REPUBLIC OF TURKEY
FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THERMOCHEMICAL AND SPECTROSCOPIC PROPERTIES OF MOLECULES IN ASTROPHYSICAL INTEREST

Henar Sleman HASSAN
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Master Thesis

Department: Physics
Program: Atomic And Moleculer Physics
Supervisor: Prof. Dr. Niyazi BULUT

JANUARY -2017

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Summary

The properties of atom and molecules be obtained from atom-molecule or molecule-molecule collisions or from spectroscopic and thermodynamic analysis of ro-vibrational and translational motion of components of molecule. There have been many spectroscopic analysis of Astrophysical molecules that observed every recently in parallel to the development of technology of Orion, Herschel telescopes etc . With these telescopes very recently many molecules from diatom to poly-atomic molecules was observed and investigated as a spectroscopic analysis. The outputs form all these spectroscopic analysis are consist of many quantum effects like tunneling and zero point energies which are not possible to calculate by using the classical physics. That is why, it is important to implement quantum mechanical methods to atom-molecule or molecule-molecule interaction to calculate quantum mechanical quantities. Depending of the size of molecule (number of molecule) it is important to implement accurate or approximate quantum methods to the system like Hartree fock (HF), Density Function Theory (DFT) or Configuration Interaction (CI) and so on.

Some of molecules which are important in Astrophysics interest, would be studied in this theses are C_2H_5, C_2H_6, NO_3, CH_3OCH_2OO. Depending on the molecule quantum mechanical HF, DFT , CI, etc. theories will be implemented and thermodynamic quantities from contribution of transition, electronic motion, and ro-vibration motion have been calculated.

Keywords: Spectroscopic, Thermodynamic, Astrophysical, Poly-atomic, Hartree fock (HF), Density Function Theory (DFT), Configuration Interaction (CI)

ÖZET

ASTROFİZİK ALANDAKİ MOLEKÜLLERİN TERMOKİMYASAL VE SPEKTROSKOPİK ÖZELLİKLERİ

Atom moleküllerin özellikleri, atom-molekül ve molekül-molekül çarpışmalarından elde edilir. Ayrıca moleküllerin öteleme hareketleri ve titreşim dönme hareketlerinin termo dinamiksel ve spektroskopik olarak incelenmesi de moleküllerin özelliklerini verir. Oriaon ve Herschel teleskopları ile çoksayıdaki astro fiziksel öneme sahip molekülün spektroskopik özellikleri incelenmiştir. Bu teleskoplar ile son zamanlarda iki atomlu moleküllerden çok atomlu moleküllere kadar bazı gözlemler yapılmıştır. Bu spektroskopik analizlerden çıkan sıfır nokta enerjisi ve tüneleme olayları gibi kuantum mekaniksel olaylar klasik olarak incelenememektedir. Bundan dolayı atom molekül etkileşmelerinde kuantum meknaiksel metotların uygulanması önem kazanmıştır. Moleküldeki atom sayılarının fazlalığına bağlı olarak gerçek yada yaklaşık metotların, Hartree Fock (HF) ve Density Function Theory (DFT) yada configürasyon etkileşmesi (CI) kullanılması dikkate alınır.

Bu tez çalışmasında astro fizikte önemli olan C_2H_5, C_2H_6, NO_3, CH_3OCH_2OO. Gibi moleküller ele alınacaktır. Moleküle bağlı olarak HF, DFT ya da CI metotları uygulanıp elektronik olarak ve ayrıca moleküllerin titreşim dönmelerinden kaynaklana termodinamik özellikler hesaplanacaktır.

Anahtar kelimeler: Spekotroskopi, Termodinamik, Astrofizik, poliatom, Hartree fock (HF), Density Function Theory (DFT), Configuration Interaction (CI)

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SYMBOL/S LIST

$\hat{\mathbf{H}}$	:	*Hamiltonian Operator*
$\mathbf{\Psi}$	:	*Wave Function*
$\mathbf{T}$	:	*Kinetic Energy Operator*
$\mathbf{Z}$	:	*Atomic Number*
∇^2	:	*Laplacian Operator*
$\hbar$	:	*Planck Constant*
O	:	*Corresponding Operator*
$\boldsymbol{\alpha}$	:	*Alpha (spin function (up))*
$\boldsymbol{\beta}$	:	*Beta (spin function (down))*
$\mathbf{c}$	:	*Molecular Orbital Coefficient*
$\mathbf{P}$	:	*Permutation Operator*
$\boldsymbol{\varepsilon}$	:	*Associated Orbital Energy*
χ_p	:	*electronegativity scale*
E_{MP2}	:	*second order in Møller − Plesset perturbation*
$\mathbf{E}_{xc}$	:	*Exchange − Correlation Energy*
$\boldsymbol{\mu}$	:	*Electronic chemical potential*
$\boldsymbol{\rho}$	:	*Electron Density*

Abbreviation

HF	:	$Hartree - Fock\ Method$
BOA	:	$Born{-}Oppenheimer\ Approximation$
MO	:	$Molecular\ Orbital$
SCF	:	$Self - Consistent\ Field$
SCRF	:	$Self - Consistent\ Reaction\ Field$
UHF	:	$Unrestricted\ Hartree - Fock$
RHF	:	$Restected\ Hartree - Fock$
ECP	:	$Effective\ Core\ Potential$
CE	:	$Configuration\ Energy$
CI	:	$Configuration\ Interaction$
MPT	:	$Møller - Plesset\ Theory$
MBPT	:	$Many - Body\ Perturbation\ Theory$
MPPT	:	$Møller - Plesset\ perturbation\ Theory$
DFT	:	$Density\ Functional\ Theory$
M^+	:	$Molecular\ ion$
LSD	:	$Local\ Spin\ Density$
LDA	:	$Local\ Density\ \ Approximation$
GGA	:	$Generalized\ Gradiant\ Approximation$
QMA	:	$Quantum\ Morte\ Carlo$
KS	:	$Kohn - Sham\ Approximation$
IR	:	$Infrared\ Spectroscopy$
UV	:	$Ultraviolet\ Spectroscopy$

1. INTRODUCTION

Hartree-Fock (HF) and Density Function Theory (DFT) methods is the underlying treatment of electron correlation. In the Hartree-Fock method, electron correlations beyond a mean field picture are entirely neglected, whereas in DFT they are included approximately with a functional. DFT methods consequently require careful calibration to establish their accuracy (or inaccuracy) on a case by case basis. Both methods provide a relatively inexpensive route to performing computational physics, chemistry and materials science, provided only trends and not highly accurate quantitative predictions are required. Both methods are used to describe the quantum states of many-electron systems, e.g. molecules and crystals. Both methods also use the Born-Oppenheimer approximation, in which you first solve for the electronic degrees of freedom[1, 2, 3, 4].

The Hartree-Fock method assumes that the many-electron wavefunction takes the form of a determinant of single-electron wavefunctions, called a Slater determinant. The problem with this assumption is that a general many-electron wavefunction cannot be expressed as a single determinant. As a result, Hartree-Fock methods do not fully incorporate electronic correlation and the resulting energies tend to be too high. Luckily, if you find a complete basis of single-electron wave functions, then you can (in principle) express the exact many-electron wavefunction as a linear combination of all possible determinants made of these wavefunctions. This is called Configuration interaction. There are also many more post-Hartree-Fock techniques which expand on this [5].

Born-Oppenheimer approximation, the difficulty is mainly due to the two-electron terms of the Hamiltonian that introduce a correlation between the motions of the electron, In the field of the attractive potential of nuclei. For this reason one has to look for approximate solution, whose accuracy is determined by the observable one wants to evaluate and by the computer resources at disposal. One of the most popular approximation is Hartree-fock method in which the wave function is as simple as possible , provided in accordance with the principles of quantum mechanics and in particular with the indistinguishability principle if identical particle . This principle imposes the electron wave function should be antisymmetric with respect to the exchange of any

two electrons, that is, it must change its sign when the position of two electron is interchanged [6]. In density functional theory (DFT), the many-electron wavefunction is completely by passed in favor of the electron density. Hohenberg-Kohn Theorems [7, 8] the ground state energy of the system depends uniquely on the electron density, i.e. the total energy is a functional of the electron density [9, 10, 11, 46]. Therefore, one can apply the vibrational principle to minimize the energy with respect to the electron density. The problem with this technique is that no one knows what the energy functional is. At the first level of approximation, one can use the local density approximation (LDA), where you assume that the energy depends locally on the density in the same way it does for a uniform electron gas. Modern methods use generalized gradient approximations (GGAs) where you take into account the gradient of the density to produce a more accurate functional. However, the exact energy functional is still unknown and is a big open problem in computational chemistry and condensed matter physics [12, 13].

The general theoretical framework of DFT, involving the Hohenberg–Kohn free energy $F_{HK}[n(\mathbf{r})]$ which for simplicity focuses on classical systems. The generalization to the quantum mechanical electron gas, together with discussion of the Kohn-Sham formula and of the local density approximation, which is the simplest practical approximation for the exchange-correlation energy. Various issues relating to the accuracy of this approach [14, 15].

Traditionally, Hartree-Fock and its descendants were considered more reliable than DFT, but this has been changing recently as DFT techniques have become more refined. Moreover, whereas in Hartree-Fock type calculations you need to keep track of the spatial and spin coordinates of all NN electrons, DFT offers the potential benefit of dealing with only a single function of a single spatial coordinate. For this reason, DFT has been steadily gaining in popularity.

2. HARTREE FOCK METHOD

2.1. Electronic Hamiltonian Operator

The Electronic Schrödinger equation can be written as

$$H^e\Psi = E^e\Psi \tag{2.1.1}$$

Here Ψ is the wave function which demonstrate the electron distribution. The E^e is the expectation value and H^e. The *Hamiltonian operator*

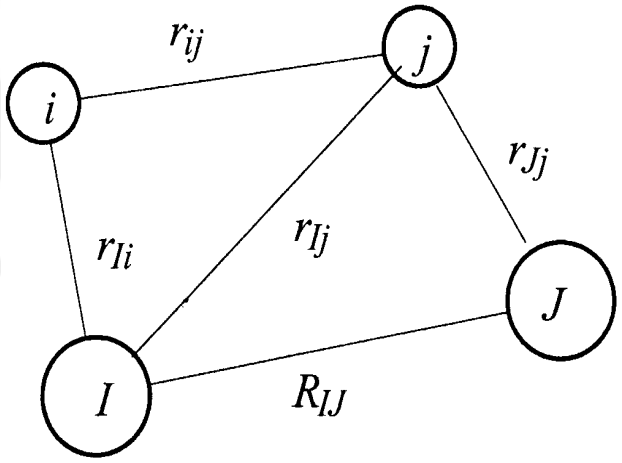

Fig.2.1. Hypothetical molecule with nuclei $I, J$and electrons, i, j and interparticle separations as shown.

The solution of (2.1.1) consists of finding a function of the coordinates of all of the electrons, is carried out by eigen value problem. Still no exact solution for equation (2.1.1) one can solve it using same approximation methods We describe these procedures and carry out anaccurate solution of the Schrödinger equation, beginning with a definition of H^e Let consider the system consist of four electron like in (**Fig.2.1**) if we follows on this system. The potential energy of interaction between any two electrons is $\frac{e^2}{r_{ij}}$, where r_{ij} is the distance between the electrons i and j and e is the electron charge. For any two nuclei I and J with atomic numbers Z_I and Z_J separated by a distance R_{IJ} , the interaction potential is $Z_I Z_J\ e^2/R_{IJ}$. The potential energy of an electron i with a nucleus I is $-Z_I e^2/r_{Ii}$. The kinetic energies of the i th electron and the $I\ th$ nucleus in momentum equations are $p_i^2/2m_e$ and $P_i^2/2M_I$, respectively, and

M_e and M_I one masses. Here $FLAE$ lowercase letters refer to electrons and capital letters refer to nuclei. For a general system the total energy can be written as

$$E = \sum_{i=1}^{x_N} \frac{P_i^2}{2M_I} + \sum_{I=1}^{N_N} \frac{P_I^2}{2M_I} - \sum_{i=1}^{x_N}\sum_{i=1}^{x_N} \frac{Z_{Ie^2}}{r_{iI}} + \sum_{I=1}^{x_N-1}\sum_{j=i+1}^{x_N} \frac{e^2}{r_{ji}} + \sum_{I=1}^{N_N-1}\sum_{J=I+1}^{N_N} \frac{Z_I Z_{Je^2}}{R_{IJ}} \quad (2.1.2)$$

Here the first two terms are the kinetic energy of the system. The last three terms are potential energy of the system.The nucler mass is more heavier than the electron mass like $\frac{1}{1820}$, that is why here we can use Born Openheimer Approximation (BOA) the second term on the right-hand side of (2.1.2) is zero. The total energy for nucluer coordinate is:

$$E(\mathbf{R}) = \sum_{i=1}^{x_N} \frac{P_i^2}{2m_e} - \sum_{i=1}^{x_N}\sum_{I=1}^{N_n} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{x_N-1}\sum_{j=i+1}^{x_N} \frac{e^2}{r_{ij}} + \sum_{I=1}^{N_N-1}\sum_{J=I+1}^{N_N} \frac{Z_I Z_J e^2}{R_{IJ}} \quad (2.1.3)$$

The electronic *Hamiltonian operator* H^e might be written as

$$H^e(\mathbf{R}) = -\sum_{i=1}^{x_N} \frac{\hbar^2}{2m_e}\nabla(i)^2 - \sum_{i=1}^{x_N}\sum_{I=1}^{N_N} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{x_N-1}\sum_{j=i+1}^{x_N} \frac{e^2}{r_{ij}} \quad (2.1.4)$$

$$= \sum_{i=1}^{x_N} h(i) + \sum_{i=1}^{x_N-1}\sum_{j=i+1}^{x_N} \frac{e^2}{r_{ij}} \quad (2.1.5)$$

one-electron Hamiltonian for the ith electron, $h(i)$, can be shown as

$$h(i) = -\frac{\hbar^2}{2m_e}\nabla(i)^2 - \sum_{I=1}^{N_N} \frac{Z_I e^2}{r_{iI}} \quad (2.1.6)$$

The explicit dependence on R is not represented for (2.1.6) and will not be given in subsequent equations. The Laplacian operator in equation (2.1.6) Cartesian coordinates for the ith electron can be given by

$$\nabla(i)^2 = \frac{\partial^2}{\partial \varkappa_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \quad (2.1.7)$$

2.2. Electronic Schrödinger Equation

The Electron energy E^e and potential energy of equation (2.1.3) will give us total energy of molecule the solving of electron Schrödinger equation will also give us electronic energy E^e. But the only solution of electron Schrödinger equation (2.1.1) is possible just for one electron system. Nevertheless, it must be represented that there are an infinite number of solutions, and that there is a lowest energy distribution, which is customarily denoted Ψ_0 with associated energy E_0^e. The only exception is the total energy of the molecule.

2.3.Expectation Values

In quantum mechanics the expectation value can be given as

$$o = \frac{\int \Psi O \Psi d\tau}{\int \Psi^2 d\tau} \tag{2.3.1}$$

Here o is the obsorved value of the operator O. and Ψ is the wave function which describes the distribution of particles in the system. The expectation value of equation.

$$E^{\approx} = \frac{\int \Psi^* H \Psi^* d\tau}{\int |\Psi^*|^2 d\tau} \tag{2.3.2}$$

It should be proved that for the ground state, E^* is always greater than or equal to the same energy E_0 and that the two are equal only if $\Psi^* = \Psi_0$ .This method is named as The procedure is called the *variation method* :

(a) Build a wave function with an accurate form to define the system, building in flexibility form of a set of parameters.

(b) Differentiate E^* equation (2.3.2) according to each of the parameters and set the resulting equation to zero.

(c) Solve the equation to obtain the lowest energy which is the closest to exact energy of the system. The first task is the construction of the wave function.

2.4. The Slater Determinants

The wave function of electronic motions must be antisymmetric to satisfy the Pauli exclusion principle naturally and therefore should be represented as a determinant [16]. The new electron–electron interaction resulting from the anti-summarization is called the exchange interaction. Slater constructed a general method for solving the Schrödinger equation based on the normalized determinant representing the anti-summarization wave function [17, 18]. one-electron wave functions (orbitals),$\phi(x_1)$,

$$\Phi(x_1, x_2, ..., x_N) = (N!)^{\frac{-1}{2}} \sum_{P=0}^{x_N - 1} (-1)^P P^P \left[\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] \tag{2.4.1}$$

The term in square brackets is a Hartree product. The Hartree product shows a particular assignment of the electrons to orbitals. The permutation operator P permutes the coordinates of two electrons. The orbitals form an orthonormal set; that is, for any pair ϕ_a and ϕ_b

$$\int \phi_a(x_1)\phi_b(x_2)d\tau = \delta_{ab} \tag{2.4.2}$$

Here the $d\tau_1$ is the volume element $dx_1dy_1dz_1ds_1$.:

In the case of two-electron system, the wave function

$$\Phi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(x_1) & \phi_b(x_1) \\ \phi_a(x_2) & \phi_b(x_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left[\phi_a(x_1)\phi_b(x_2) - \phi_b(x_1)\phi_a(x_2)\right] \tag{2.4.3.a}$$

For many (N) electron

$$\Phi(x_1, x_2, ..., x_N) = (N!)^{\frac{-1}{2}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \phi_3(x_1) & \cdots & \phi_{x_N}(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \phi_3(x_2) & \cdots & \phi_{x_N}(x_2) \\ \phi_1(x_3) & \phi_2(x_3) & \phi_3(x_3) & \cdots & \phi_{x_N}(x_3) \\ \ddots & \ddots & \ddots & \ddots & \ddots \\ \phi_1(x_N) & \phi_2(x_N) & \phi_3(x_N) & \cdots & \phi_{x_N}(x_N) \end{vmatrix} \tag{2.4.3.b}$$

$$(N!)^{\frac{-1}{2}} = \frac{1}{\sqrt{N!}}$$

might generate an infinite number of determinate wave functions of in a form equation (2.4.1), and without approximation, the exact wave function $\Phi(x_1, x_2, ..., x_N)$ can be stated as a linear combination of them:

$$\Psi(x_1, x_2, ..., x_N) = \sum_{a=0}^{\infty} d_a \Phi_a \tag{2.4.4}$$

2.5. Electronic Hartree-Fock Energy

The Hartree-Fock approximation, in the equation (2.4.4) might be approximated by a single wave function term , the first term of equation (2.4.4). The variations method is used to determine an optimum Φ_0 .

$$\Phi_{HF}.E_0 = \frac{\int \Phi_0 H \Phi_0 d\tau}{|\Phi_0|^2 d\tau} = \int \Phi_0 H \Phi_0 d\tau \tag{2.5.1}$$

If Before we replace equation (2.4.1) into equation (2.5.1), where equation (2.4.1) and (2.4.3.b) can be presented in terms of the antisymmetrizer operator, A,

$$\Phi(x_1, x_2, ..., x_N) = \left[A\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] \tag{2.5.2}$$

here

$$A = (x_N!)^{\frac{-1}{2}} \sum_{P=0}^{x_N!-1} (-1)^P P^P \tag{2.5.3}$$

Our first aim is to create a simpler equation for the electronic energy. We can do this by using the properties of the antisymmetrizer operator represent at the right. Thus,

$$E_0 = \int A\left[\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] HA\left[\phi_1(x_1)\phi_2(x_2)....\phi x_N(x_N)\right] d\tau$$

$$= \int \phi_1(x_1)\phi(x_2)....\phi_{x_N}(x_N) HA^2\left[\phi(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] d\tau \qquad [A, H] = 0$$

$$= (x_N!)^{\frac{1}{2}} \int \phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N) HA\left[\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] d\tau \qquad A^2 = (x_N!)^{\frac{1}{2}} A$$

$$= \int \phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N) H \sum_{P=0}^{x_N!-1} (-1)^p P^p \left[\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] d\tau \qquad (2.5.4)$$

Finally

$$E_0 = \int \phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N) \sum_{i=1}^{x_N} h(i) \sum_{P=0}^{x_N!-1} (-1)^p P^p \left[\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] d\tau$$

$$+ \int \phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N) \sum_{i=1}^{x_N-1} \sum_{j=i+1}^{x_N} \frac{e^2}{r_{ij}} \sum_{P=0}^{x_N!-1} (-1)^p P^p \left[\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] d\tau \qquad (2.5.5)$$

Consider the first term in equation (2.5.5). Specifically, take the term for the ith electron and the "do-nothing" permutation $(P = 0)$:

$$= \int \phi_1(x_1)\phi_2(x_2)....\phi_{_N}(x_N) h(i) (-1)^0 p^0 \left[\phi_1(x_1)\phi_2(x_2)....\phi_{_N}(x_N)\right] d\tau$$

$$= \int \phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N) h(i) \phi_1(x_1)\phi_2(x_2)....\phi_{X_N}(x_N) d\tau_1 d\tau_2 ....d\tau_{X_N}$$

$$= \int \phi_1(x_1)\phi_1(x_1)d\tau_1 \int \phi_2(x_2)\phi_2(x_2)d\tau_2 .... \int \phi_i(i)h(i)\phi_i(i)d\tau_i .... \int \phi_{x_N}(x_N)\phi_{x_N}(x_N)d\tau_N$$

$$= 1 \cdot 1 \cdots \int \phi_i(i)h(i)\phi_i(i)d\tau_i \cdots 1$$

$$= \int \phi_i(i)h(i)\phi_i(i)d\tau_i$$

$$= h_i \qquad (2.5.6)$$

Another permutation, say P^k , may interchange electrons i and j. For this term, the integration can be written as

$$\int \phi_1(x_1)\phi_2(x_2)....\phi_i(i)....\phi_j(j)....\phi_{x_N}(x_N) h(i) (-1)^k p^k \left[\phi_1(x_1)\phi_2(x_2)....\right.$$

$$\left.\left[\phi_i(i)....\phi_j(j)....\phi_{x_N}(x_N) d\tau\right]\right.$$

$$= -\int \phi_1(x_1)\phi_2(x_2)....\phi_i(i)....\phi_j(j)....\phi_{x_N}(x_N)h(i)\phi_1(x_1)\phi_2(x_2)....$$
$$\phi_i(j)....\phi_j(i)....\phi_{x_N}(x_N)d\tau_1 d\tau_2....d\tau_{x_N}$$

$$= -\int \phi_1(x_1)\phi_1(x_1)d\tau_1 \int \phi_2(x_2)\phi_2(x_2)d\tau_2.... \int \phi_i(i)h(i)\phi_j(i)d\tau_i....$$

$$\int \phi j(j)\phi_i(j)d\tau_j.... \int \phi_{x_N}(x_N)\phi_{x_N}(x_N)d\tau_{x_N}$$

$$= 1{\cdot}1\cdots \int \phi_i(i)h(i)\phi_j(i)d\tau_i \cdots 0 \cdots 1$$
$$= 0 \tag{2.5.7}$$

The "*zero*" result arise from the orthogonality of the orbitals equation (2.4.2). Because each electron is in a different orbital, The entire first term of equation (2.5.5) becomes

$$\int \phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N) \sum_{i=1}^{x_N} h(i) \sum_{P=0}^{x_N!-1} (-1)^p P^p \left[\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] d\tau$$

$$= \sum_{a=1}^{x_N} h_a \tag{2.5.8}$$

It is worthwhile mentioning ha explicitly using equation (2.1.6):

$$h_a = \int \phi_a(x_1) \left(-\frac{\hbar^2}{2m_e} \nabla(x_1)^2 - \sum_{I=1}^{N_N} \frac{Z_I e^2}{r_{iI}} \right) \phi_a(x_1) d\tau_1 \tag{2.5.9}$$

equation (2.5.4) is the energy of a sole electron with spatial distribution given by the MO ϕ_a. for the $(-1)^p$ permutitation the equation

$$\int \phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\frac{e^2}{r_{ij}} \left[1 - P_{ij}\right] \left[\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right] d\tau$$

$$= \int \phi_1(x_1)\phi_1(x_1)d\tau_1 \int \phi_2(x_2)\phi_2(x_2)d\tau_2.... \int\int \phi_i(i)\phi_j(j)\frac{e^2}{r_{ij}}\phi_i(i)\phi_j(j)d\tau_i d\tau_j....$$

$$\int \phi_{x_N}(x_N)\phi_{x_N}(x_N)d\tau_{x_N} - \int \phi_1(x_1)\phi_1(x_1)d\tau_1 \int \phi_2(x_2)\phi_2(x_2)d\tau_2....$$

$$\int\int \phi_i(i)\phi_j(j)\frac{e^2}{r_{ij}}\phi_i(j)\phi_j(i)d\tau_i d\tau_j \int \phi_{x_N}(x_N)\phi_{x_N}(x_N)d\tau_{x_N}$$

$$= \int\int \phi_i(i)\phi_j(j)\frac{e^2}{r_{ij}}\phi_i(i)\phi_j(j)d\tau_i d\tau_j - \int\int \phi_i(i)\phi_j(j)\frac{e^2}{r_{ij}}\phi_i(j)\phi_j(i)d\tau_i d\tau_j$$

$$= J_{ij} - K_{ij} \tag{2.5.10}$$

The total two-electron contribution to the electronic energy is

$$\int \phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N) \sum_{i=1}^{x_N-1}\sum_{j=i+1}^{x_N}\frac{e^2}{r_{ij}}\sum_{P=0}^{x_N!-1}(-1)^p P^p\left[\phi_1(x_1)\phi_2(x_2)....\phi_{x_N}(x_N)\right]d\tau$$

$$= \sum_{a=1}^{x_N-1}\sum_{b=a+1}^{x_N}(J_{ab} - K_{ab}) \tag{2.5.11}$$

The two-electron repulsion integrals J_{ab} and K_{ab} are formally can be define as

$$J_{ab} = \int\int \phi_a(x_1)\phi_b(x_2)\frac{e^2}{r_{12}}\phi_a(x_1)\phi_b(x_2)d\tau_1 d\tau_2 \tag{2.5.12}$$

$$K_{ab} = \int\int \phi_a(x_1)\phi_b(x_2)\frac{e^2}{r_{12}}\phi_a(x_1)\phi_b(x_2)d\tau_1 d\tau_2 \tag{2.5.13}$$

and the Coulomb and exchange integrals, respectively. Thus,

$$E_0 = \sum_{a=1}^{x_N} h_a + \frac{1}{2}\sum_{a=1}^{x_N}\sum_{b=1}^{x_N}(J_{ab} - K_{ab}) \tag{2.5.14}$$

we see that the restriction on the second sums may be released and the factor of $\frac{1}{2}$ introduced since $J_{aa} = K_{aa}$.

