

Ab-initio-rhf methods calculation to study the fundamental vibrational frequency of Acetone (CH₃-CO-CH₃)

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Abstract

The electronic distribution and energy level as well as modes of vibration of Acetone molecule are studied theoretically using ab-initio methods .

The geometry optimization of the acetone was obtained depending on the restricted Hartree- Fock (rhf) equation for the restricted system by using STO - 3G basis sets.

The modes of vibrations were calculated under the steady state geometry condition and presented in graphically with frequency,intensity and symmetry for each mode.

The molecular orbital calculation and energy level diagram appears that paired electron . The Ionization potential is equal to = 8.757333 eV , while the low electron affinity is equal to =8.075379 eV.

The total energy of acetone equal to (-5157.258583 eV) where calculated by Ab-initio method compared with different semi-empirical methods, indicate that Ab-initio method is very high accurate method to give the geometry more stable , because it takes in to a ccount all electron internal and external orbital but need a long time for calculation with a large process capacity .

الخلاصة

تم دراسة التوزيع الالكتروني وطاقة المستوي كذلك انماط الاهتزاز لجزيئة الاسيتون نظريا باستخدام طريقة المبادئ الاساسية المحددة لهارتري- فوك (ab-initio) .

ان تحقيق أمثلية هندسة الأسيون حصل على الإعتماد على معادلة هارترى – فوك للنظام المقيد باستعمال مجموعة القواعد STO-3G .

تم حساب انماط الاهتزاز الاساسية لجزيئة الاسيتون تحت شروط الاستقرار الجزيئي الهندسي وتمثيلها بشكل تخطيطي مع التردد والشدة والتمائل لكل نمط .

كما تم تمثيل المدارات الجزيئية ومستويات الطاقة بشكل تخطيطي يظهر فيها المزدوج الالكتروني . كما تم حساب طاقة جهد التاين والتي كانت يساوي (8.757333 eV) , بينما الالفة الالكترونية تساوي (8.075379 eV) .

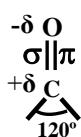
ان الطاقة الكلية المحسوبة لجزيئة الاسيتون المحسوبة بطريقة المبادئ الاساسية Ab-initio فكانت (-5157.258583eV) مقارنة بطرائق شبيه تجريبية مختلفة , تدلل مدى الدقة العالية لهذه الطريقة المستخدمة في البحث للحصول على الشكل الهندسي الفراغي الاكثر استقرارا , بسبب كون هذه الطريقة تأخذ في الحساب كل الكترونات المدار الداخلي والخارجي لكنها تحتاج الى وقت اطول في الحسابات مع قدرة عملية واسعة .

Introduction:

Theoretical computation in physics and chemistry using various methods dependant on ab-initio and semi empirical methods are widely used. These methods are very important to the studies of matter and its physical properties. The advancement in computer systems enabled the improvement in the increased accuracy and speed of evaluating theoretical results.

Many searchers used ab-initio and semi empirical methods for example , (Laref,2000) studied the band structure of Germanium crystal using semi empirical methods (Benzair and Aourag , 2003)

studied the electronic properties and total energy of Zinc-blende compounds using ab-initio and density functional methods.

In this work, the distribution , energy levels and normal modes of vibration of Acetone molecule which consist a Carbonal group  are studied using ab-initio methods .

The main goal is to classify the Acetone as an example of non-linear molecule theoretically according to group theory using the linear combination of Atomic orbitals (LCAO) .

Methods:

I- Hartree - Fock theory .

In Hartree Fock HF theory , the wave function is represented by a single N-dimensional slater determinant $\phi(x_1, x_2, \dots, x_N)$ made up of N orthonormal spin orbital $\{X_i(x)\}$, where x represents both the position r and the spin ω of an electron . Each spin orbital can be have both a spin up α and spin down β part; $\psi_i^\alpha(r)$ and $\psi_i^\beta(r)$ respectively (parr and yang 1989). Hence , the spin orbitals can be written as :

$$X_i(x) = \psi_i^\alpha(r) \alpha(\omega) + \psi_i^\beta(r) \beta(\omega) \dots\dots\dots(1)$$

In restricted Hartree - Fock (RHF) and unrestricted Hartree - Fock (UHF) methods, each spin orbital is either pure α or pure β .In UHF theory , the two sets of molecular orbitals are defined by two sets of coefficients $C_{\mu i}^\alpha, C_{\mu i}^\beta$

$$\Psi_i^\alpha = \sum_{\mu=1}^N C_{\mu i}^\alpha \phi_\mu \quad \Psi_i^\beta = \sum_{\mu=1}^N C_{\mu i}^\beta \phi_\mu \dots\dots\dots(2)$$

