.27
12	1357.205	1342.81
13	1340.575	1305.37
14	1327.66	1257.31
15	1307.268	1247.11
16	1292.997	1220.63
17	1261.837	1218.05
18	1257.392	1212.4
19	1248.739	1207.55
20	1230.974	1179.03

mode	This work	Ref. [27]
21	1207.73	1177.01
22	1201.444	1123.89
23	1193.294	1116.24
24	1095.764	1059.2
25	1072.365	1034.71
26	345.1833	341
27	328.1559	320.2
28	273.1423	269.86
29	239.5582	243.75
30	226.5197	227.16
31	204.5121	210.08
32	189.6654	181.94
33	161.9408	171.36
34	144.1857	129.63
35	123.0799	111.31
36	110.6408	100.07
37	92.07286	98.36
38	83.79469	82.4
39	75.38673	68.94
40	49.30222	56.79

Table 6 : Calculated vibrational frequencies (cm^{-1}) of 5'-dGMP

Mode	This work	Ref. [27]
1	3683.056	3705.98
2	3164.426	3056.08
3	2994.466	2896.87
4	2928.004	2858.36
5	2917.127	2850.92
6	1017.005	1114.07
7	879.1751	950.67
8	844.433	893.17
9	817.2975	874.15
10	804.1059	844.15
11	789.8577	827.98
12	759.743	818.36
13	736.8269	728.33
14	714.6982	721.23
15	684.5945	703.04
16	670.4689	702.32
17	662.7489	682.4
18	643.4267	655.73
19	637.6719	641.98
20	620.9497	611.75

Mode	This work	Ref. [27]
21	603.0356	580.96
22	568.8046	568.83
23	512.566	553.78
24	481.4125	477.45
25	480.1469	465.34
26	459.4744	460.42
27	436.6485	420.17
28	407.7645	407.36
29	388.8625	399.03
30	377.5436	395.69
31	364.6958	388.05
32	350.4559	358.1
33	343.7974	350.29
34	323.5478	320.07
35	203.7729	200.02
36	198.2778	180.44
37	92.20446	102.58
38	82.06892	97.35
39	60.77074	61.18
40	57.12797	50

Table 7: Calculated vibrational frequencies (cm⁻¹) of 5'-dTMP

Mode	This work	Ref. [27]	Mode	This work	Ref. [27]
1	3733.759	3703.85	21	603.4892	585.87
2	3062.864	2924.45	22	596.192	566.12
3	3032.184	2892.17	23	536.6611	521.32
4	3006.883	2863.06	24	472.0423	472.46
5	2981.718	2850.82	25	454.3706	468.68
6	1210.26	1264.55	26	438.8008	446.04
7	1026.909	1088.83	27	419.7629	439.52
8	953.3601	989	28	412.7625	428.17
9	909.2697	951.11	29	391.6735	400.73
10	877.9687	901.45	30	374.3642	396.26
11	856.6032	883.18	31	363.3179	394.54
12	849.9243	848.98	32	329.457	368.05
13	835.8049	831.71	33	301.7802	327.8
14	764.7489	821.55	34	265.9833	248.23
15	743.4429	747.21	35	250.4181	226.79
16	727.4579	707.65	36	170.6517	175.77
17	721.2459	706.43	37	160.6132	160.67
18	703.8722	697.39	38	82.53162	80.31
19	655.0544	686.22	39	73.75671	68.94
20	646.4973	620.76	40	68.96502	55.27

4.3 Principal Moment of Inertia and Zero point point Energy for the Five Nucleotide

Table 8 shows the results for the principal moment of inertia for all the nucleotides while Table 9 shows the results of zero point energy.

Table 8. Principal Moment of Inertia for the Four Nucleotides

Nucleotide	Principle Moment of Inertia (kg m ²)	Product of Principle Moment of Inertia (kg ³ m ⁶)
5'-dAMP	0.23934611E-0043; 0.35415681E-0043; 0.50448240E-0043	0.42762984E-0130
5'-dCMP	0.20594265E-0043; 0.34682548E-0043 0.50277898E-0043	0.35911572E-0130
5'-dGMP	0.25094125E-0043; 0.39715529E-0043 0.58254110E-0043	0.58057585E-0130
5'-dTMP	0.23542600E-0043; 0.36007102E-0043 0.52265668E-0043	0.44305648E-0130

Table 9 : Zero point energy, E_{ZPE} (eV)

Nucleotide	This work	Ref. [27]
5'-dAMP	7.18166535	7.34377405
5'-dCMP	6.81893068	7.05930309
5'-dGMP	7.28501111	7.66683940
5'-dTMP	7.26390674	7.47126561

Conclusion

Results obtained for relaxation runs show that 5'-dGMP is the most stable molecule because it has the lowest energy of -0.417086638607448E+05 eV when compared with the other nucleotides. However, 5'-dGMP took more CPU time, more number of self consistency cycles and more relaxation steps to converge. The atoms (H,O,N,C and P) which formed the nucleotides under study appeared at the ir-spectra at different bonding and vibrations and were interpreted using IRPal 2.0. The vibrational frequencies calculated for this work were compared with a previously reported work [27]. Similarly, the zero point energy calculated for this work agreed with a previously reported work [27]. In all the nucleotides, the total free energy was found to depend on temperature showing an increase in temperature leads to a decrease in total free energy.

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