Once the orbitals have been "optimized" (see below) to yield the lowest possible value of the energy equation (2.5.14), the energy will be the Hartree-Fock energy E_{HF}

2.6. Variation of E_{HF}

The variation of E_{HF} equation (2.5.14) with respect to variation of the orbitals can be written as formally

$$\delta E_{HF} = \sum_{a=1}^{x_N} \delta h_a + \frac{1}{2} \sum_{a=1}^{x_N} \sum_{b=1}^{x_N} (\delta J_{ab} - \delta K_{ab}) = 0 \tag{2.6.1}$$

where

$$\delta h_a = \int \phi_a(x_1) h(x_1) \delta\phi_a(x_1) d\tau_1 + \int \phi_a(x_1) h(x_1) \delta\phi_a(x_1) d\tau_1$$

$$= 2 \int \phi_a(x_1) h(x_1) \delta\phi_a(x_1) d\tau_1 \tag{2.6.2}$$

$$\delta h_{ab} = \int\int \delta\phi_a(x_1)\phi_b(x_2) \frac{e^2}{r_{12}} \phi_a(x_1)\phi_b(x_2) d\tau_1 d\tau_2 + \int\int \phi_a(x_1)\delta\phi_b(x_2) \frac{e^2}{r_{12}} \phi_a(x_1)\phi_b(x_2) d\tau_1 d\tau_2$$

$$+ \int\int \phi_a(x_1)\phi_b(x_2) \frac{e^2}{r_{12}} \delta\phi_a(x_1)\phi_b(x_2) d\tau_1 d\tau_2 + \int\int \phi_a(x_1)\phi_b(x_2) \frac{e^2}{r_{12}} \phi_a(x_1)\delta\phi_b(x_2) d\tau_1 d\tau_2$$

$$= 2\int\int \delta\phi_a(x_1)\phi_b(x_2) \frac{e^2}{r_{12}} \phi_a(x_1)\phi_b(x_2) d\tau_1 d\tau_2 + 2\int\int \phi_a(x_2)\delta\phi_b(x_1) \frac{e^2}{r_{12}} \phi_a(x_2)\phi_b(x_1) d\tau_1 d\tau_2 \tag{2.6.3}$$

And

$$\delta K_{ab} = \int\int \delta\phi_a(x_1)\phi_b(x_2) \frac{e^2}{r_{12}} \phi_a(x_2)\phi_b(x_1) d\tau_1 d\tau_2 + \int\int \phi_a(x_1)\delta\phi_b(x_2) \frac{e^2}{r_{12}} \phi_a(x_2)\phi_b(x_1) d\tau_1 d\tau_2$$

$$+ \int\int \phi_a(x_1)\phi_b(x_2) \frac{e^2}{r_{12}} \delta\phi_a(x_2)\phi_b(x_1) d\tau_1 d\tau_2 + \int\int \phi_a(x_1)\phi_b(x_2) \frac{e^2}{r_{12}} \phi_a(x_2)\delta\phi_b(x_1) d\tau_1 d\tau_2$$

$$= 2\int\int \delta\phi_a(x_1)\phi_b(x_2) \frac{e^2}{r_{12}} \phi_a(x_2)\phi_b(x_1) d\tau_1 d\tau_2 + \int\int \delta\phi_b(x_1)\phi_a(x_2) \frac{e^2}{r_{12}} \phi_b(x_2)\phi_a(x_1) d\tau_1 d\tau_2 \tag{2.6.4}$$

The combination of terms takes advantage of the Hermitian nature of the operators,

$$\int\int \phi_a(x_1)\phi_b(x_2) \frac{e^2}{r_{12}} \delta\phi_a(x_2)\phi_b(x_1) d\tau_1 d\tau_2 = \int\int \delta\phi_a(x_2)\phi_b(x_1) \frac{e^2}{r_{12}} \phi_a(x_1)\phi_b(x_2) d\tau_1 d\tau_2$$

and the indistinguishability of electrons,

$$\int\int \delta\phi_a(x_2)\phi_b(x_1)\frac{e^2}{r_{12}}\phi_a(x_1)\phi_b(x_2)d\tau_1 d\tau_2 = \int\int \delta\phi_a(x_1)\phi_b(x_2)\frac{e^2}{r_{12}}\phi_a(x_2)\phi_b(x_1)d\tau_1 d\tau_2$$

for all pairs of orbitals a and b,

$$\int \delta\phi_a(x_1)\phi_b(x_1)d\tau_1 + \int \delta\phi_a(x_1)\phi_b(x_1)d\tau_1 = 0 \tag{2.6.5}$$

Constraints must be imposed on a set of simultaneous linear equations by the method of Lagrangian multipliers.

$$\sum_{a=1}^{x_N}\sum_{b=1}^{x_N}(-\varepsilon_{ab})\left[\int \delta\phi_a(x_1)\phi_b(x_1)d\tau_1 + \int \delta\phi_b(x_1)\phi_a(x_1)d\tau_1\right] \tag{2.6.6}$$

Here the complete set of simultaneous equations for the variation are

$$\begin{aligned}
0 = {} & 2\sum_{a=1}^{x_N}\int \delta\phi_a(x_1)h(x_1)\phi_a(x_1)d\tau_1 \\
& + \sum_{a=1}^{x_N}\sum_{b=1}^{x_N}\iint \delta\phi_a(x_1)\phi_b(x_2)\frac{e^2}{r_{12}}\phi_a(x_1)\phi_b(x_2)d\tau_1 d\tau_2 \\
& + \sum_{a=1}^{x_N}\sum_{b=1}^{x_N}\iint \delta\phi_b(x_1)\phi_a(x_2)\frac{e^2}{r_{12}}\phi_a(x_2)\phi_b(x_1)d\tau_1 d\tau_2 \\
& - \sum_{a=1}^{x_N}\sum_{b=1}^{x_N}\iint \delta\phi_a(x_1)\phi_b(x_2)\frac{e^2}{r_{12}}\phi_a(x_2)\phi_b(x_1)d\tau_1 d\tau_2 \\
& - \sum_{a=1}^{x_N}\sum_{b=1}^{x_N}\iint \delta\phi_b(x_1)\phi_a(x_2)\frac{e^2}{r_{12}}\phi_b(x_2)\phi_a(x_1)d\tau_1 d\tau_2
\end{aligned}$$

$$-\sum_{a=1}^{x_N}\sum_{b=1}^{x_N}-\varepsilon_{ab}\int \delta\phi_a(x_1)\phi_b(x_1)d\tau_1 - \sum_{a=1}^{x_N}\sum_{b=1}^{x_N}-\varepsilon_{ab}\int \delta\phi_b(x_1)\phi_a(x_1)d\tau_1 \tag{2.6.7}$$

or

$$0 = 2\sum_{a=1}^{x_N}\int \delta\phi_a(x_1)h(x_1)\phi_a(x_1)d\tau_1$$

$$+2\sum_{a=1}^{x_N}\sum_{b=1}^{x_N}\int\int \delta\phi_a(x_1)\phi_b(x_2)\frac{e^2}{r_{12}}\phi_a(x_1)\phi_b(x_2)d\tau_1 d\tau_2$$

$$-2\sum_{a=1}^{x_N}\sum_{b=1}^{x_N}\int\int \delta\phi_a(x_1)\phi_b(x_2)\frac{e^2}{r_{12}}\phi_a(x_1)\phi_b(x_2)d\tau_1 d\tau_2$$

$$-2\sum_{a=1}^{x_N}\sum_{b=1}^{x_N}\varepsilon_{ab}\int \delta\phi_a(x_1)\phi_b(x_2)d\tau_1 \tag{2.6.8}$$

where $J_b(x_1)$ and $K_b(x_1)$, is Coulomb and exchange one-electron operators, obtained as

$$0=\sum_{a=1}^{X_N}\int d\tau\delta\phi_a(x_1)\left[\left(h(x_1)+\sum_{b=1}^{X_N}\left[J_b(x_1)-K_b(x_1)\right]\right)\phi_a(x_1)-\sum_{b=1}^{X_N}\varepsilon_{ab}\phi_b(x_1)\right] \tag{2.6.9}$$

$$\int \phi_a(x_1)J_b(x_1)\phi_a(x_1)d\tau_1=\int \phi_a(x_1)\left(\int \frac{\phi_b(x_2)\phi_b(x_2)e^2}{r_{12}}d\tau_2\right)\phi_a(x_1)d\tau_1=J_{ab} \tag{2.6.10}$$

$$\int \phi_a(x_1)K_b(x_1)\phi_a(x_1)d\tau_1=\int \phi_a(x_1)\left(\int \frac{\phi_b(x_2)\phi_a(x_2)e^2}{r_{12}}d\tau_2\right)\phi_a(x_1)d\tau_1=K_b \tag{2.6.11}$$

Since the individual variations of the orbitals are linearly independent,where equation (2.6.4) can only be true if the quantity inside the large square brackets is zero for every value of a, namely

$$\left(h(x_1)+\sum_{b=1}^{x_N}\left[J_b(x_1)-K_b(x_1)\right]\right)\phi_a(x_1)-\sum_{a=1}^{x_N}\varepsilon_{ab}\phi_b(x_1)=0 \tag{2.6.12}$$

The group of orbitals can be rotated so that the ε matrix becomes diagonal, that is,

$$\left(h(x_1)+\sum_{b=1}^{x_N}\left[J_b(x_1)-K_b(x_1)\right]\right)\phi_a(x_1)-\varepsilon_{ab}\phi_b(x_1)=0 \tag{2.6.13}$$

The quantity in huge parentheses is the Fock operator, $F\ (x_1)$

$$F(x_1) = h(x_1) + \sum_{b=1}^{x_N} [J_b(x_1) - K_b(x_1)] \tag{2.6.14}$$

So , the condition that the orbitals yield a stationary point on the energy hyper-surface with respect to variations is that the orbitals are eigenfunctions of the Fock operator, with associated orbital energy, ε,

$$F(x_1)\phi_a(x_1) = \varepsilon_a\phi_a(x_1) \tag{2.6.15}$$

to get a many-electron wave function of the sole determinantal form equation (2.4.3.b) which will let the lowest electronic energy equation (2.5.1) or (2.5.14), one should use one-electron wave functions

2.7. LCAO Solution Fock Formulas

Here we would like to gererate moleculer orbitals which are combination of function the basis set:

$$\phi_a(x_1) = \sum_{i=1}^{n} \chi_i(x_1)c_{ia} \qquad\qquad \boldsymbol{\phi} = \boldsymbol{\chi}\mathbf{c} \quad (in\ matrix\ form) \tag{2.7.1}$$

If χ_i as known and proceed to determining the expansion cofficients c_{ia}. Substitution of equation (2.7.1) into equation (2.6.15) we can obtain

$$F(x_1)\sum_{i=1}^{n} \chi_i(x_1)c_{ia} = \varepsilon_a \sum_{i=1}^{n} \chi_i(x_1)c_{ia} \tag{2.7.2}$$

Multiplication on the left by χ_j and integration over the range of the coordinates of the electron give us

$$\sum_{i=1}^{n} \int \chi_j(x_1)F(x_1)\chi_i(x_1)d\tau_1 c_{ia} = \varepsilon_a \sum_{i=1}^{n} \int \chi_j(x_1)\chi_i(x_1)d\tau_1 c_{ia} \tag{2.7.3}$$

or

$$\sum_{i=1}^{n} F_{ji}c_{ia} = \sum_{i=1}^{n} S_{ji}c_{ia}\varepsilon_a \tag{2.7.4}$$

in equation (2.7.4) may be cast as a matrix equation

$$\mathbf{Fc} = \mathbf{Sce} \tag{2.7.5}$$

The overlap matrix **S** can be defined as

$$\mathbf{S}_{ij} = \int \chi_i(x_1)\chi_j(x_1)d\tau_1 \tag{2.7.6}$$

The Fock matrix **F** is given as

$$\mathbf{F}_{ij} = \int \chi_i(x_1)F(x_1)\chi_i(x_1)d\tau_1$$

$$= \chi_i(x_1)\left[h(x_1) + \sum_{b=1}^{x_N}[J_b(x_1) - K_b(x_1)]\right]\chi_j(x_1)d\tau_1$$

$$= \int \chi_i(x_1)h(x_1)\chi_j(x_1)d\tau_1 + \sum_{b=1}^{x_N}\left[\int \chi_i(x_1)J_b(x_1)\chi_j(x_1)d\tau_1 - \int \chi_i(x_1)K_b(x_1)\chi_j(x_1)d\tau_1\right]$$

$$= \int \chi_i(x_1)h(x_1)\chi_j(x_1)d\tau_1 + \sum_{b=1}^{x_N}\iint (\ \chi_i(x_1)\phi_b(x_2)\frac{e^2}{r_{12}}\phi_b(x_2)\chi_i(x_1)d\tau_2 d\tau_1$$

$$-\iint \chi_i(r_1)\phi_b(x_2)\frac{e^2}{r_{12}}\chi_i(x_2)\phi_b(r_1)d\tau_2 d\tau_1\ ) \tag{2.7.7}$$

For the Fock matrix, one must already know the molecular orbitals. For this reason, the Fock equation (2.7.5) must be solved iteratively. After repeating this operation a number of times, a point will be reached where the MOs achieved from solution of the Fock equations are the same as were obtained from the previous cycle and used to create the Fock matrix. When this point is reached, one is said to have reached self-consistency or to have reached a self-consistent field (SCF).

2.8. Integrals

To solve Fock equations requires integrals involving the basis functions, either in pairs or four at a time. The S matrix elements are whose element are shown by equation (2.7.6) as

$$\mathbf{S}_{ij} = \int \chi_i(x_1)\chi_i(x_1)d\tau_1$$

The Fock integrals first encountered in equation (2.7.3) are constructed from kinetic energy integrals, nuclear-electron attraction integrals, and two-electron repulsion integrals, as follows, continuing from equation (2.7.7):

$$\mathbf{F}_{ij} = \int \chi_i(r_1) \left[\frac{-\hbar^2}{2m}\nabla^2(r_1)\right] \chi_i(r_1) d\tau_1 + \int \chi_i(r_1) \left[\sum_{I=1}^{N_N} \frac{-Z_I e^2}{r_{1i}}\right] \chi_i(r_1) d\tau_1 \sum_{k=1}^{n}\sum_{l=1}^{n}\sum_{b=1}^{n} c_{kb}c_{lb}$$

$$\left[\iint \chi_i(r_1)\chi_k(r_2)\frac{e^2}{r_{12}}\chi_l(r_2)\chi_j(r_1)d\tau_2 d\tau_1 - \iint \chi_i(r_1)\chi_k(r_2)\frac{e^2}{r_{12}}\chi_j(r_2)\chi_l(r_1)d\tau_2 d\tau_1\right] \tag{2.8.1}$$

$$= \mathbf{T}_{ij} + \mathbf{V}_{ij}^{ne} + \sum_{k=1}^{n}\sum_{l=1}^{n} \mathbf{P}_{kl}\mathbf{G}_{ijkl} \tag{2.8.2}$$

The kinetic energy integrals are collected as the matrix T, whose elements are defined by

$$\mathbf{T}_{ij} = \frac{-\hbar^2}{2m} \int \lambda_j(r_1)\nabla^2(r_1)\lambda_j(r_1)d\tau_1 \tag{2.8.3}$$

The nuclear-electron attraction integrals are collected as the matrix V^{ne} , whose elements are defined by

$$\mathbf{V}_{ij}^{ne} = -\sum_{I=1}^{N_N} -Z_I e^2 \int \chi_i(x_1)\frac{1}{r_{1I}}\chi_i(x_1)d\tau_1 \tag{2.8.4}$$

The supermatrix $\mathbf{G}$, which contains the two-electron repulsion integrals, has elements defined by

$$\mathbf{G}_{ijkl} = \iint \chi_i(x_1)\chi_k(x_2)\frac{e^2}{r_{12}}\chi_l(x_2)\chi_j(x_1)d\tau_2\ d\tau_1 - \iint \chi_i(x_1)\chi_k(x_2)\frac{e^2}{r_{12}}\chi_j(x_2)\chi_l(x_1)d\tau_2\ d\tau_1 \tag{2.8.5}$$

In equation (2.8.2) we also introduced a useful matrix, the density matrix $\mathbf{P}$, whose elements are defined by

$$\mathbf{P}_{ij} = \sum_{a=1}^{N_e} c_{ia}c_{ja} \tag{2.8.6}$$

where the sum runs over all of the occupied Molecule orbitals.

2.9. Basis Sets

A basis set in theoretical and computational physical is a set of functions (called basis functions) which are combined in linear combinations to create molecular orbitals. For convenience these functions are typically atomic orbitals centered on atoms

a) [STO-3G] is a minimal basis set the fastest, contain only minimal required contracted functions for each atom.

b) [3-21G] is a simple basis set with added flexibility, and polarization functions on atoms heavier than N_e. This is the simplest basis set that gives reasonable results.

c) [6-31G, 6-311G, cc-pCVTZ, cc-pCVTZ, aug-cc-pCVQZ)], For this branch of basis function most molecules, valence orbitals mainly contribute to chemical bonds, while core orbitals hardly participate in the bonds. The Pople-type basis functions, including the 6-31G basis, are included. "6-31G" indicates the extent of the contraction and section, here "6" means the use of contracted basis functions of 6 primitive functions for core orbitals and "31" means the use of double-Split basis functions for describe valence orbitals of 3 primitive functions with one uncontracted basis function for valence orbitals. "6-311G" uses triple-Split basis functions for valence orbitals. In this type of basis function,("CC-PVDZ;" "CC-PVTZ,"and "CC-PVQZ") this type functions are described as for doubly, triply, and quadruply basis functions for valence orbitals, this branch of basis set named by Split valence basis functions

d) [6-31G*, 6-31G**, 6-31G(d)] For branch of basis function, the Pople-type basis functions we can describe basis functions represented by star "* " such as "6-31G " For a one star " * " one polarization function is added for all atoms except hydrogen atoms, However for a double star "**" one p orbital function is also added to each hydrogen atom. Where the form of polarization function is often written explicitly, such that, "6-31G(d)" (for this basis function, a d orbital function is added). This branch of basis set named by Polarization function-supplemented because Polarization functions usually have big angular momenta than the biggest angular momenta of the atomic orbitals that mainly make up the molecular orbitals.

e) [6-31+G(d), 6-311++G(2df,2pd), aug-cc-pCVQZ] For this branch basis function, the Pople-type basis functions is shown by a plus "+" , "6-311CG(d)" augments s p diffuse functions mixing s and p orbitals for all atoms except hydrogen atoms, and "6-311++G($2df$, $2pd$)" adds two d and one f diffuse functions for all atoms except

hydrogen and two p and one d orbital functions for hydrogen in addition. For correlation consistent basis functions, augmenting diffuse functions is represented by "aug-" at the head of the names and one diffuse function is added to each angular momentum type of basis function. In the "aug-CC-PVDZ" function, containing up to d orbital functions, diffuse functions are added to s through d orbital functions one by on [20, 23, 25, 26].

Basis Set	# basis functions	Energy (au)	SCF cycles
STO-3G	26	-189.534 688 69	14
3-21G	48	-190.886 407 54	14
6-31G	48	-191.874 189 82	14
6-31G*	72	-191.960 613 31	15
6-311G*	90	-192.001 883 12	15
6-311+G*	106	-192.005 994 08	15
6-311++G**	130	-192.015 295 56	15
6-311++G(2df,2pd)	226	-192.029 578 61	15
6-311++G(3df,3pd)	264	-192.031 627 88	31
cc-pCVTZ	209	-192.032 898 46	15
cc-pCVQZ	400	-192.046 642 88	30
aug-cc-pCVQZ	712	-192.047 735 33	19

Table 1. Effect of Basis Set Choice on Computation Cost

2.10. Orbital Energies and Total Electronic Energy

To solve of the Hartree Fock equations crop molecule orbitals and their linked energies. The energy of ϕ_a is

$$\varepsilon_a = \int \phi_a(x_1) F(x_1) \phi_a(x_1) d\tau_1 = h_a + \sum_{b=1}^{x_N} (J_{ab} - K_{ab}) \tag{2.10.1}$$

however the integrals h_a , J_{ab} , and K_{ab} were shown in (2.5.6), (2.5.12), and (2.5.13), respectively. The total electronic energy in expression of the same integrals was shown in (2.5.14) as

$$E_{HF} = \sum_{a=1}^{x_N} h_a + \frac{1}{2}\sum_{a=1}^{x_N}\sum_{b=1}^{x_N}(J_{ab} - K_{ab})$$

It is clear that

$$E_{HF} = \sum_{a=1}^{x_N} \varepsilon_a - \frac{1}{2}\sum_{a=1}^{x_N}\sum_{b=1}^{x_N}(J_{ab} - K_{ab}) \tag{2.10.2}$$

The average electronic energy is not simply the sum of the orbital energies, which by themselves would over count the electron-electron repulsion.

2.11. Restricted Hartree-Fock Theory

For the HF theory we have been discuss is called unrestricted Hartree-Fock theory (UHF). The spin should be taken into account when the exchange integrals are being evaluated since when the two spin orbitals involved in this integral did not have the same spin function, α or β, the integral value is zero by virtue of the orthonormality of the electron spin functions

$$\int \alpha(x_1)\alpha(x_1)d\sigma_1 = \int \beta(x_1)\beta(x_1)d\sigma_1 = 1 \qquad \int \alpha(x_1)\beta(x_1)d\sigma_1 = \int \beta(x_1)\,\alpha(x_1)d\sigma_1 = 0 \tag{2.11.1}$$

If a molecule has the same number of electrons with spin up (α) as with spin down (β), the solution of the Hartree Fock equations in the vicinity of the equilibrium geometry and for the ground electronic state yields the result that the spatial part of the MOs describing α and β electrons are equal in pairs. In other words, the Hartree Fock determinantal wave function may be written as

$$\Phi_{RHF}(x_1, x_2, x_3, ..., x_N) = (x_N!)^{\frac{1}{2}} \left|\phi_1^{'}(x_1)\alpha(x_1)\phi_1^{'}(x_2)\beta(x_2)\phi_2^{'}(x_3)\alpha(x_3)....\phi_M^{'}(x_N)\beta(x_N)\right| \tag{2.11.2}$$

If one reformulates the HF equations and total energy expression for a wave function which must have the form of equation (2.11.2), then one is doing restricted Hartree Fock (RHF) theory. The RHF electronic energy is

$$E_{RHF} = 2\sum_{a=1}^{x_N} \varepsilon_a - \sum_{a=1}^{M}\sum_{b=1}^{M}(2J_{ab} - K_{ab}) \tag{2.11.3}$$

and the molecular orbitals energy is given by

$$\varepsilon_a = \int \phi_a^{'}(x_1)F(x_1)\phi_a^{'}(x_1)d\tau_1 \ = h_a + \sum_{b=1}^{M}(2J_{ab} - K_{ab}) \tag{2.11.4}$$

and RHF energy

$$E_{RHF} = 2\sum_{a=1}^{M} h_a + \sum_{a=1}^{M}\sum_{b=1}^{M}(2J_{ab} - K_{ab}) \tag{2.11.5}$$

and

$$E_{RHF} = \sum_{a=1}^{M}(h_a + \varepsilon_a) \tag{2.11.6}$$

The energy of the determinant for the molecular ion, M^+ , obtained by removing an electron from orbital o of the RHF determinant, is given as

$$\Phi_{RHF}^{M^+}(x_1, x_2, x_3, \cdots, x_N - 1)$$

$$= [(x_N - 1)]^{\frac{1}{2}} \begin{vmatrix} \phi_1^{'}(x_1)\alpha(x_1)\phi_1^{'}(x_1)\beta(x_1)\cdots \\ \phi_{_0}^{'}(x_0)\alpha(x_0)\phi_{_{0+1}}^{'}(x_0 + x_1)\alpha(x_0 + x_1)\cdots\phi_M^{'}(x_N - 1)\beta(x_N - 1) \end{vmatrix} \tag{2.11.7}$$

is given by

$$E_{RHF}^{M^+} = 2\sum_{a\neq 0}^{M} h_a + h_{_0} + \sum_{a\neq 0}^{M}\sum_{b\neq 0}^{M}(2J_{ab} - K_{ab}) \ + \sum_{b\neq 0}^{M}(2J_{b_0} - K_{b_0}) \tag{2.11.8}$$

The energy of the molecule itself, equation (2.11.5), could have been written as

$$E_{RHF}^{M} = 2\sum_{a\neq 0}^{M} h_a + 2h_{_0} + \sum_{a\neq 0}^{M}\sum_{b\neq 0}^{M}(2J_{ab} - K_{ab}) + 2\sum_{b\neq 0}^{M}(2J_{b_0} - K_{b_0}) + J_{_{00}} \tag{2.11.9}$$

Then the energy difference becomes

$$\begin{aligned} E_{RHF}^{M^+} - E_{RHF}^{M} &= -h_{_0} - \sum_{b\neq 0}^{M}(2J_{b_0} - K_{b_0}) - J_{_{00}} \\ &= -h_{_0} - \sum_{b=0}^{M}(2J_{b_0} - K_{b_0}) \\ &= -\varepsilon_{_0} \end{aligned} \tag{2.11.10}$$

Thus the ionization potential corresponding to removal of the electron from occupied MO $_o$ is just the negative of that MO/s energy. In fact, ionization potentials estimated by Koopmans' theorem are fairly accurate.

2.12. Total Energys of Hartree-Fock Energies

The summation of electronic energy and the nuclear-nuclear repulsion can given us total energy

$$E = E_{HF} + \sum_{I=1}^{N_N-1} \sum_{J=I+1}^{N_N} \frac{Z_I Z_J e^2}{R_{IJ}} \tag{2.12.1}$$

the second part is constant which is shown as geometry. The total energy depends on the choice of basis set through the HF energy.

2.13. Configuration Energies

There have been many calculation on canfiguration energy [22, 27, 28]. It is proposed that the missing third dimension is the configuration energy (CE),[28]. The total one-electron valence shell energy of a ground state free atom, which may be defined as follows:

$$CE = \frac{a\varepsilon_s + b\varepsilon_p}{a+b} \tag{2.13.1}$$

If a and b are the occupancies of the valence shell s and p orbitals, respectively, and ε_s and ε_p are the multiplet-averaged s and p shell ionization potentials. For the d -block transition elements, a parallel definition applies, namely,

$$CE = \frac{a\varepsilon_s + b\varepsilon_d}{a+b} \tag{2.13.2}$$

such that the occupancy of the d orbital may be difficult to assign. Values of CE closely parallel the established electronegativity scales of Pauling [29, 30]. A comparison of the three electronegativity scales for selected main group elements is shown in Table 2. [21].

	H
CE	2.300
χ_P	2.200
$\chi A\&R$	2.200

	Li	Be	B	C	N	O	F	Ne
CE	0.912	1.576	2.051	2.544	3, 066	3.610	4.193	4.787
χ_P	0.98	1.57	2.04	2.55	3.04	3.44	3.98	
$\chi A\&R$	0.97	1.47	2.01	2.50	3.07	3.50	4.10	

	Na	Mg	Al	Si	P	S	Cl	Ar
CE	0.869	1.293	1.613	1.916	2.253	2.589	2.869	3.242
χ_P	0.93	1.31	1.61	1.90	2.19	2.58	3.16	
$\chi A\&R$	1.01	1.23	1.47	1.74	2.06	2.44	2.83	

	K	Ca	Ga	Ge	As	Se	Br	Kr
CE	0.734	1.034	1.756	1.994	2.211	2.424	2.685	2.966
χ_P	0.82	1.00	1.81	2.01	2.18	2.55	2.96	
$\chi A\&R$	0.91	1.04	1.82	2.02	2.20	2.48	2.74	

	Rb	Sr	In	Sn	Sb	Te	I	Xe
CE	0.706	0.963	1.656	1.824	1.984	2.158	2.359	2.582
χ_P	0.82	0.95	1.78	1.96	2.05	2.10	2.66	
$\chi A\&R$	0.89	0.99	1.49	1.72	1.82	2.01	2.21	

Table 2. Comparison of Configuration Energy with Electronegativity Scales of Pauling (χ_P) and Allred and Rochow ($\chi A\&R$)[a]

2.14. Configuration Interaction Theory

We wrote the expanded equation for many-electron wave function (2.4.4).

$$\Psi(x_1, x_2, x_3, \cdots x_N) = \sum_{a=1}^{\infty} d_a \Phi_a$$

where each of thedeterminants is of the form equation (2.14.1).

$$\Phi(x_1, x_2, \cdots x_N) = (x_N!)^{\frac{-1}{2}} = \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \phi_3(x_1) & \cdots & \phi_{x_N}(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \phi_3(x_2) & \cdots & \phi_{x_N}(x_2) \\ \phi_1(x_3) & \phi_2(x_3) & \phi_3(x_3) & \cdots & \phi_{x_N}(x_3) \\ \ddots & \ddots & \ddots & \ddots & \ddots \\ \phi_1(x_N) & \phi_2(x_N) & \phi_3(x_N) & \cdots & \phi_{x_N}(x_N) \end{vmatrix} \tag{2.14.1}$$

The Hartree Fock equations were solved in a finite basis of dimension, n, and so yielded n MOs which form an orthonormal set. The determinants are called electron configuration. This configuration describe the distribution of all of the electrons. If determinants are constructed from all possible *single excitations*, the number of singly excited determinants can be $x_N \times (n - x_N)$ The many- electron wave function can be written (2.4.4) to yield a CI wave function,

$$\Psi^{CI}(x_1, x_2, x_3, \cdots x_N) = \sum_{a=1}^{n_{CI}} d_a \Phi_a \tag{2.14.2}$$

The variational method is used to find the best expansion in terms of the configurations; that is, the energy is expressed as an expectation value as was done in equation (2.3.2),

$$E^{CI} = \frac{\int \Psi^{CI} H \Psi^{CI} d\tau}{\int |\Psi^{CI}|^2 d\tau} = \frac{\sum_{a=1}^{n_{CI}} \sum_{b=1}^{c_{CI}} d_a d_b \int \Phi_a H \Phi_b d\tau}{\sum_{a=1}^{n_{CI}} d_a^2} \tag{2.14.3}$$

and differentiated with respect to each of the coefficients, d_a , and setting the result equal to zero,

$$\frac{\partial E^{CI}}{\partial d_a} = 2 \sum_{b=1}^{c_{CI}} d_b \left(\int \Phi_a H \Phi_b d\tau - E^{CI} \delta_{ab} \right) = 0 \tag{2.14.4}$$

This is obtained by diagonalization of the Hamiltonian matrix $\mathbf{H}$, which is

$$\mathbf{H}_{ab} = \int \Phi_a H \Phi_b d\tau \tag{2.14.5}$$

It can be shown that most of the correlation error in HF theory, may be corrected if one includes in the CI calculation all singly and doubly excited configurations (SDCI). GAUSSIAN codes [40, 41] will perform SDCI.

2.15. Møller-Plesset Perturbation Theory

Møller-Plesset perturbation theory (MPPT) aims to make more correction the correlation error incurred in Hartree-Fock theory for the ground state wavefunction $\mathbf{\Phi_{HF}}$ The difference between the sum of Fock operators and the exact Hamiltonian:

$$\begin{aligned} H^{(0)} &= \sum_{i=1}^{x_N} F(i) \\ &= \sum_{i=1}^{x_N} \left(h(i) + \sum_{b=1}^{x_N} [J_b(i) - K_b(i)] \right) \end{aligned} \tag{2.15.1}$$

$$H^P = \sum_{i=1}^{x_N} \sum_{j=i+1}^{x_N} \frac{1}{r_{ij}} - \sum_{i=1}^{x_N} \sum_{b=1}^{x_N} [J_b(i) - K_b(i)] \tag{2.15.2}$$

For second order in Møller-Plesset perturbation theory the E_{MP2} derivation can be corrected.

$$\begin{aligned} E_{MP2} &= \sum_{a=1}^{x_N} \varepsilon_a - \frac{1}{2} \sum_{a=1}^{x_N} \sum_{b=1}^{x_N} [J_b - K_b] \\ &+ \frac{1}{4} \sum_{a=1}^{x_N} \sum_{b=1}^{x_N} \sum_{u=x_N+1}^{n} \sum_{\upsilon=x_N+1}^{n} \frac{|\langle ab \| u\upsilon \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_u - \varepsilon_\upsilon} \end{aligned} \tag{2.15.3}$$

where the notation $\langle ab \| u\upsilon \rangle$ means;

$$\begin{aligned} \langle ab \| u\upsilon \rangle &= \iint \phi_a(x_1)\phi_b(x_2) \frac{1}{r_{12}} \phi_u(x_1)\phi_\upsilon(x_2) d\tau_1 d\tau_2 \\ &- \iint \phi_a(x_1)\phi_b(x_2) \frac{1}{r_{12}} \phi_\upsilon(x_1)\phi_u(x_2) d\tau_1 d\tau_2 \end{aligned} \tag{2.15.4}$$

Notice the last term in this equation is the sum of all doubly excited configurations, the first two terms in equation (2.15.4) correspond to the Hartree-Fock energy, (2.10.2).

3. DENSITY FUNCTIONAL THEORY (DFT)

3.1. Kohn-Sham Formulation

Hohenberg-Kohn method shows it is imaginable to use the ground state density to calculate properties of the system, its not way to get supply a way of finding the ground state density. A way to this is provided by the Kohn-Sham formula [48]. Through the ground state energy, for get a function of the charge density we must To derive these equations

$$E[\rho(r)] = T[\rho(r)] + \rho(r)\upsilon(r)dr + E_{ee} \tag{3.1.1}$$

the kinetic energy is in the the first section in (3.1.1), interaction and external potential the second section, including the electron-nuclei interaction, and the last is the electron-electron interaction

$$E_{ee}[\rho(r)] = 1l2 \int \frac{\rho(r)}{|r - \grave{r}|} dr \; d\grave{r} + E_{xc}[\rho(r)] \tag{3.1.2}$$

Equation (3.1.2) is shown the the electron-electron interaction which is the right hand side the first part is the electron-electron electrostatic interaction other part is the non-classical exchange-correlation energy. we can derive a set of Kohn and Sham for a set of single particle SEs by reintroducing wave functions

$$\rho(r) = \sum_{i=1}^{n} \psi_i^*(r)\psi_i(r) \tag{3.1.3}$$

Thus n is the number of electrons.

$$T[\rho(r)] = -\frac{\hbar^2}{2m} \sum_{i}^{n} \left\langle \psi_i \left| \nabla^2 \right| \psi_i \right\rangle \tag{3.1.4}$$

this Equation represent the The kinetic energy. Then If the wavefunctions are required to be orthonormal can be write as,

$$\int \psi_i^*(r)\psi_i(r)dr = \delta_{ij} \tag{3.1.5}$$

Then we can define a functional of the wavefunctions

$$\Omega(\psi_i) = E[\rho(r)] \sum_i \sum_j \varepsilon_{ij} \int \psi_i^*(r)\psi_i(r)dr \tag{3.1.6}$$

where ε_{ij} are Lagrange multipliers to ensure the wavefunctions are orthonormal. Minimization of $\Omega(\psi_i)$ with respect to $\psi_i^*(r)$ gives the Kohn-Sham formulas

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \upsilon_{eff}(r)\right]\psi_i(r) = \varepsilon_i\psi_i(r) \tag{3.1.7}$$

$$\upsilon_{eff}(r) = \upsilon(r) + \int \frac{\rho(r)}{|r-\grave{r}|}d\grave{r} + \upsilon_{xc}(r) \tag{3.1.8}$$

$$\upsilon_{xc}(r) = \frac{\delta E_{xc}}{\delta\rho(r)} \tag{3.1.9}$$

which $\upsilon_{xc}(r)$ is the exchange-correlation potential .

then in equations (3.1.6) to (3.1.7) a unitary convert is perfect to include the wave-functions are orthonormal . In the equation (3.1.7) can be seen is of the same form as the single particle Schrödinger equation with an effective local potential defined in equation (3.1.8) [47]. The Hartree-Fock equations is in contrast in which there is a non-local potential in the one-electron equations [45, 49].

3.2. Application For Kohn-Sham Formulation

The single quantity that residue to be static is $E_{xc}[n]$, the exchange–correlation energy functional. It is officially define by the adiabatic connection equation [49, 50]. For computation, the terms for $E_{xc}[n]$ has to be accurately constructed. When great efforts have gone into constructing some approximate terms, namely called LDA, GGA, GEA, ODF, hybrid functionals and ect.. [51, 11].

3.2.1. Density Functional Approximations

(1) Local Density Approximation (**LDA**): The natural and simplest approximation is to assume that the density can be treated locally as an regular electron gas, the exchange and correlation energy for every point in the method is the same as that of an regular electron gas of the same density. This approximation was originally introduced and holds for a slowly varying density. Empoly this approximation the exchange-correlation energy for a density can be shown as [48] .

$$E_{xc}^{LDA} = \rho(r)\varepsilon_{xc}(\rho)dr \tag{3.2.1.1}$$

The exchange-correlation energy per particle is shown by $\varepsilon_{xc}(\rho)$.

The regular electron gas of density is ρ.

$$E_{xc}^{LDA} = \frac{\delta E_{xc}^{LDA}}{\delta \rho(r)} = \varepsilon_{xc}(\rho) + \rho(r)\frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} \tag{3.2.1.2}$$

when

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho) \tag{3.2.1.3}$$

the equation (3.2.1.1) is shown exchange-correlation potential [31].The exact values for have been determined from Quantum Monte Carlo (QMC) computation [24]. Those have then been interpolated to provide an analytic form for [34].

(2) Gradient-Expansion Approximation (GEA): If the density variation is high , we can try to include systematically the gradient corrections to the LDA terms, running as $|n(r)|, |n(r)|^2$. In practice, low-order gradient corrections nearly never improve the LDA results and higher-order corrections are exceedingly difficult to calculate. In any case, for real systems the results of GEA are worse than those of LDA [49].

(3) Generalised Gradient Approximation (**GGA**): We can say that the local density approximation can be considered to be the zeroth order approximation to the semi-classical expansion of the density matrix in formula of the density and its derivatives [53]. A natural progression beyond the LDA is thus to the gradient expansion approximation (GEA) in which first order gradient terms in the expansion are included. In the generalised gradient approximation (GGA) a functional form is adopted which include the normalisation case and that the exchange hole is negative shown [55], [56]. This leads to an energy functional that depends on both the density and its gradient but keep the analytic properties of the exchange correlation hole inherent in the LDA. The typical form for a GGA functional is;

$$E_{xc} = \int \rho(r)\varepsilon_{xc}(\rho, \nabla\rho)d\mathbf{r} \tag{3.2.1.4}$$

$$E_{xc} = E_x + E_c \tag{3.2.1.5}$$

We will see below the **GGA** progress significantly on the **LDA**'s characractrization of the binding energy of molecules it was this advantage which lead to the very wide

spread acceptance of DFT in the chemistry community during the early 1990's. A number of functionals within the **GGA** group [55, 56, 57, 58, 59, 60] have been developed. The performance of these functionals will be discussed below

(4) Hybrid functionals : All these set group of approximate types for exchange-correlation energies, incorporating a part of the accurate exchange formula with Kohn-Sham wave functions

with each other with connection estimates for experimental sources.There are much parameterized hybrid forms, several from them are of use in atomic and molecular calculations. One of the forms we shown given here,

$$E_{xc}^{hybrid} \equiv aE_x^{exact} + (1-a)E_x^{GGA} + E_c^{GGA} \tag{3.2.1.6}$$

(5) Orbital dependent functionals : "third generation" of DFT this is a name which known as [49]. Here, instead of only density-dependent functionals, single uses orbital-dependent functionals. However the orbitals will clearly incarante more microscopic information, there are many advantages of this approach to much correlated methods.

3.3. Exchange-Correlation Energy E_{xc}

The Local Density Approximation (LDA) proposed employ by the Kohn and Sham

$$E_{xc}^{LD} = \int d\mathbf{r}\ n(\mathbf{r})\ \varepsilon_{xc}\left[n(\mathbf{r})\right] \tag{3.3.1}$$

when $\varepsilon_{xc}[n]$ is the correlation and exchange energy for all particle of a homogeneous electron gas with density n. This approximation is accurate in the limits of bit by bit varying densities and very large densities. This approximation " has no validity " at the " surface " of atoms and in the interfere regions of molecules and concluded [48]. "We do not expect an accurate description of chemical bonding"

Whether this is true or not depends, of course, on the definition of "accurate", but I sometimes feel that it set back chemical applications of DF theory by a decade or more generalizations to spin-polarized systems [62, 63].given by

$$E_{xc}^{LSD} = \int d\mathbf{r}\ n(\mathbf{r})\ \varepsilon_{xc}\left[n\uparrow(\mathbf{r}), n\downarrow(r)\right] \tag{3.3.2}$$

Which $\varepsilon_{xc}[n\uparrow, n\downarrow]$ is the exchange and correlation energy per particle of a homogeneous, spin-polarized, with spin-up and spin-down densities $n\uparrow$ and $n\downarrow$ for electron gas, respectively the "$X\alpha$" approximation [63].

$$E_{xc}^{X\alpha} = -\frac{3}{2}\alpha C \int d\mathbf{r}\{(n\uparrow(\mathbf{r}))^{\frac{4}{3}} + (n\downarrow(r))^{\frac{4}{3}}\} \tag{3.3.3}$$

where $C = 3(3/4\pi)^{1/3}$.

The α-dependence of energy variations for a given atom or molecule is low for values near 2/3.[64, 9, 65, 66] .

We can say that the electron density in molecules and solids is generally faraway from that of a homogeneous electron gas, and the validity of calculations based on properties of a gas of constant density has often been questioned. [67, 17, 18].

3.4.The Local Density Approximation for E_{xc}

The local density Approximation (LDA) in formula (3.3.1) with local spin density (LSD) in formula (3.3.2) approximations principal to overbidding of several molecules, deprived interchange energy changes if the nodal constructions of the orbitals change, and the conforming Kohn-Sham eigenvalues frequently underestimate measured optical band gaps. However, calculations that used them supplied insight into several physical problems, and the reasons for the errors will be clearer. Though, if insight is not enough and reliable numbers are needed, improved approximations are essential.

The first generalized gradient approximations did principal to well results, and "hybrid" functional, which include a Hartree-Fock similar exchange component,. This formula of E_x has three strictures, and its combination with E_c (B3LYP) is still the so popular approximation applied in chemical applications . Several extra experiential and hybrid functional have been developed since, with parameters often fit to thermochemical data for particular groups of molecules [52, 68, 69, 70].

The employ of experimental data for fitting functional formulas may be logical, but the result was that DF theory was now viewed by some as "semi-empirical" in nature [71, 72].

There is no doubt that the increased focus on Hartree-Fock like exchange and its role in “hybrid” functionals has been one of the most significant developments in recent years. The use of the standard technique of chemists has brought the world of “chemistry” and “materials science” closer, as the need for approximations that gave satisfactory results in both areas became obvious [73]. The implementation of HF like exchange usually comes with a high computational price, especially in calculations

using very large plane-wave basis sets. However, new algorithms on massively parallel computers have reduced or even eliminated this drawback [74, 76]. Models of the exchange-correlation hole continue to provide a way of developing DFT approximations [77, 78], and systematic ways of correcting for the results of DFT calculations are still being pursued. A recent example is the use of multi-determinant wave functions for hybrid functionals [79].

3.5. Successes And Failures

Over the years, many different types of applications of DFT have been developed. This variety evolved because knowledge of the electronic ground–state energy as a function of the position of the atomic nuclei determines molecular and crystal structure, and gives the forces acting on the atomic nuclei when they are not at their equilibrium positions. At present, DFT is being used routinely to solve problems in atomic and molecular physics, such as the calculation of ionization potentials [80] and vibration spectra, the study of chemical reactions, the structure of bio–molecules [81], and the nature of active sites in catalysts [82], as well as problems in condensed matter physics, such as lattice structures [83], phase transitions in solids [84], and liquid metals [85]. Furthermore these methods have made possible the development of accurate molecular dynamics schemes in which the forces are evaluated quantum mechanically "on the fly" [86].

It is important to stress that all practical applications of DFT rest on essentially uncontrolled approximations, such as the LDA discussed above. Thus the validity of the method is in practice established by its ability to reproduce experimental results. A discussion of the accuracy achieved by DFT, compared to other alternative approaches, necessarily depends very much on the specific applications one has in mind, as detailed below.

For atoms and small molecules, the simplest version of the LDA already provides a very useful qualitative and semi–quantitative picture. It is of course a dramatic improvement over the Thomas–Fermi model. It even improves on the more labor–intensive Hartree-Fock method in many cases, especially when one is calculating the strength of molecular bonds, which are substantially overestimated in Hartree-Fock calculations. This can only be considered as a surprising success, keeping in mind that

an isolated atom or molecule is as inhomogeneous an electronic system as possible, and therefore the last place where one might expect a local approximation to work. In other words, electronic correlations in such systems are in a sense weak, and are on average similar to those of a uniform electron gas .

However, the many–body quantum states of such relatively small systems can be solved for extremely accurately using well–known techniques of quantum chemistry, specifically the configuration interaction (CI) method [87]. Furthermore, these techniques use controlled approximations, so that the accuracy can be improved indefinitely, given a powerful enough computer, and indeed impressive agreement with experiment is routinely achieved. For this reason, most quantum chemists did not embrace DFT at an early stage. It is in studies of larger molecules that DFT becomes an indispensable tool [88].

The computational effort required in the conventional quantum chemistry approaches grows exponentially with the number of electrons involved, whereas in DFT it grows roughly as the third power of this number. In practice, this means that DFT can be applied to molecules with hundreds of atoms, whereas using CI, one is limited to systems with only a few atoms. Simply solving the non-interacting problem for a complicated molecule may also be prohibitive, and various methods are used in order to reduce the problem to a computationally manageable task. Of these, we mention the well-known pseudopotential method [89], which allows one to avoid recalculating the wave functions of the inert core electrons over and over again, and the recent attempts to develop "order N" methods [90], which make use of the fact that the behavior of the densities at each point is determined primarily by the atoms in its immediate vicinity, rather than by the whole molecule. It is for this problem that more and more accurate density functionals are most obviously needed.[91]: "Accurate atomization energies are found [using the GGA] for seven hydrocarbon molecules, with a rms error per bond of $0.1eV$, compared with $0.7eV$ for the LSD approximation and $2.4eV$ for the Hartree-Fock approximation."

The remarkable usefulness of DFT for solid–state physics was apparent from the outset. For example, the lattice constants of simple crystals are obtained with an accuracy of about 1% already in the LDA [92]. In such applications, the electronic structure of a single unit cell with periodic boundary conditions is studied; more am-

bitious applications are also common, e.g. a supercell containing many unit cells with a single impurity or defect [93]. Admittedly, this method is inappropriate for treating some more complicated situations, such as anti-ferrimagnets or systems with strong electronic correlations. In other cases, such as for the work–function of metals, local approximations such as the **LDA** obviously miss an important part of the physics: for a point **r** a short distance away from the surface of a metal, the exchange-correlation hole $\rho_{xc}(r, r\prime)$ is concentrated at points $r\prime$ in side or very near the surface of the metal; this results in image forces, i.e. a $1/r$ behavior of vxc (where r is the distance from the surface) which is nonlocal. However, this deficiency can be corrected for "by hand", yielding satisfactory results [94]. In general it is useful to note that, in contrast to approximations using free parameters which are empirically optimized to fit a certain set of data and may thus be used reliably for interpolation, the LDA and the GGA have proved to exhibit a consistent degree of accuracy or inaccuracy for a wide variety of problems when applied to a new problem, the results can thus be interpreted with some confidence. One should of course also be aware of the cases for which these approximations are known to fail, such as the image forces mentioned above, and van der Waals forces [95], which are important e.g. for biological molecules. Both of these are manifestations of the significance of nonlocal correlations a nonlocality which is by definition absent from the LDA and its immediate extensions. These examples of practical failure, together with the unattractiveness of uncontrolled approximations, spur research towards new and more exact exchange–correlation energy functionals. Our discussion would not be complete without mentioning the existence of many other uses of density–functional methods, for electronic systems and for other physical systems. The former include time-dependent

DFT, which relates interacting and non-interacting electronic systems moving in time–dependent potentials, and relativistic DFT, which uses the Dirac equation rather than the Schrodinger equation to calculate the Kohn-Sham states [96]. The latter include applications in nuclear physics, in which the densities of protons and neutrons and the resulting energies are studied [97], and in the theory of liquids.

4. RESULTS AND DISCUSSION

In this section the theory that given above have implemented to big molecules which one important in astrophysics interest to obtain some physical quantities like IR and UV. For this, at first all molecules optimized with an ultra fine grid and we found thermodynamic quantities from contribution of transition, electronic motion, then the calculation have done by important Gaussian software program. For all the molecule calculation done by HF and DFT methods with different basis sets .

4.1. Nitrate NO_3

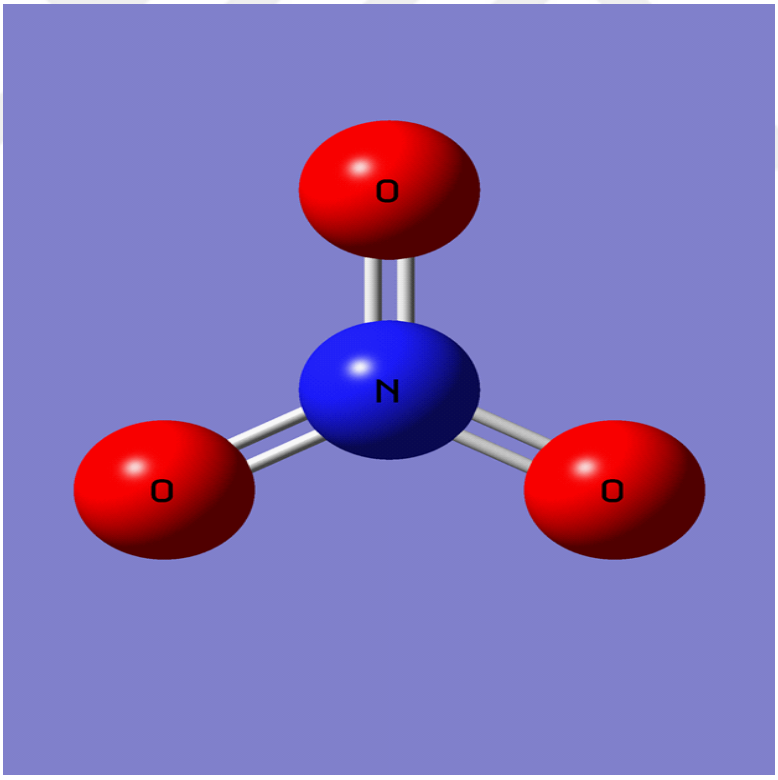

Fig 4.1.1. The optimized geometric structure with atoms numbering for Nitrate (**NO_3**).

Nitrate ion is the conjugate base of nitric acid. A nitrate salt forms when a positively charged ion (such as a metal ion) attaches to the negatively charged oxygen atoms of the ion, forming an ionic compound.Nitrate is formed from the chemical combustion of nitrogen and oxygen. Although nitrogen constitutes almost 79% of earth's atmosphere, nitrogen is mostly inert. Almost all nitrates are soluble in water at standard temperature and pressure. Nitrate is a common contaminant found in groundwater and play a major part in Nitrogen cycle and nitrate pollution. Nitrate is colorless, odorless and tasteless. Low levels of naturally occurring nitrate can be normal, but excess amounts can pollute groundwater. Natural events such as lightning and cosmic radiation create nitrates in the atmosphere, which are then brought out of the atmosphere and to the ground by precipitation (rain, snow, sleet, etc.). This process of nitrate formation is known as nitrogen fixation. Common sources of nitrate in groundwater are fertilizers, livestock waste, and human waste associated with septic and municipal wastewater systems. Excess nitrate in the soil is most often found in rural and agricultural areas. Nitrate travels easily through the soil carried by rain or irrigation water into groundwater. Inorganic nitrates are formed by bacteria and are an essential component of agricultural soil. Organic nitrates are manufactured compounds and, because they generate oxygen when heated, are used in explosives such as nitrocellulose and nitroglycerin

- $Molecular\ Formula$ $\mathbf{NO_3}$
- $molecular\ mass$ $62.0049 g/mol$
- $Monoisotopic\ mass$ $61.988365 Da$
- $ChemSpider$ $ID 918$

Thermochemistry for Nitrate $(\mathbf{NO}_3)$

Temperature 298.150 Kelvin. Pressure 1.0 Atm.

Atom 1 has atomic number 7 and mass 14.00307

For each O has atomic number 8 and mass 15.99491

Molecular mass: 61.98782 amu.

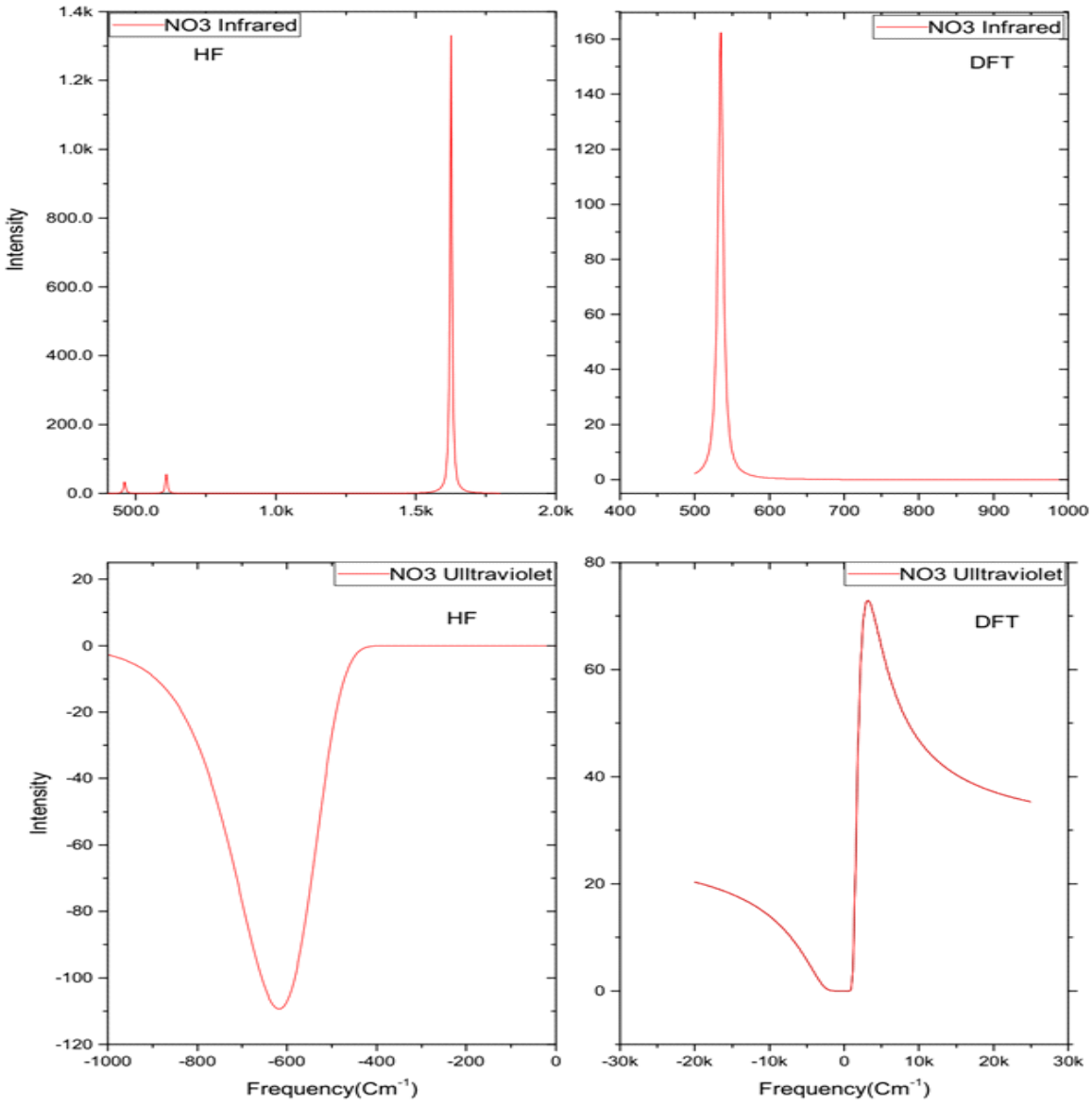

Fig 4.1.2. Infrared and Ultraviolet spectra of the $\mathbf{NO_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{STO-3G}$ basis set

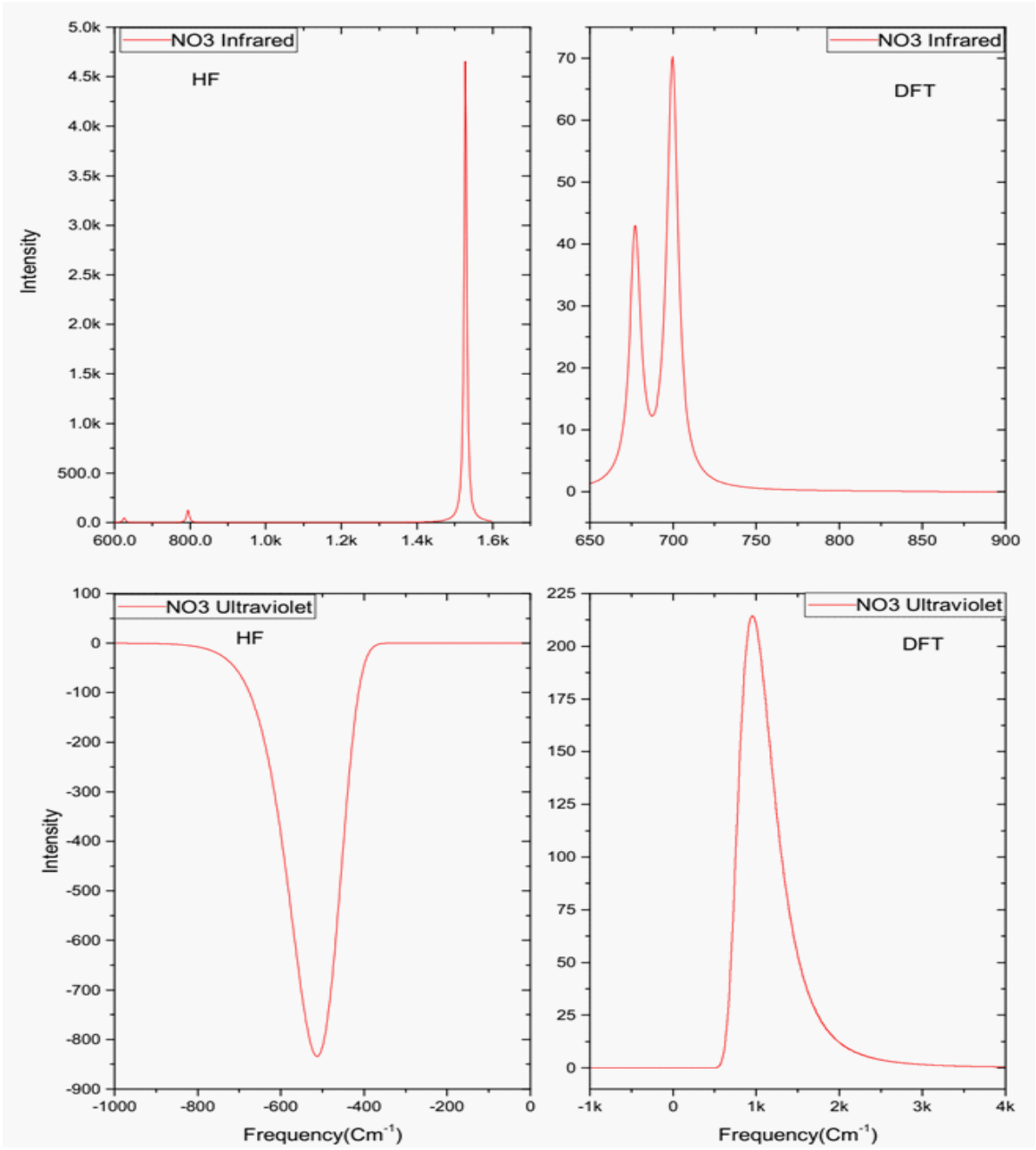

Fig 4.1.3. Infrared and Ultraviolet spectra of the $\mathbf{NO_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{3-21G}$ basis set

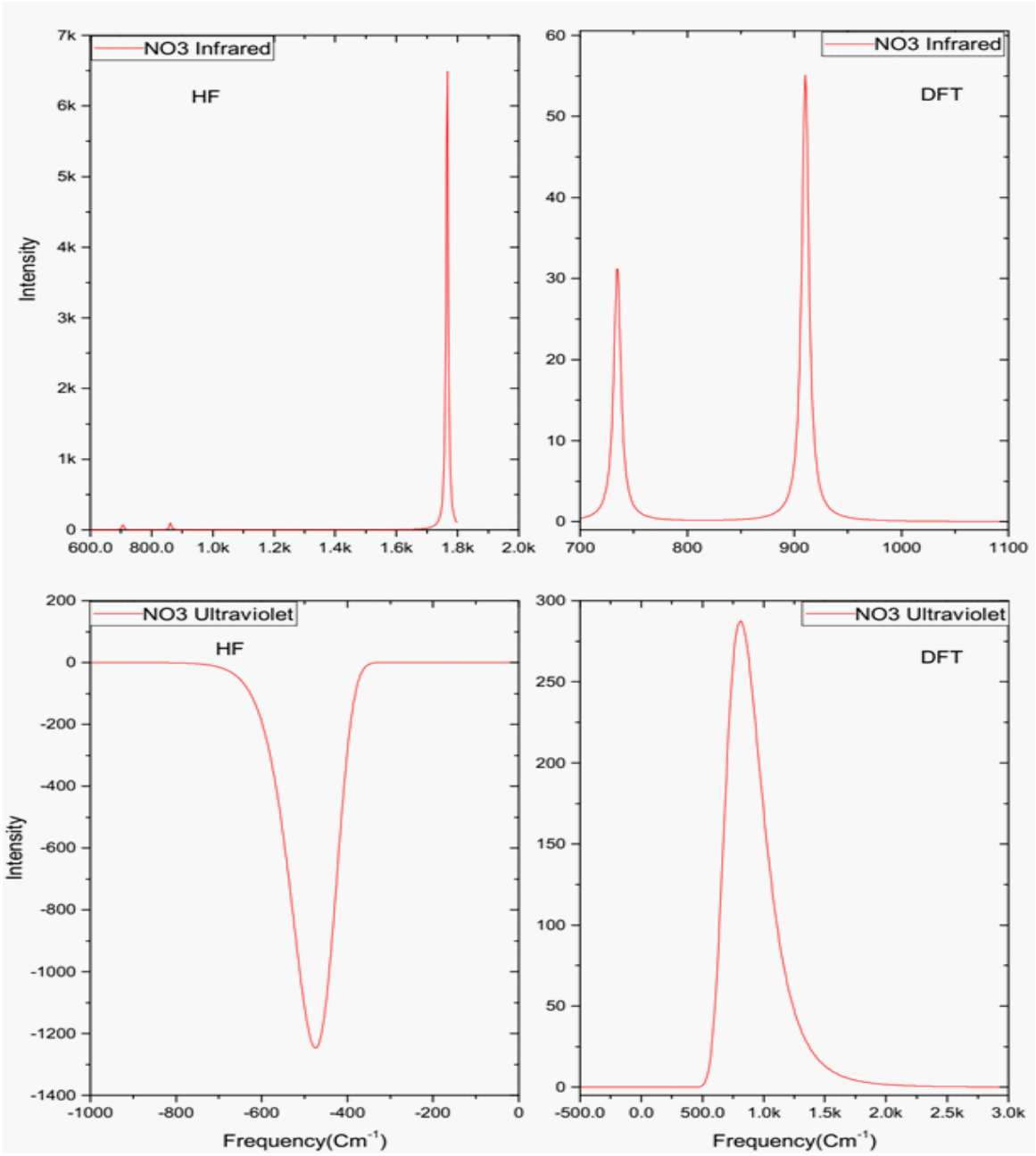

Fig 4.1.4. Infrared and Ultraviolet spectra of the $\mathbf{NO_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{6-31G}$ basis set

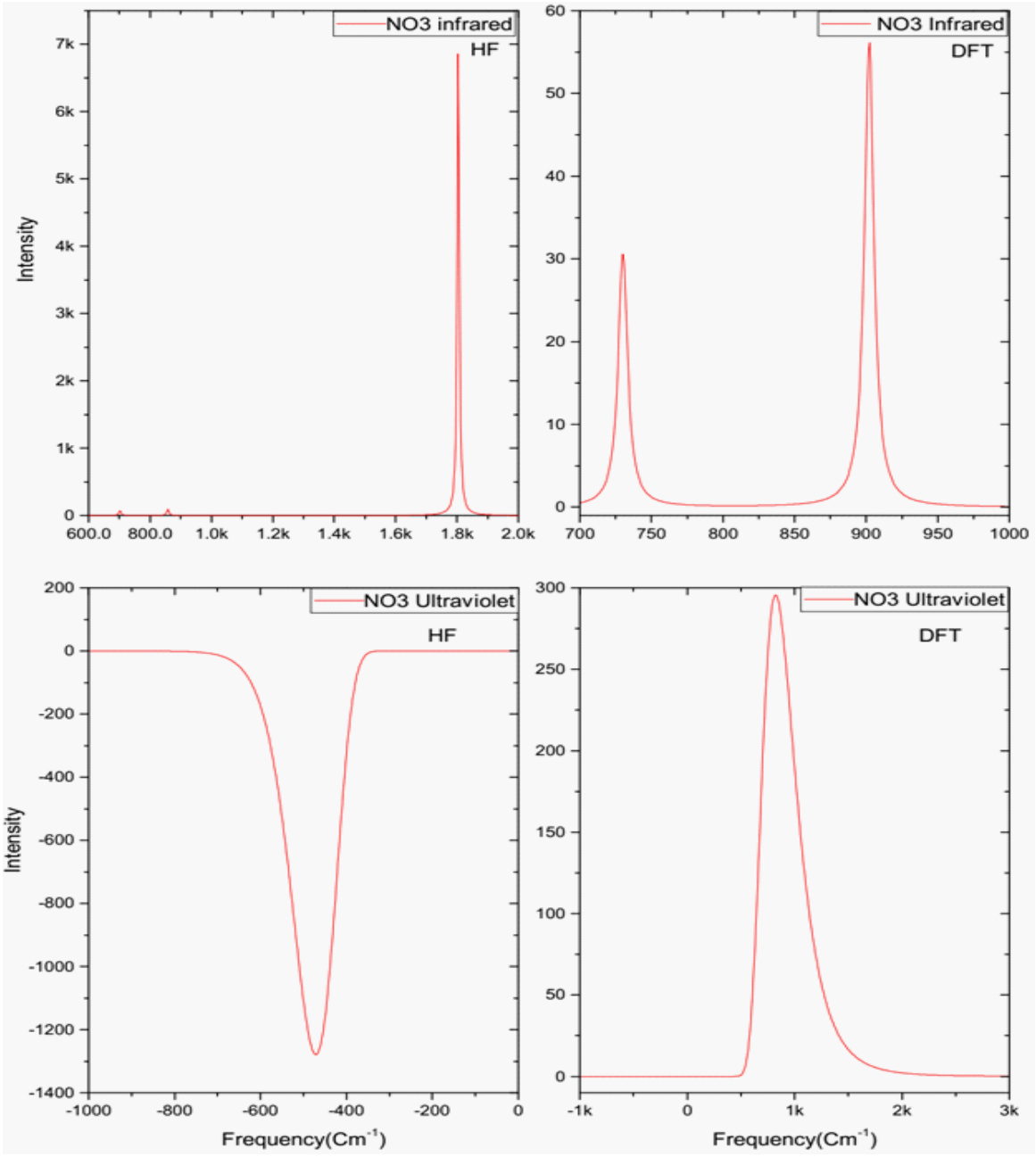

Fig 4.1.5. Infrared and Ultraviolet spectra of the $\mathbf{NO_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{6-311G}$ basis set

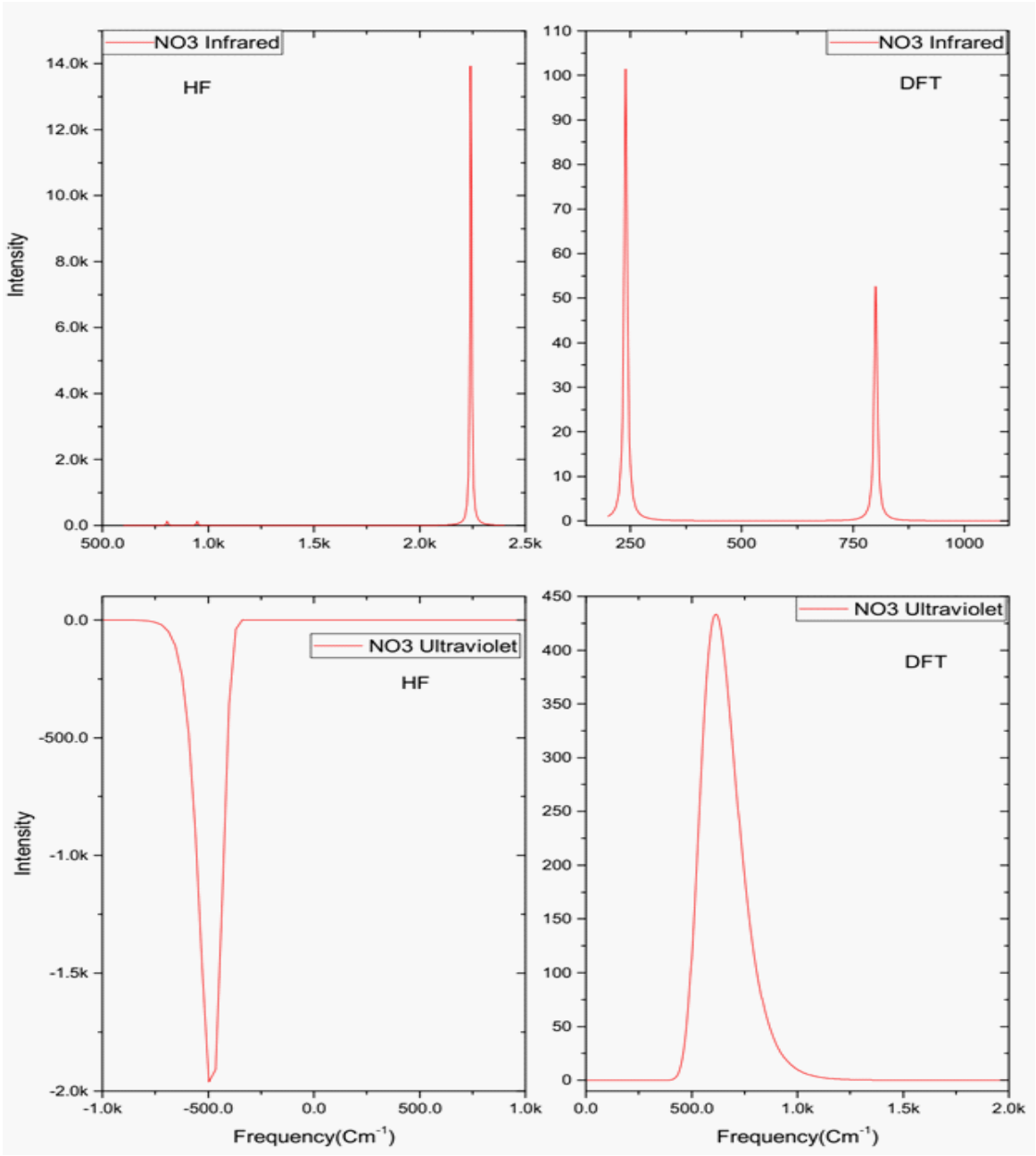

Fig 4.1.6. Infrared and Ultraviolet spectra of the $\mathbf{NO_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVDZ}$ basis set

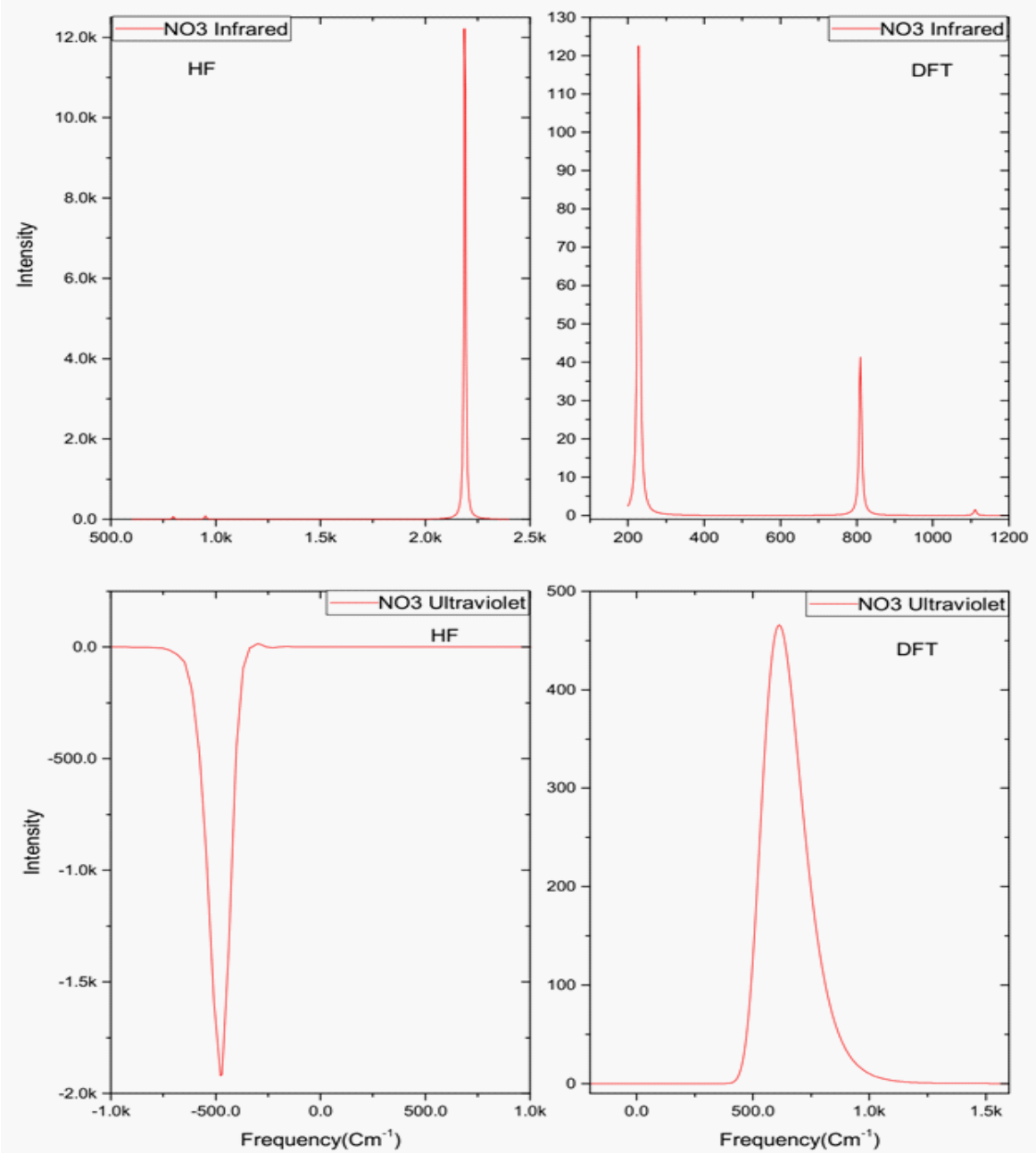

Fig 4.1.7. Infrared and Ultraviolet spectra of the $\mathbf{NO_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVQZ}$ basis set

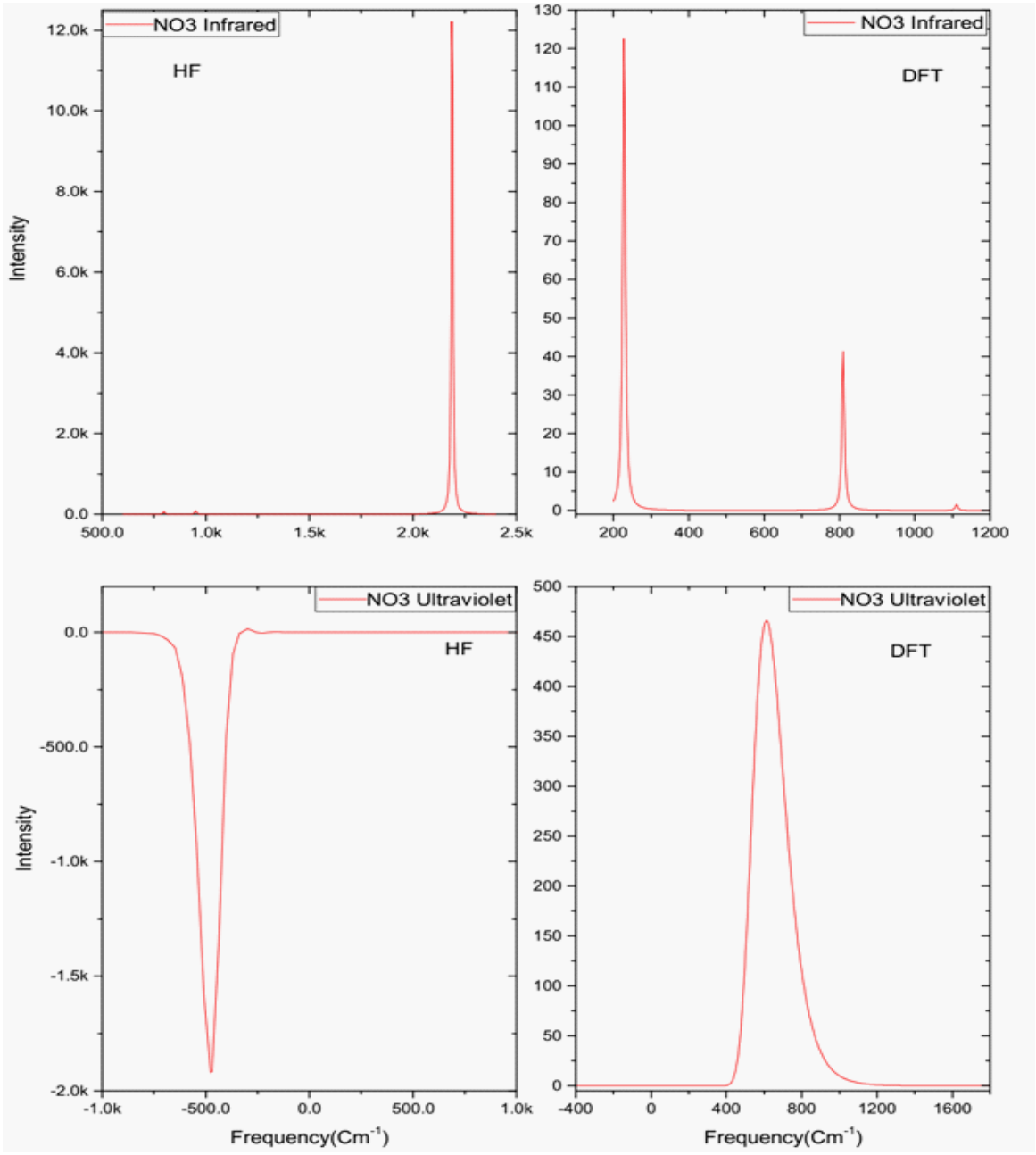

Fig 4.1.8. Infrared and Ultraviolet spectra of the $\mathbf{NO_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVTZ}$ basis set

In all the figures different basis sets have used and one of the aim was to see the change of the IR spectrum with the basis sets. Of was found out that the basis sets have a big effect or computation. When the computation the quantities close to accurate values. If all of the IR figures there are same peaks which are corresponds of the vibration mods of NO3 molecule.

4.2. Methoxymethyl peroxy radical CH_3OCH_2OO :

The methoxymethyl peroxy radical, CH3OCH2OO, is an important molecule in atmospheric chemistry and in combustion with combined the nitrate radical (NO3).This molecule of also important in astrochemistry and here the main idea is to obtain the vibrational motion of the often in this big molecule. we expect more oscillation in the IR results. the number of peak. In the IR figures are proportionl to the number of atoms in molecule.

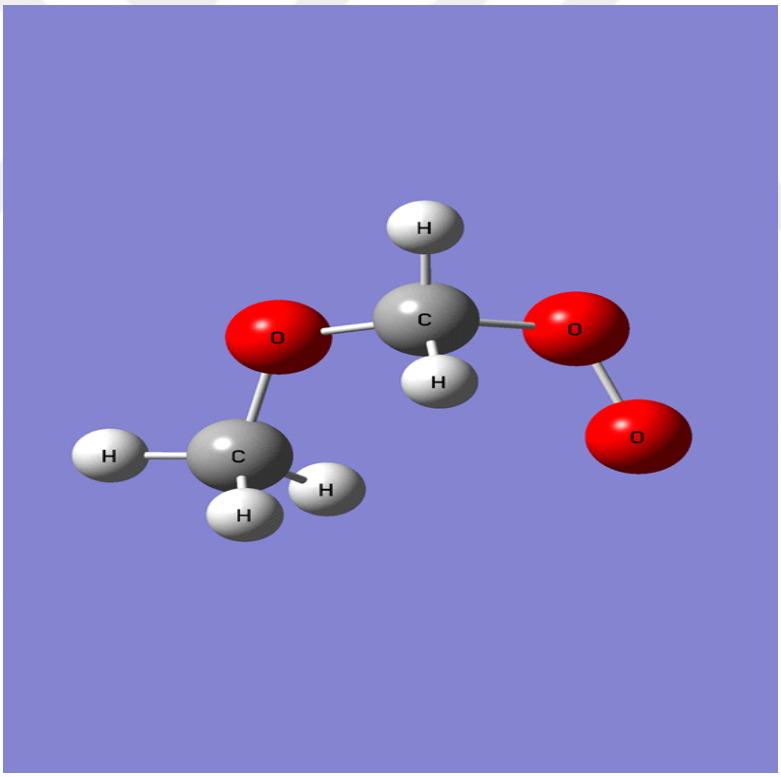

Fig 4.2.1. The optimized geometric structure with atoms numbering for $\mathbf{CH_3OCH_2OO}$.

Here also we have obtain the Thermochemistry poremeters for $\mathbf{CH_3OCH_2OO}$

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 1 and mass 1.00783

Atom 3 has atomic number 1 and mass 1.00783

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 8 and mass 15.99491

Atom 6 has atomic number 6 and mass 12.00000

Atom 7 has atomic number 1 and mass 1.00783

Atom 8 has atomic number 1 and mass 1.00783

Atom 9 has atomic number 8 and mass 15.99491

Atom 10 has atomic number 8 and mass 15.99491

Molecular mass: 77.02387 amu

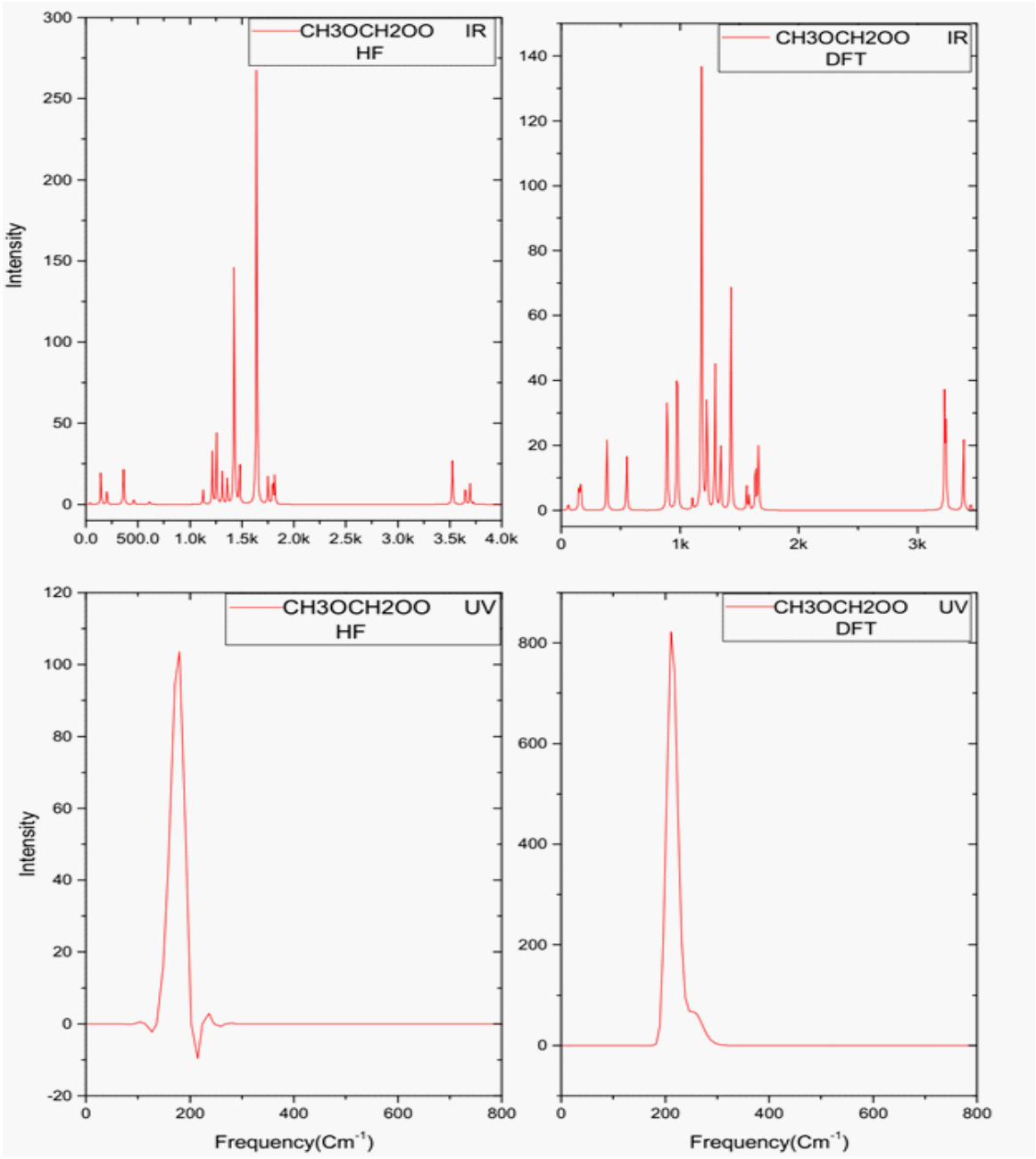

Fig 4.2.2. Infrared and Ultraviolet spectra of the $\mathbf{CH_3OCH_2OO}$ optimized structure determined with HF and DFT approximations, by $\mathbf{STO-3G}$ basis set

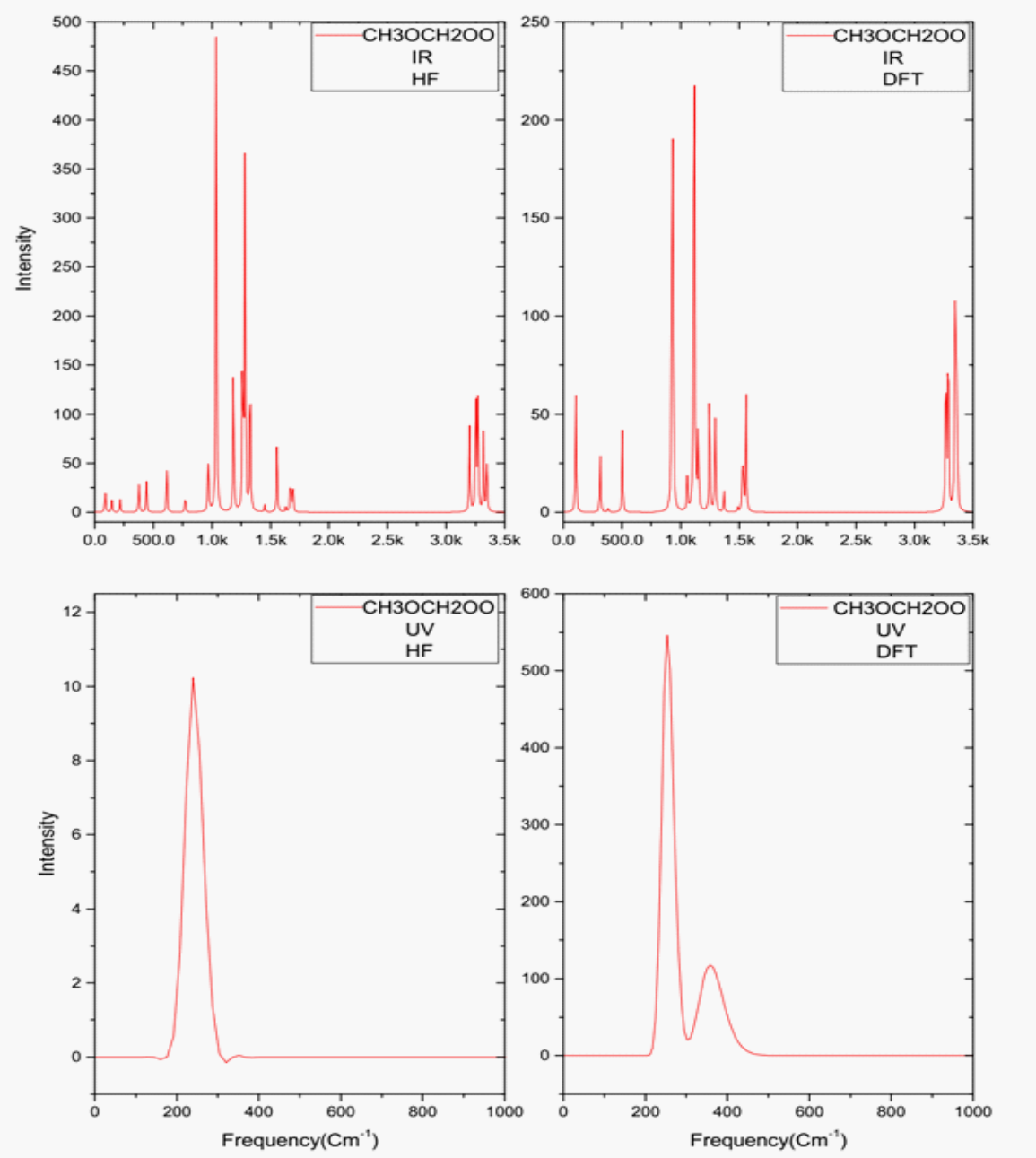

Fig 4.2.3. Infrared and Ultraviolet spectra of the $\mathbf{CH_3OCH_2OO}$ optimized structure determined with HF and DFT approximations, by $\mathbf{3-21G}$ basis set

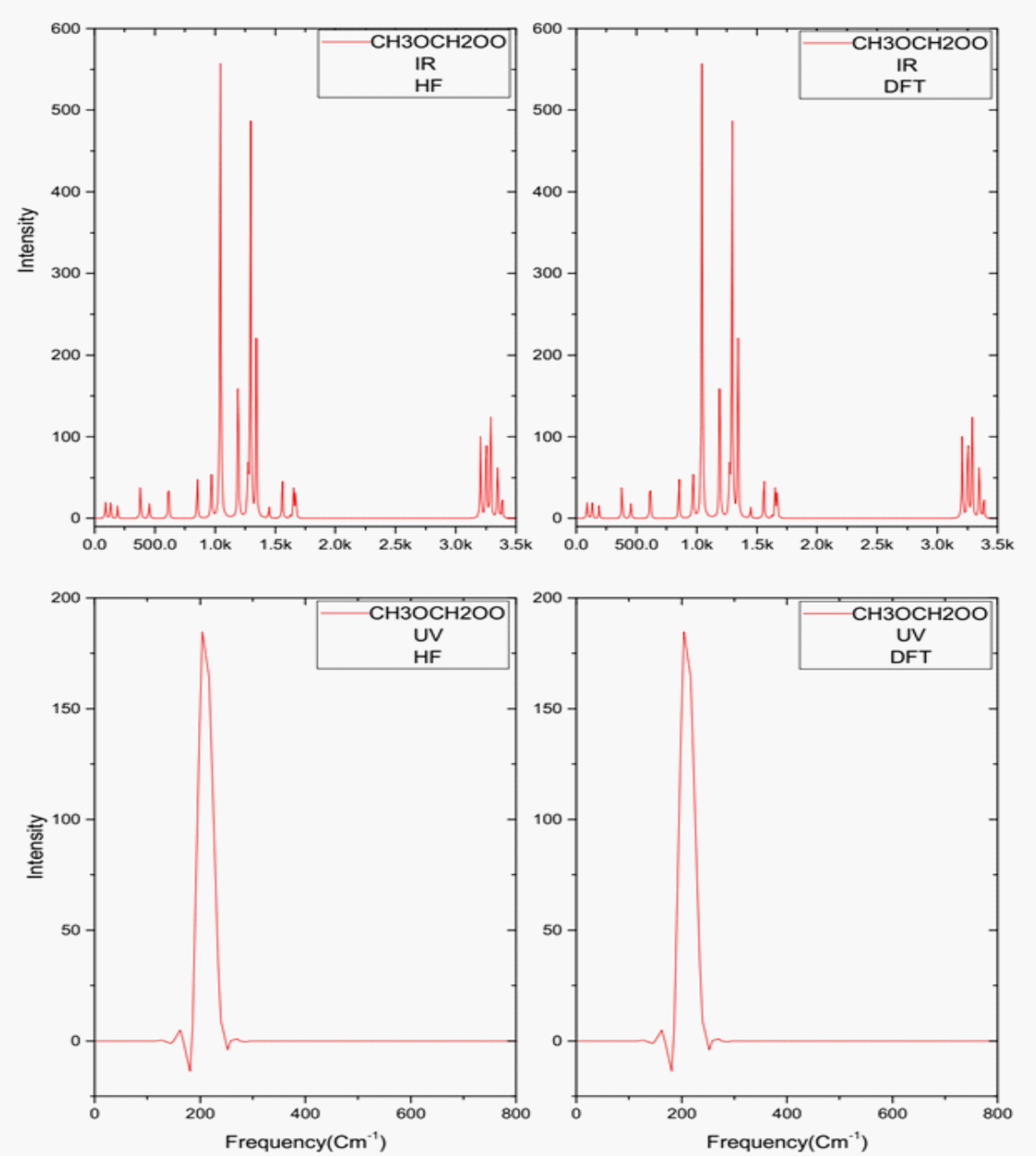

Fig 4.2.4. Infrared and Ultraviolet spectra of the $\mathbf{CH_3OCH_2OO}$ optimized structure determined with HF and DFT approximations, by $\mathbf{6-31G}$ basis set

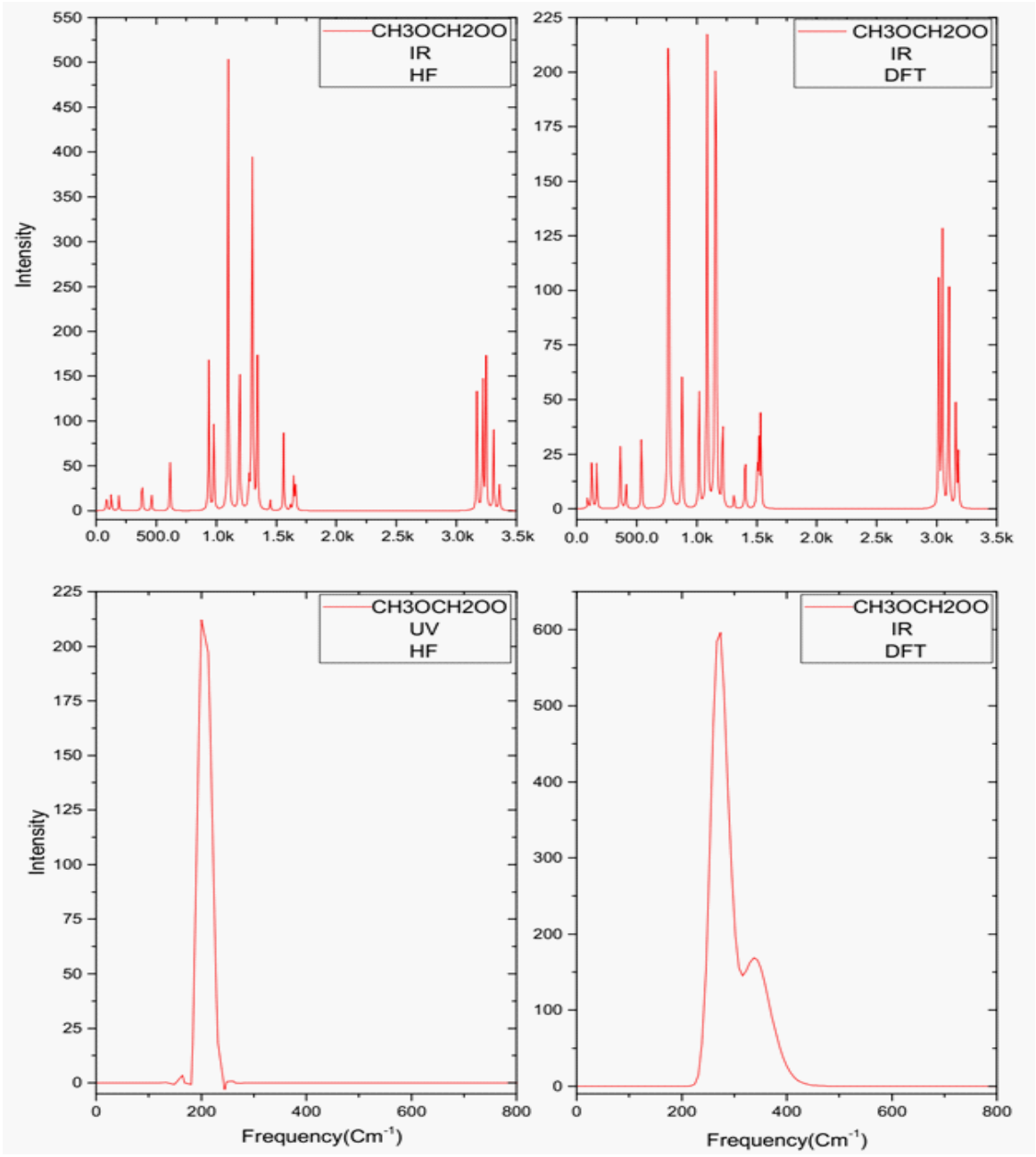

Fig 4.2.5. Infrared and Ultraviolet spectra of the $\mathbf{CH_3OCH_2OO}$ optimized structure determined with HF and DFT approximations, by $\mathbf{6-311G}$ basis set

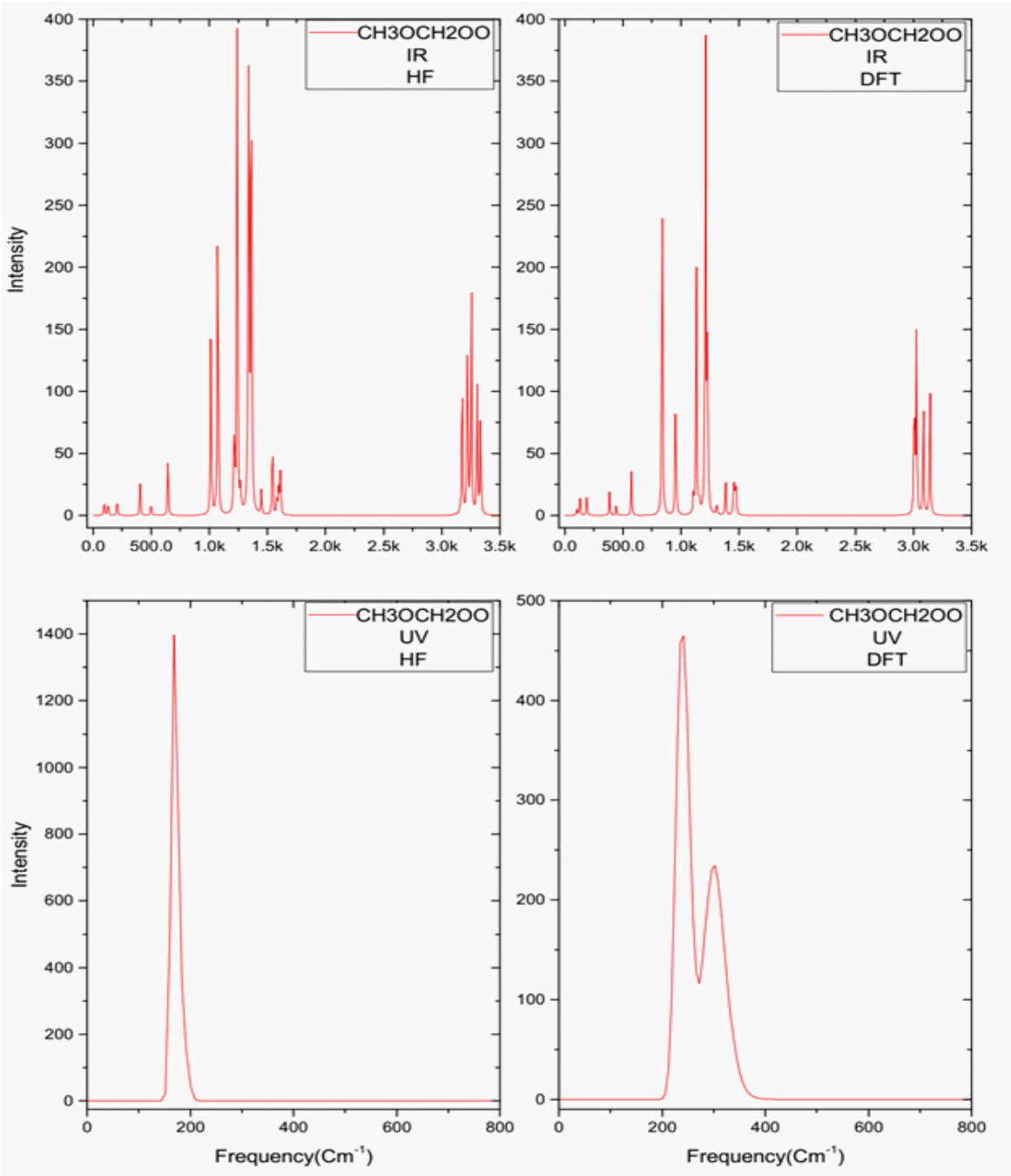

Fig 4.2.6. Infrared and Ultraviolet spectra of the $\mathbf{CH_3OCH_2OO}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVQZ}$ basis set

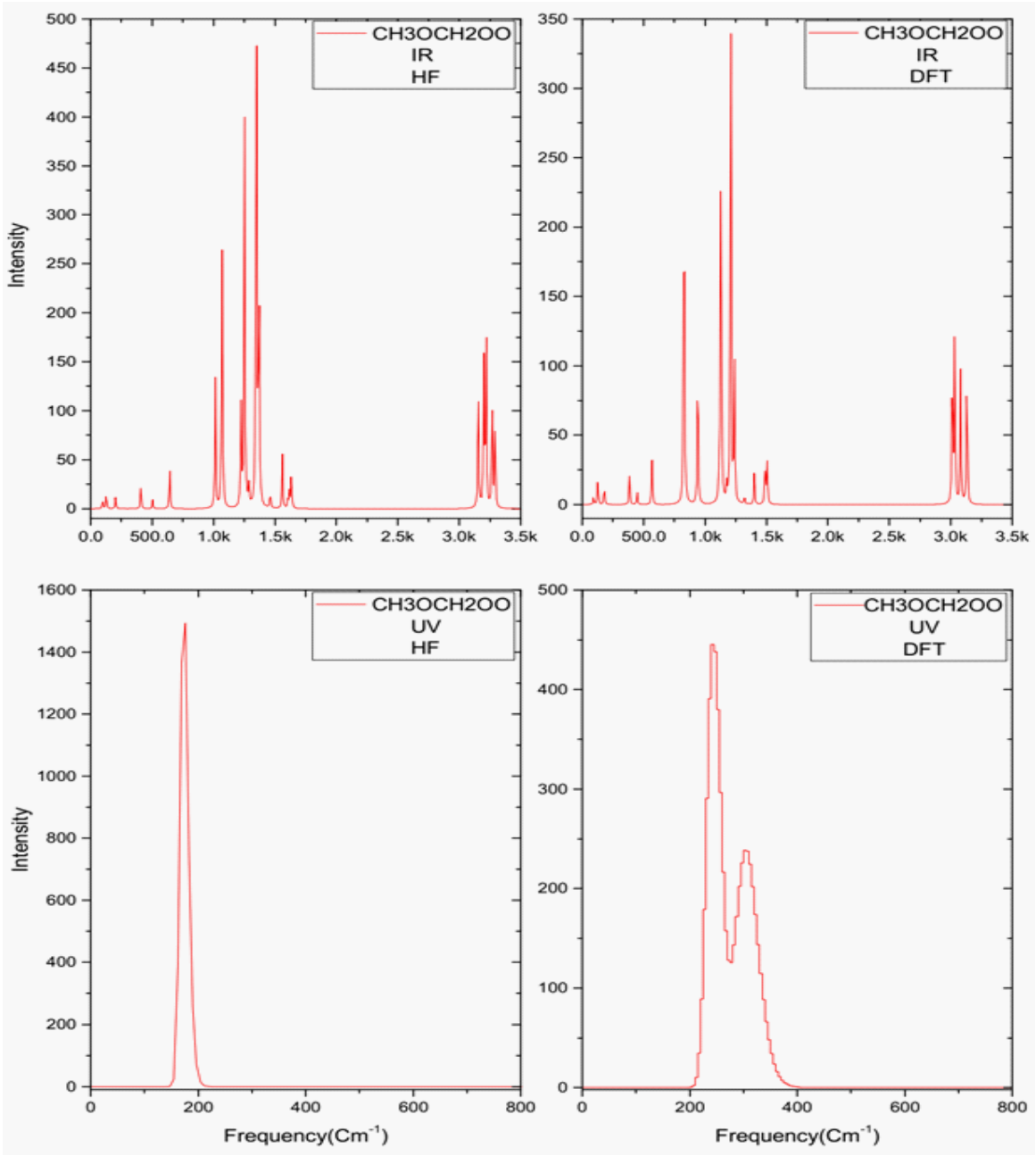

Fig 4.2.7. Infrared and Ultraviolet spectra of the $\mathbf{CH_3OCH_2OO}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVQZ}$ basis set.

As can be seen in all the figure there have been many peaks in the IR figures here also we can see the big difference between $\mathbf{CH_3OCH_2OO}$ and $\mathbf{NO_3}$ molecule in repeat of the number on the results .In the different basis set it have different vibration if we use the last basis set its give us more oscillation also. Here again we try to out the effect of basis sets on the results.

4.3. Ethane C_2H_6

Ethane as one of the important molecule in chemistry and it has been well known in literature

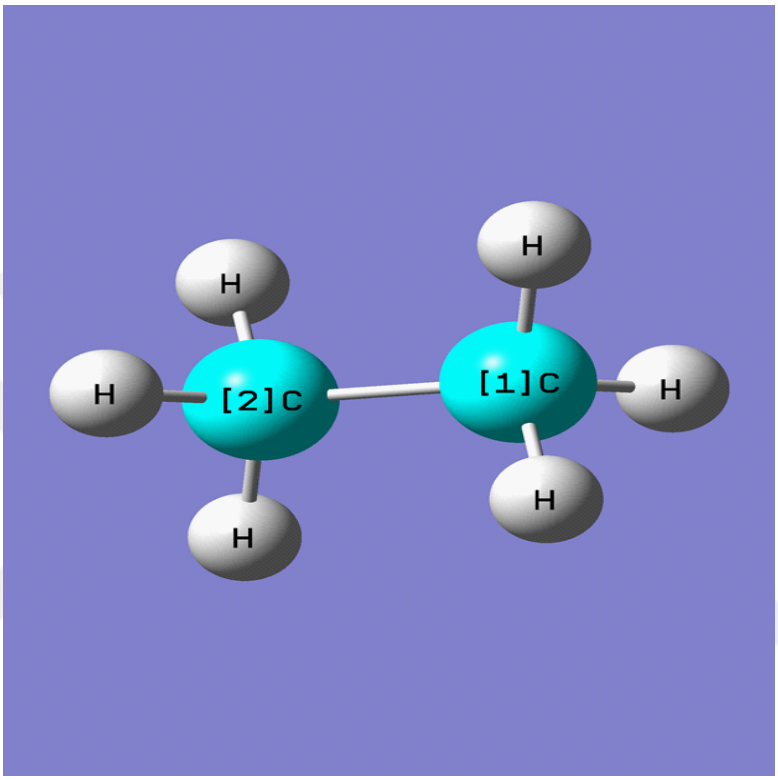

Fig 4.3.1. The optimized geometric structure with atoms numbering for $\mathbf{CH_3CH_3}$

Ethane is found in all parts of the world, in natural gas deposits, petroleum and many minerals. It exists as a colorless, odorless gas at room temperature and is the primary chemical used to create ethylene, the most widely used organic compound in the world. Ethane heavier than air and can creep along the ground or gather in low places, and if they encounter an ignition source, can flash back to the body of ethane from which they evaporated. Ethane occurs as a trace gas in the Earth's atmosphere, at a current concentration at sea level of around 0.5 parts per billion by volume (ppbv) It has also been detected as a trace component in the atmospheres of all four giant planets, Atmospheric ethane results from the Sun's photochemical action on methane gas, also present in these atmospheres: ultraviolet photons of shorter wavelengths than 160 nanometer (nm) can photo-dissociate the methane molecule into a methyl radical and a hydrogen atom. When two methyl radicals recombine, the result is ethan and in

the atmosphere of Saturn's moon Titan. Containers recently emptied of ethane may contain insufficient oxygen to support life. Beyond this asphyxiation hazard, ethane poses no known acute or chronic toxicological risk. It is not known or suspected to be a carcinogen more than 109 million tons of ethylene are produced from ethane each year.

Ethane

- $Molecular\ Formula$ $C_{\mathbf{2}}H_{\mathbf{6}}$
- $Molar\ mass$ $30.07g/mol$
- $Monoisotopic\ mass$ $30.046949Da$
- $Appearance$ $colourlessgas$
- $Density$ $1.212kg/m^3, gas$
- $Melting\ point$ $-182.76°C(90.34K)$
- $Boiling\ point$ $-88.6°C(184.5K)$
- $ChemSpider$ $ID6084$

Thermochemistry for Ethane ($\mathbf{C_2H_6}$)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 6 and mass 12.00000

Atom 3 has atomic number 1 and mass 1.00783

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 1 and mass 1.00783

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 1 and mass 1.00783

Atom 8 has atomic number 1 and mass 1.00783

Molecular mass: 30.04695 amu.

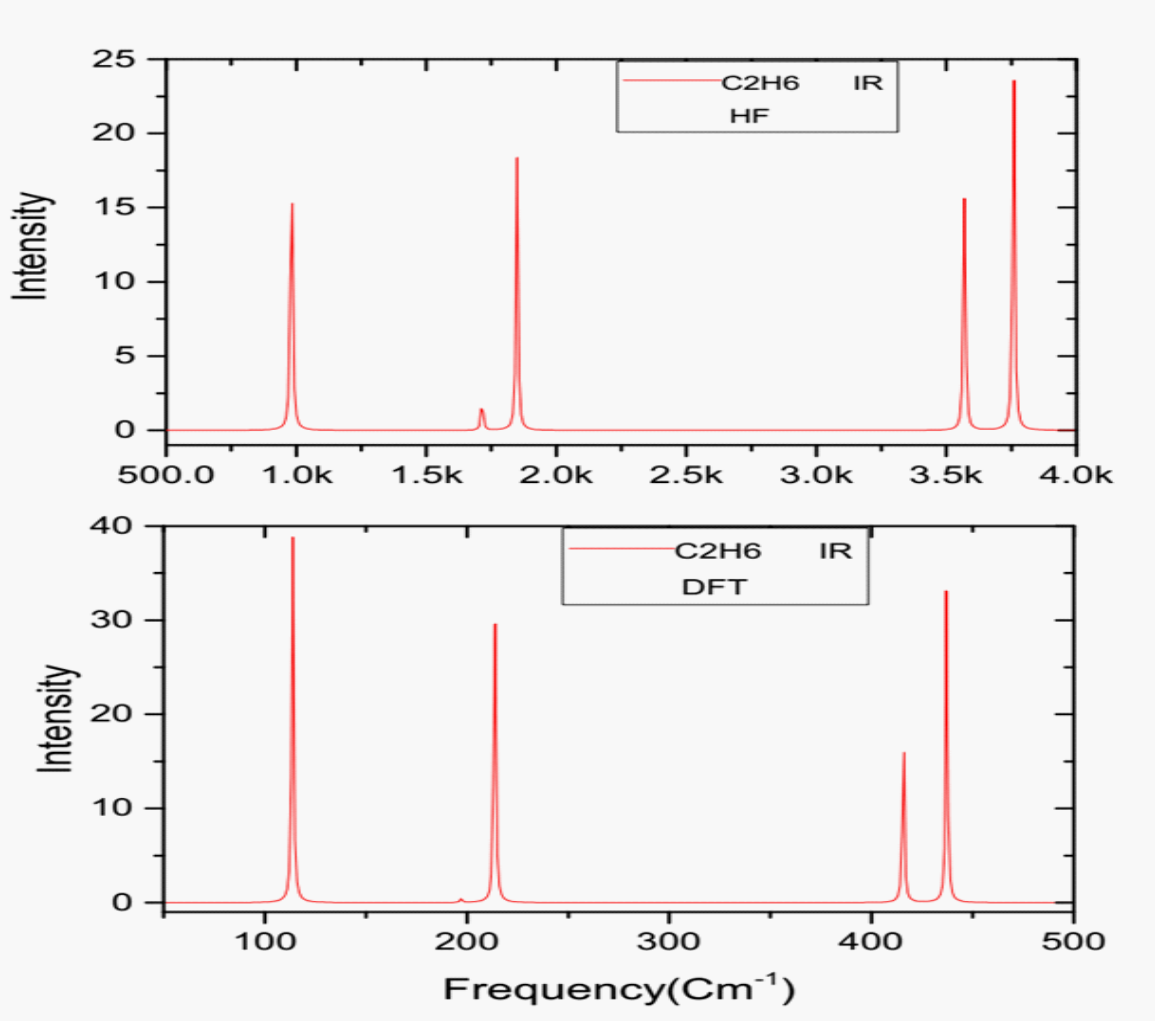

Fig 4.3.2. Infrared spectra of the $\mathbf{CH_3CH_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{STO-3}$ basis set

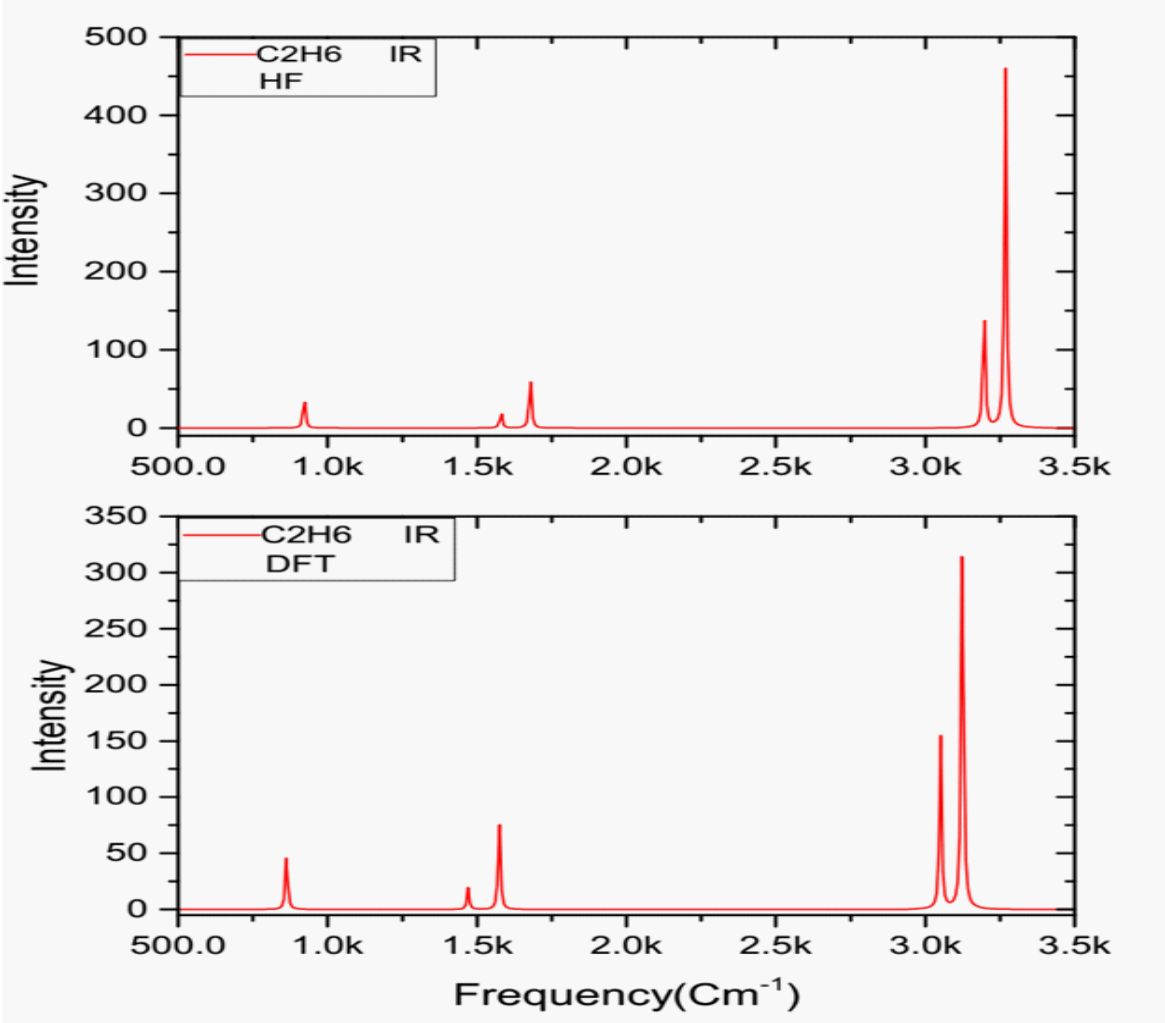

Fig 4.3.3. Infrared spectra of the $\mathbf{CH_3CH_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{3-21G}$ basis set

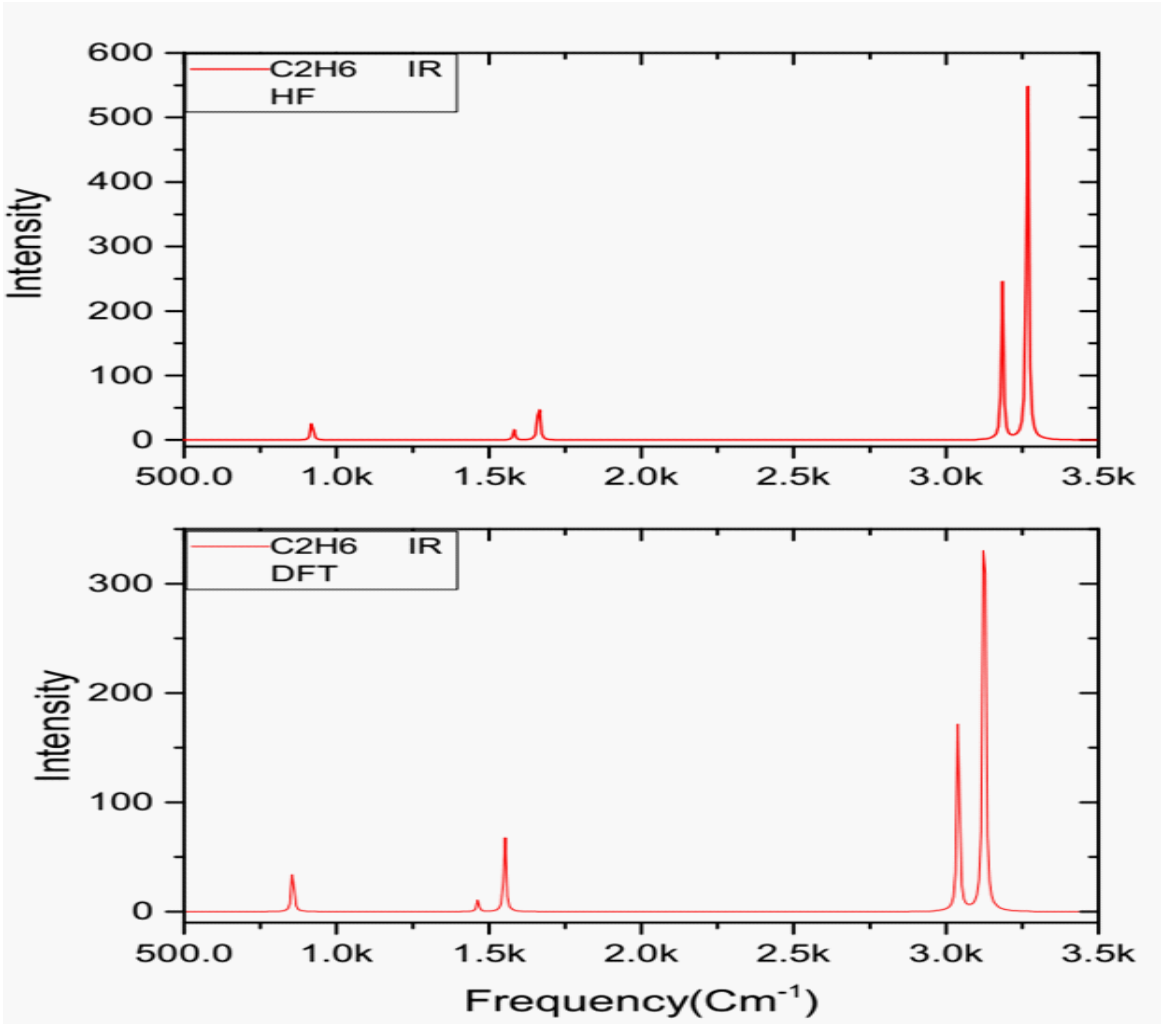

Fig 4.3.4. Infrared spectra of the $\mathbf{CH_3CH_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{6-31G}$ basis set

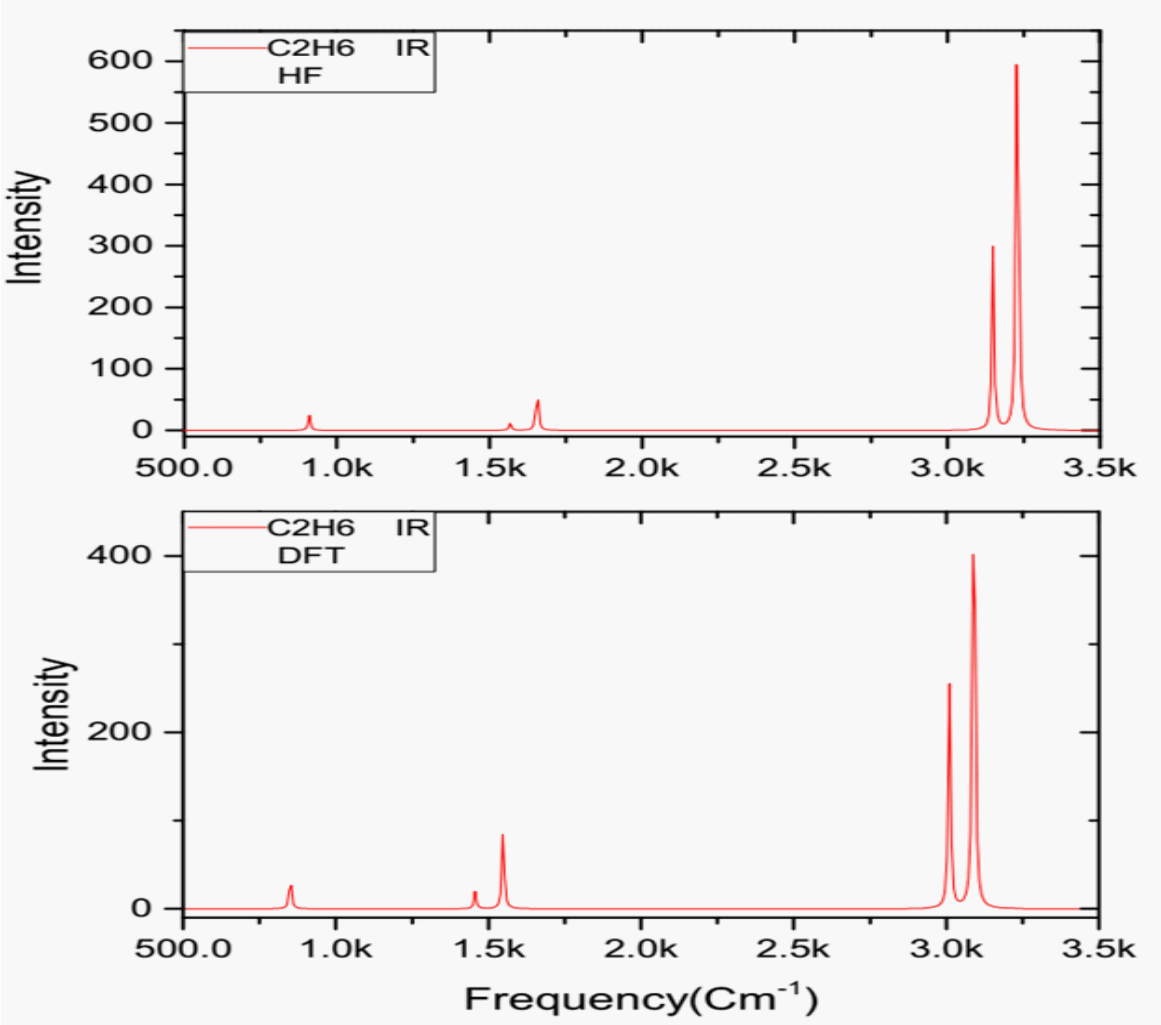

Fig 4.3.5. Infrared spectra of the $\mathbf{CH_3CH_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{6-311G}$ basis set

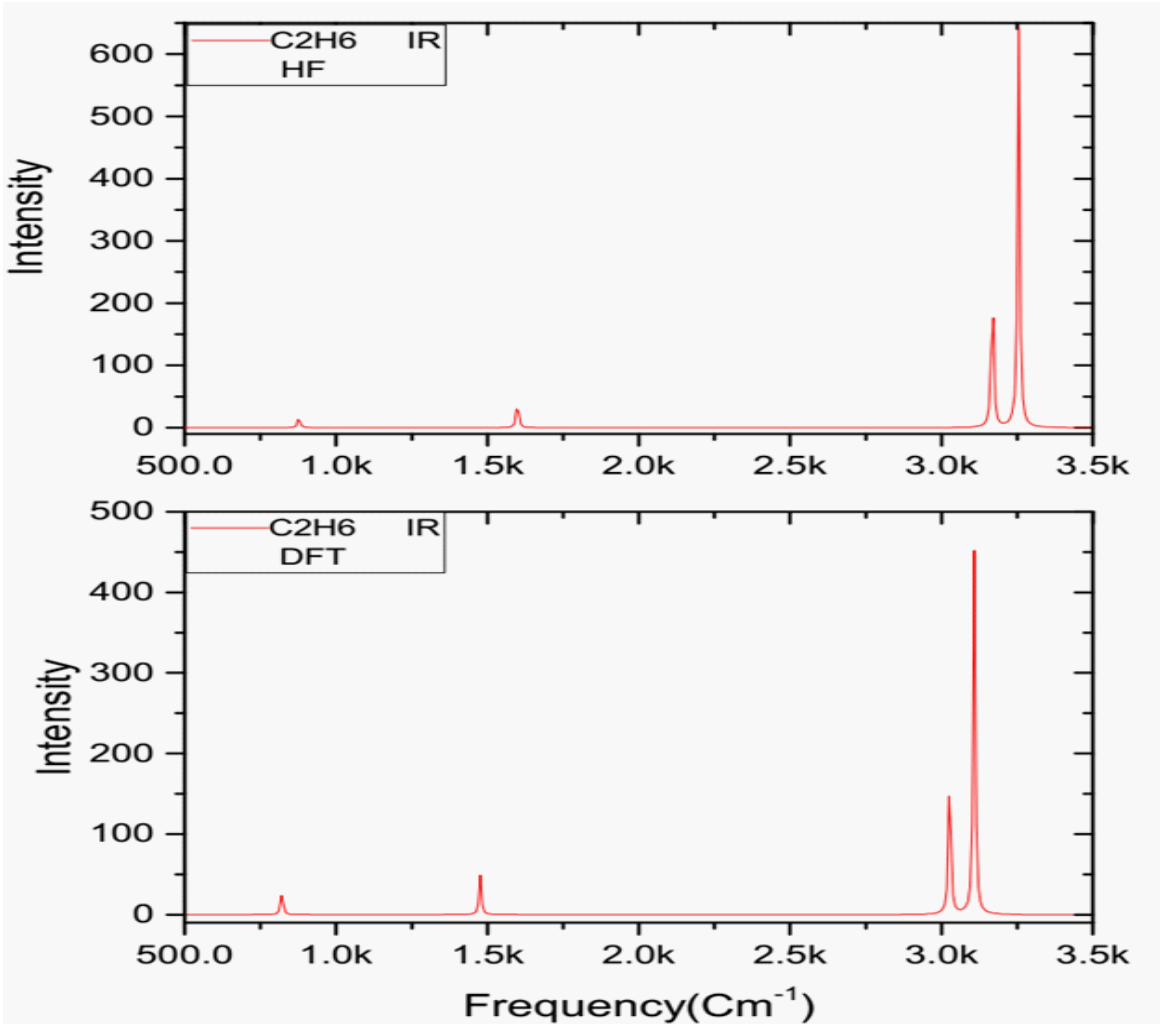

Fig 4.3.6. Infrared spectra of the $\mathbf{CH_3CH_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVDZ}$ basis set.

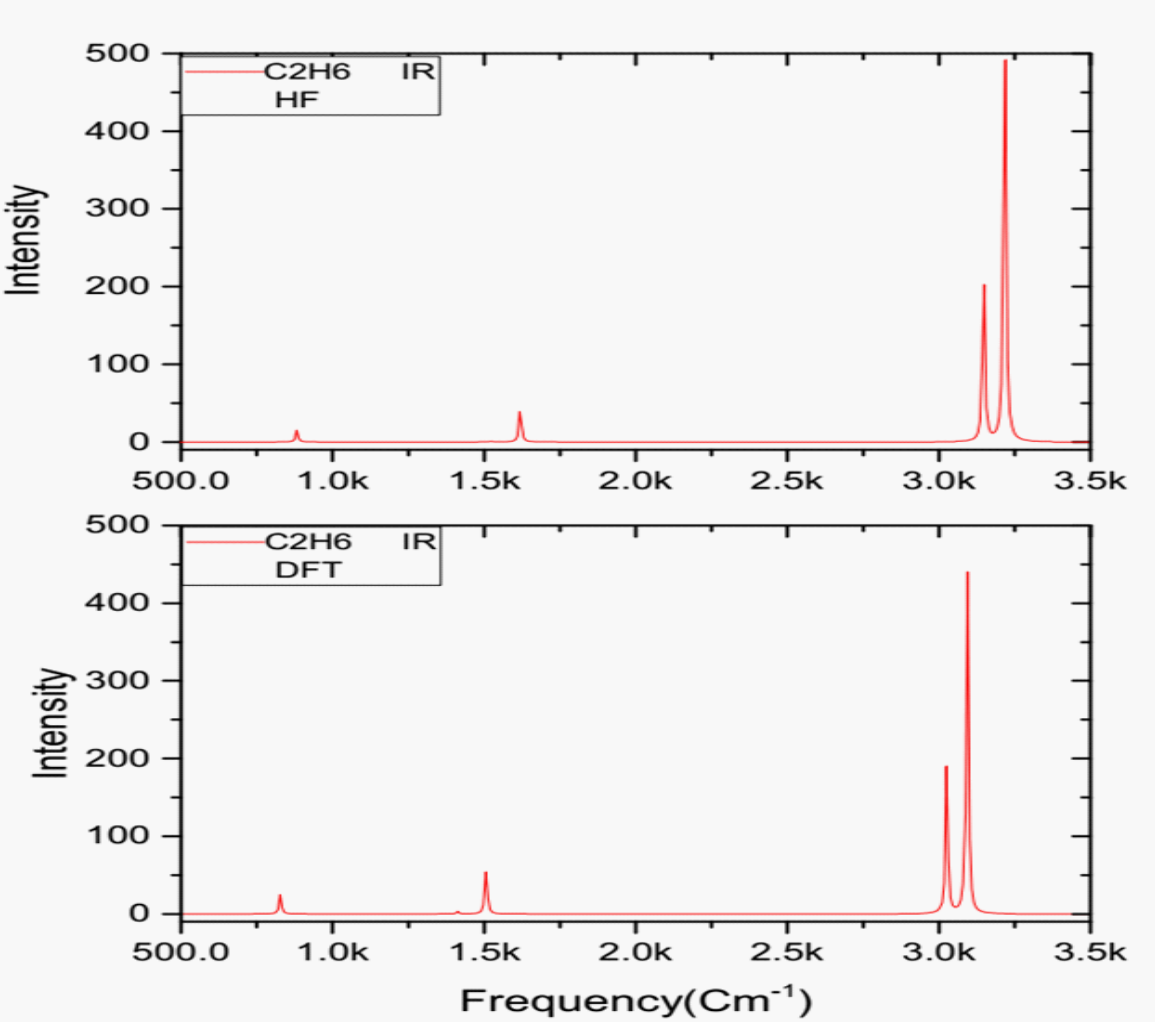

Fig 4.3.7. Infrared spectra of the $\mathbf{CH_3CH_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVQZ}$ basis set.

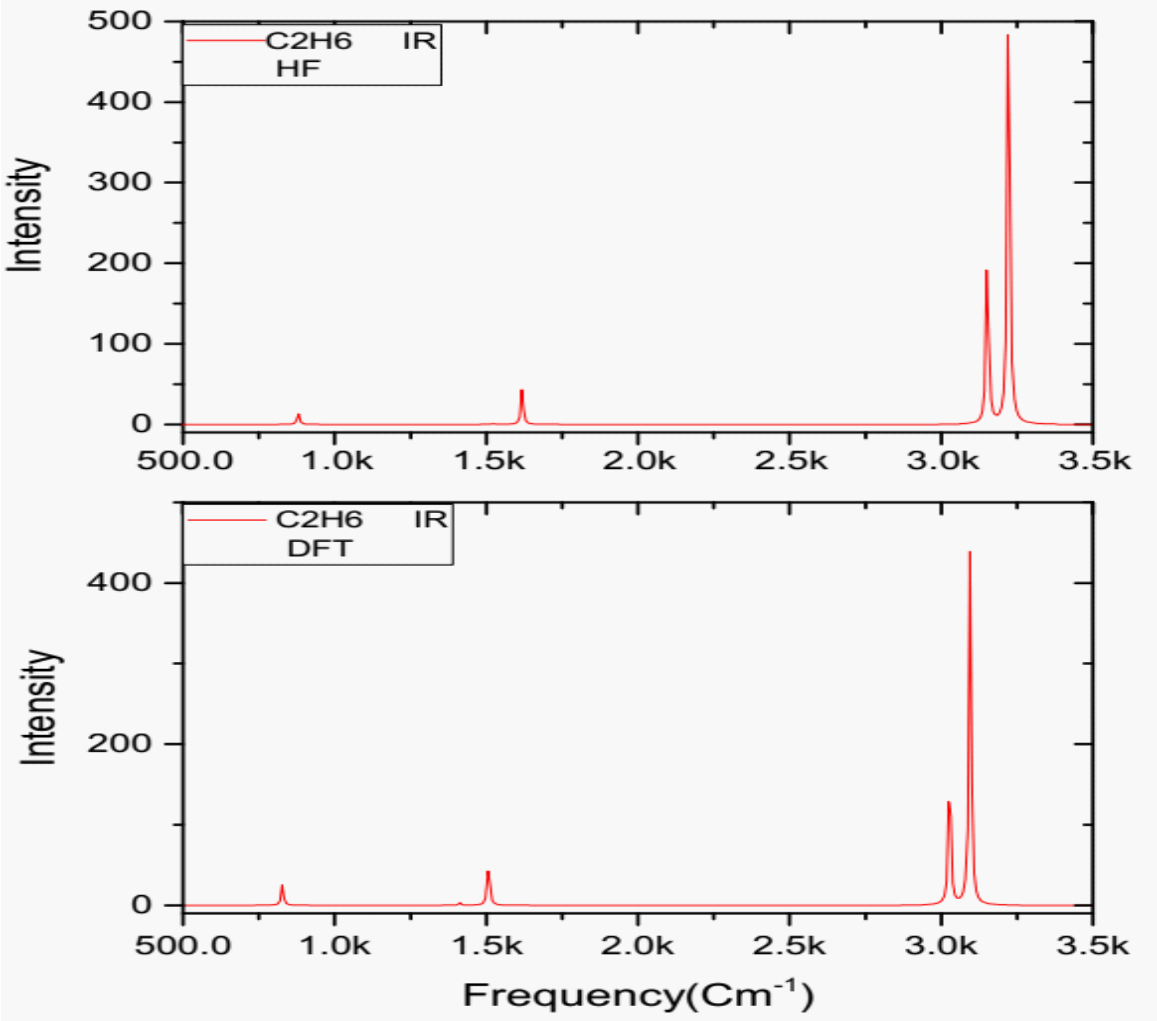

Fig 4.3.8. Infrared spectra of the $\mathbf{CH_3CH_3}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVTZ}$ basis set.

For this molecule the obtained values are compared with literature and it is found that our results one very well reproduced the literature. Here again the number of peaks are proportion to the number of vibration motion of molecule. For this molecule we could not find out the UV spectrum because Ethane in origin is colourless Ethene only have IR spectrum.

4.4. Ethyl radical CH_3CH_2

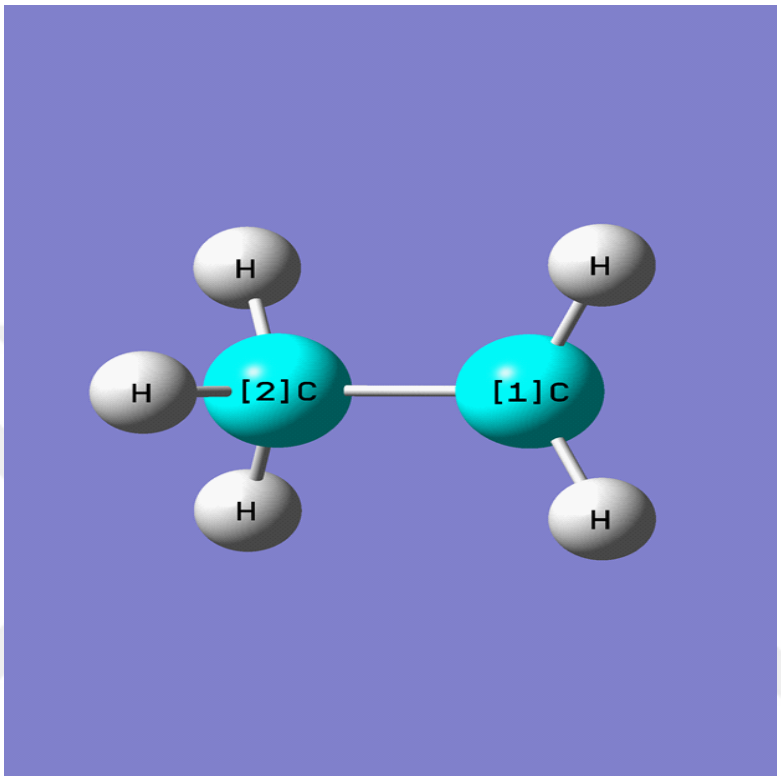

Fig 4.4.1. The optimized geometric structure with atoms numbering for $\mathbf{C_2H_5}$.

CH_3CH_3 is ethane. If you remove an H, and attach the CH_3CH_2 to something else, we remove the "ane" and attach a "yl" and call it an "ethyl group" or "Ethyl radical"

- $Molecular\ Formula$ C_2H_5
- $Molar\ mass$ $29.0611 g/moL$
- $Monoisotopic\ mass$ $29.039125\ Da$
- $ChemSpider\ ID$ 109753

Thermochemistry for $\mathbf{CH_3CH_2}$

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Atom 1 has atomic number 6 and mass 12.00000

Atom 2 has atomic number 6 and mass 12.00000

Atom 3 has atomic number 1 and mass 1.00783

Atom 4 has atomic number 1 and mass 1.00783

Atom 5 has atomic number 1 and mass 1.00783

Atom 6 has atomic number 1 and mass 1.00783

Atom 7 has atomic number 1 and mass 1.00783

Molecular mass: 29.03913 amu.

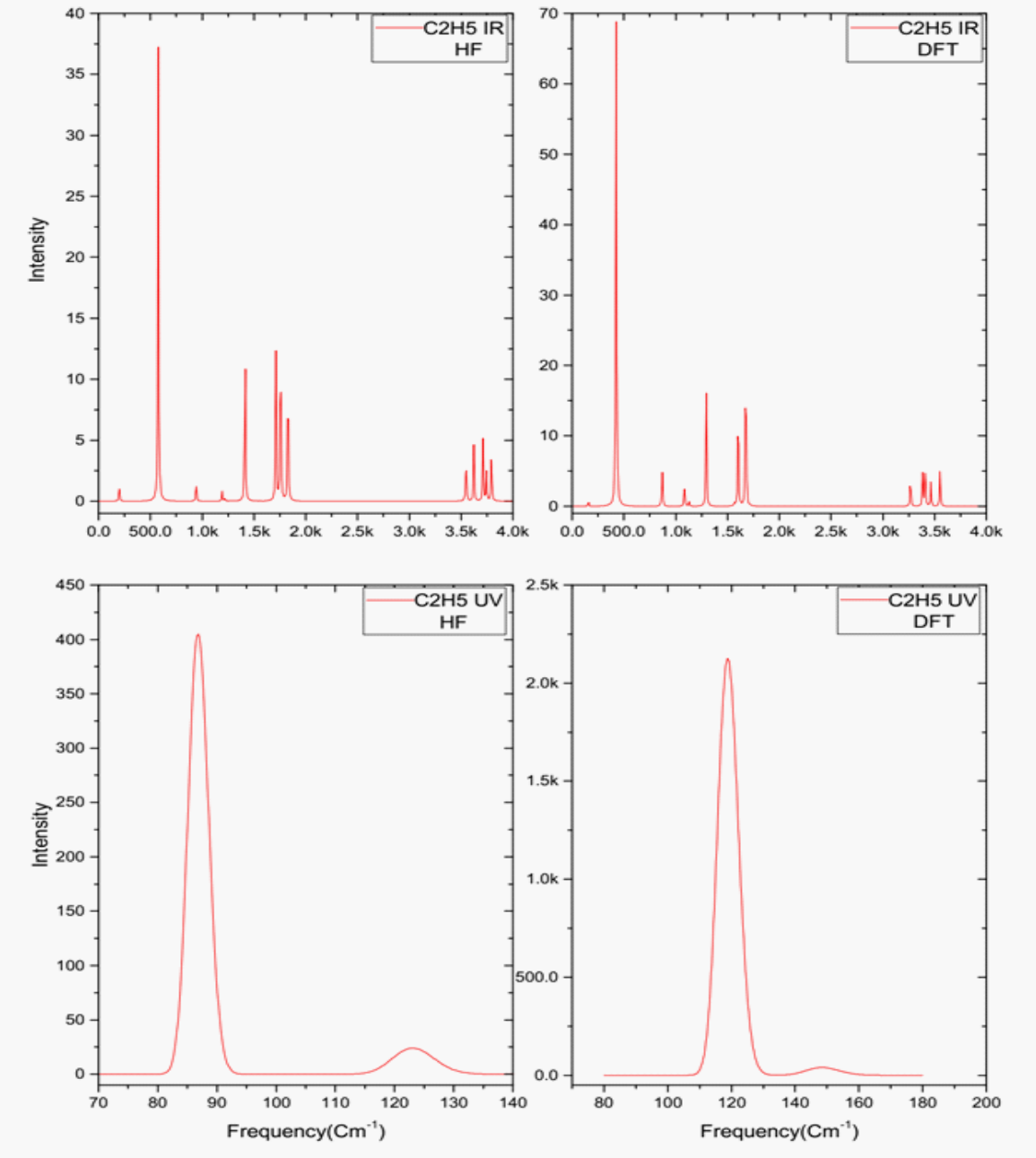

Fig 4.4.2. Infrared and Ultraviolet spectra of the $\mathbf{C_2H_5}$ optimized structure determined with HF and DFT approximations, by $\mathbf{STO-3G}$ basis set

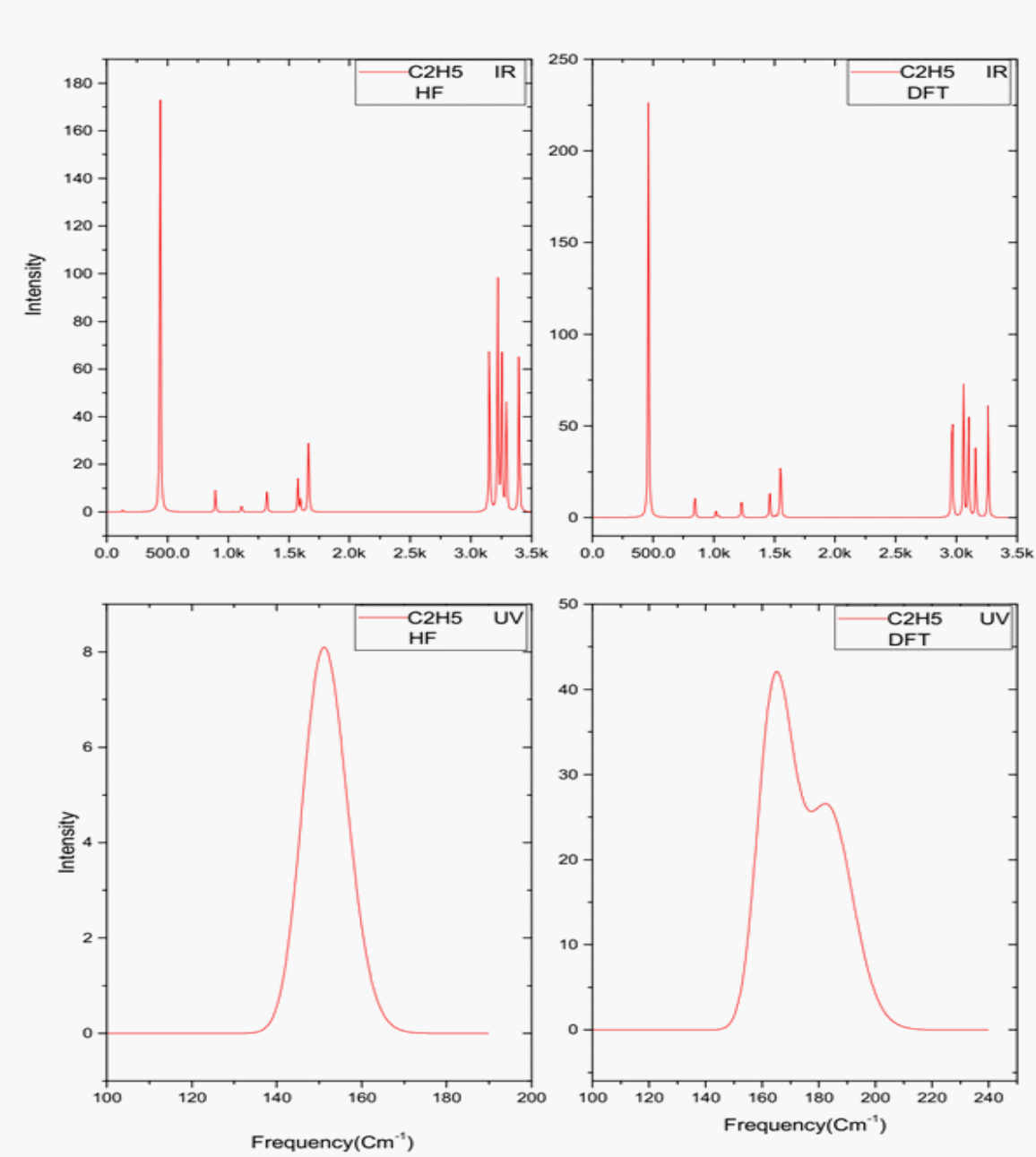

Fig 4.4.3. Infrared and Ultraviolet spectra of the $\mathbf{C_2H_5}$ optimized structure determined with HF and DFT approximations, by **3.21G** basis set

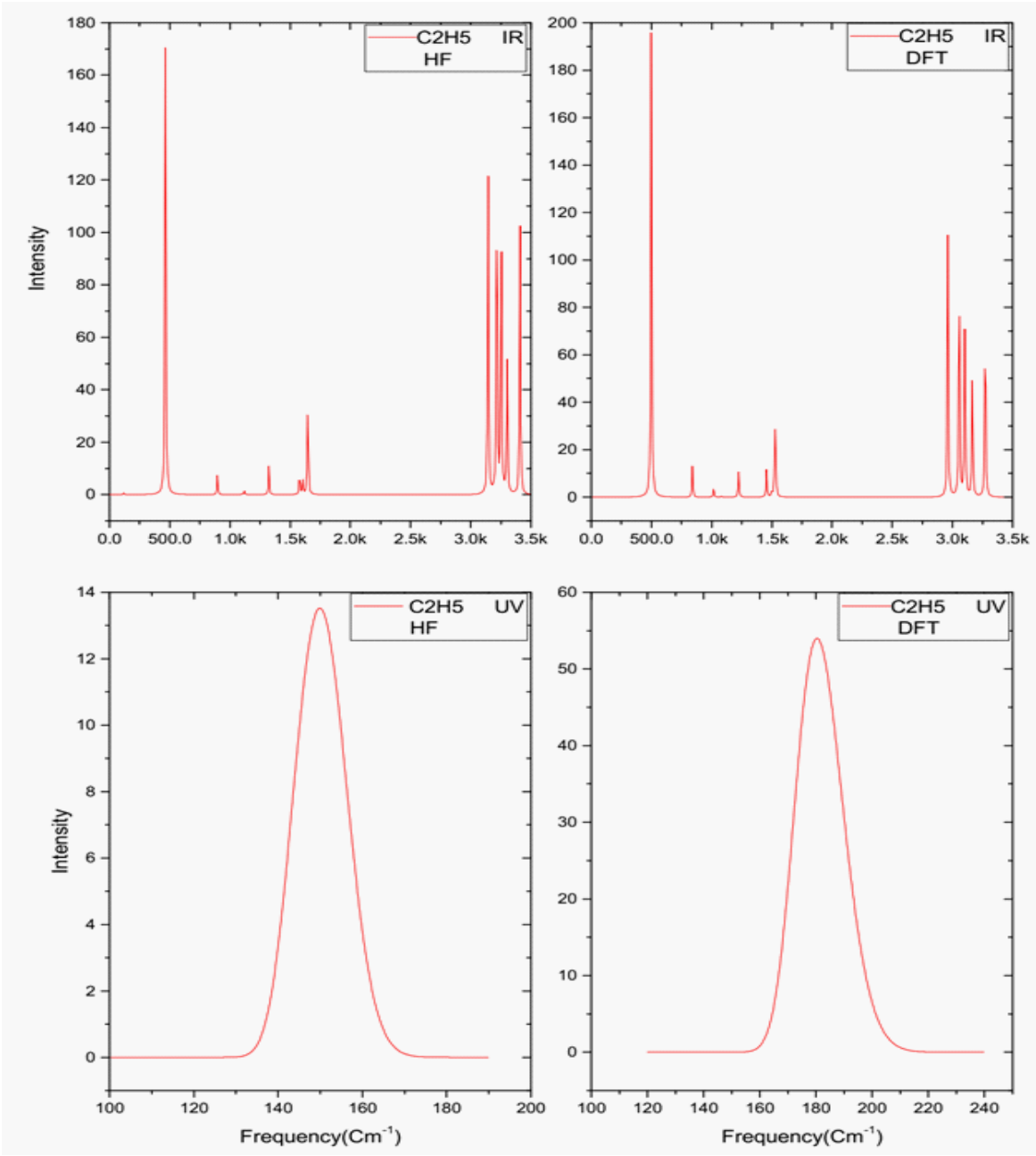

Fig 4.4.4. Infrared and Ultraviolet spectra of the $\mathbf{C_2H_5}$ optimized structure determined with HF and DFT approximations, by $\mathbf{6-31G}$ basis set

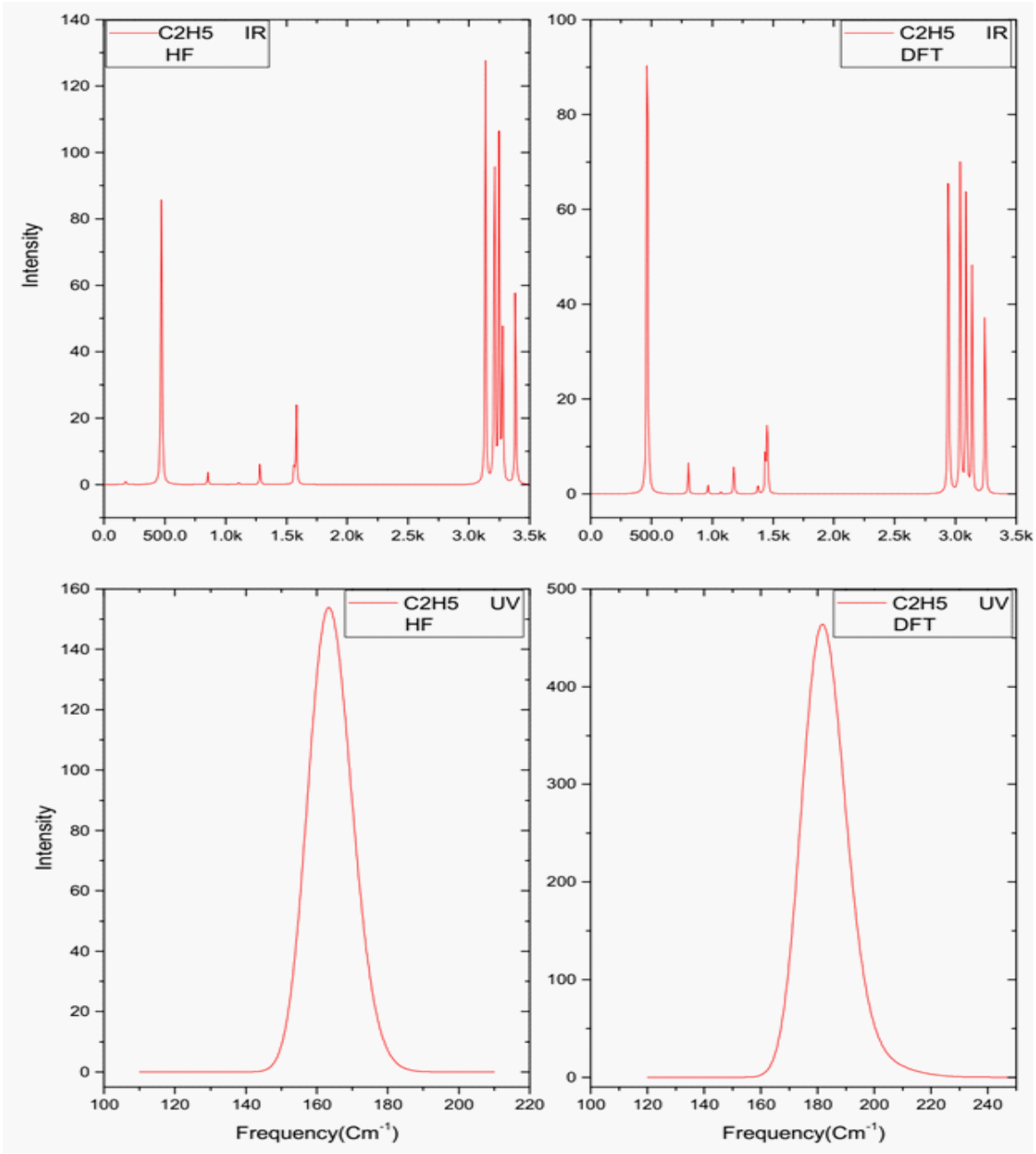

Fig 4.4.6. Infrared and Ultraviolet spectra of the $\mathbf{C_2H_5}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVDZ}$ basis set

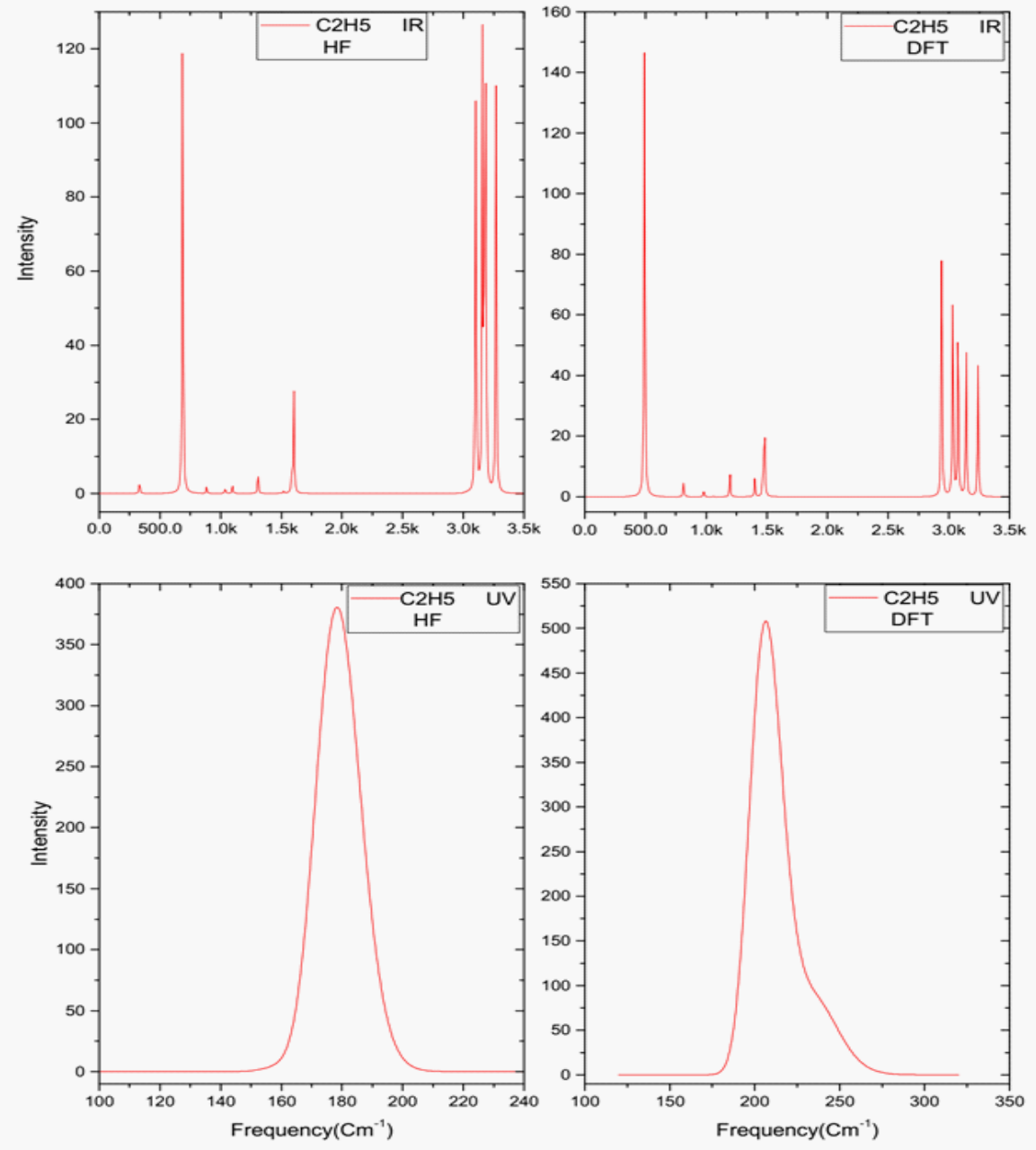

Fig 4.4.7. Infrared and Ultraviolet spectra of the $\mathbf{C_2H_5}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVQZ}$ basis set

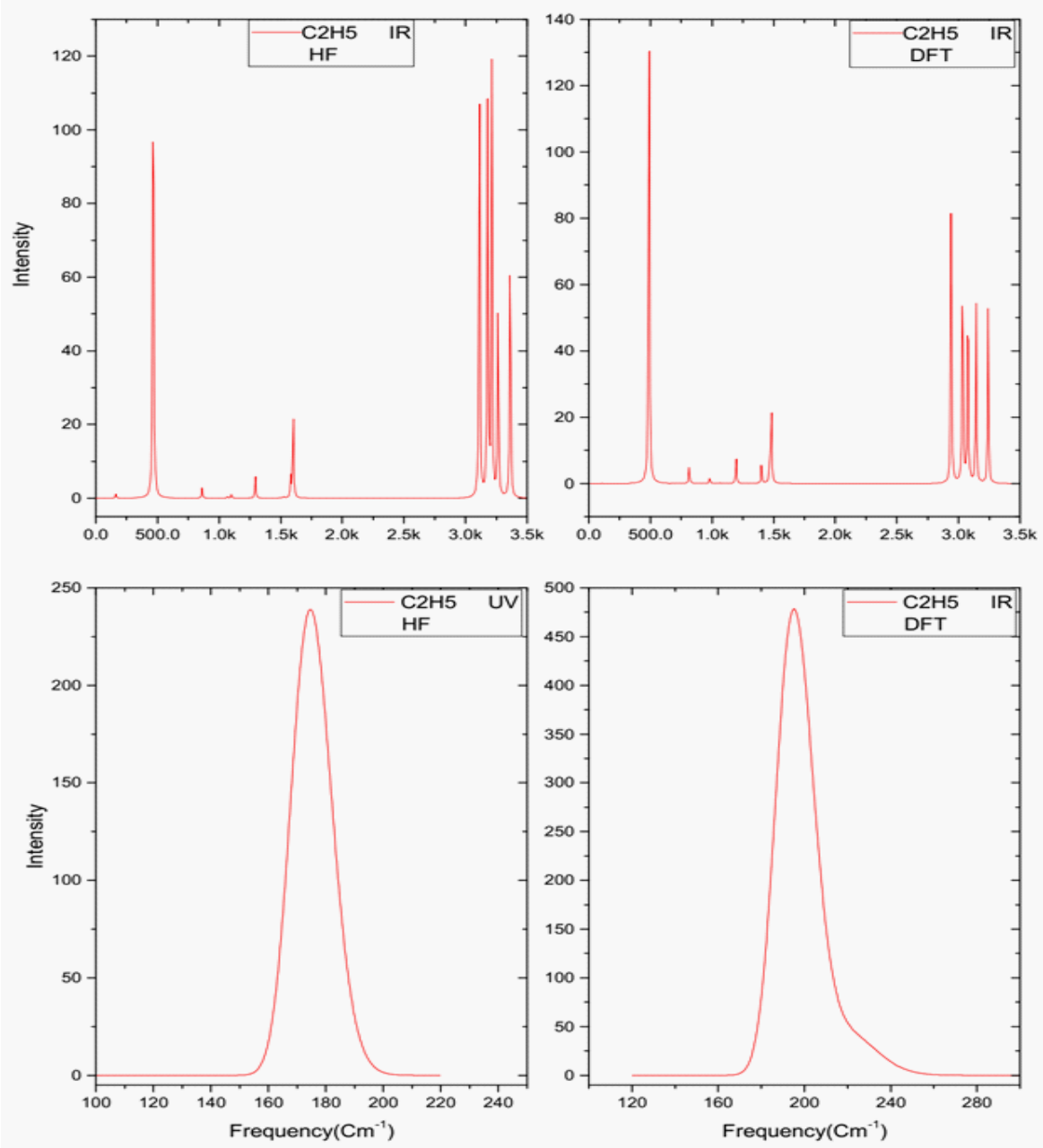

Fig 4.4.8. Infrared and Ultraviolet spectra of the $\mathbf{C_2H_5}$ optimized structure determined with HF and DFT approximations, by $\mathbf{cc-pVTZ}$ basis set

This C_2H_5 radical is also important in chemistry and astrophysics, in the simple basis set we can see the its not have resonance but in the last basis set As can be seen there have been many resonance in increased in the high frequency which is corresponds to vibrational motion of CH molecule.

5. Conclusion

As results, in this thesis different molecule which are important in astrophysics have been investigated by HF and DFT method, All molecule optimized with a fine grid and the IR and UV calculation have been done for each molecule by important thing different basis sets increase the accurate of calculation increases, Also depending of the molecule the vibration motion of molecule is proportion with respect to the number of modes of the system that one consider in this thesis.

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