For agiven nuclear configuration R_i that includes a system of M nuclei and a given set of orthonormal spin orbitals , the electronic energy $E_e(\{C_{\mu i}^\alpha, C_{\mu i}^\beta\}, \{R_i\})$ is (Sherrill,2000) :

$$E_e = \sum_{i=1}^N \langle X_i | -\frac{1}{2}V_I + \sum_{l=1}^N V_l(r_i, R_l) | X_i \rangle + \sum_{i=1}^N \sum_{j < i} \left[\langle X_i X_j | X_i X_j \rangle - \langle X_i X_j | X_i X_j \rangle \right] \dots\dots\dots(3)$$

Where

$$V_I(r_i, R_I) = \frac{Z_I}{|r_i - R_I|} \text{ for the electronic } r_i \text{ and nuclear } R_I$$

The Born-oppenheimer (Sherrill,2000;klienert,1990) approximation separates the electron and nuclear motions because the nuclear mass is so much larger than that of the electrons , and the nuclei move on a potential energy surface given by :

$$E(\{C_{\mu i}^{\alpha}, C_{\mu i}^{\beta}\}, \{R_i\}) = E_{ele} E(\{C_{\mu i}^{\alpha}, C_{\mu i}^{\beta}\}, \{R_i\}) + \sum_{I,J \in \{1\}}^M \frac{Z_I Z_J}{|R_I R_J|} \dots\dots\dots(4)$$

Where Z_I, Z_J are the atomic number for I and J atoms respectively .

II - Ab-initio Methods.

In ab-initio ,the calculations of electronic structure are based on the HF wave functions. The approximation ab-initio treatments are based on the variation principle which requires an evaluation of (szabo,and ostlund 1982) .

$$E [\Psi] = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \dots\dots\dots(5)$$

$$H = \sum_i h(i) + \sum_{i < j} \frac{1}{r_{ij}} \dots\dots\dots(6)$$

Where $h(i)$ represents the single i^{th} electron term which includes the kinetic energy of the electron as well as its energy associated with its interaction with the nucleus . The two electron term r_{ij} denotes the distance between electron i and j .

An application of the variation principle implies that all, integrals for Ψ should factorize into low dimensional cases .

This condition is achieved by building Ψ from the one electron function ϕ_i that are called molecular orbitals (Mo) , and this leads to the general properties :

$$\psi = \sum C_I \phi_I \dots\dots\dots(7)$$

$$\phi_I = [\phi_{i1} \dots\dots \phi_{in}] \dots\dots\dots(8)$$

$$\langle \phi_i | \phi_j \rangle = s_{ij} \dots\dots\dots(9)$$

Results and discussion

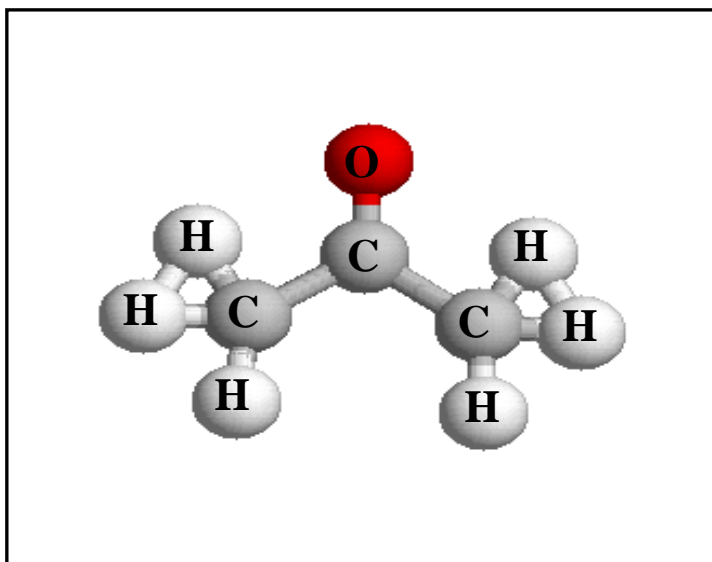
Before starting the calculation , it is necessary to select a geometry that enables the optimization of the compound studied in order to minimize its energy .

In this geometry , the force on the atoms can be calculated by evaluating the gradient of the energy with respect to atomic coordinates analytically .

In quantum mechanics computer programs, such as Mopac 7.21 and hyperchem 6.01, the form of geometry in put called z-matrix . This matrix specifies the positions of an atom(n) by three geometric parameters :

- 1- The bond length r between two atoms $r(i,j)$.
- 2- The bond angle θ at atom j between lines $j-i$ and $j-k$, $\theta(i,j,k)$.
- 3- The dihedral angle ϕ between the two planes defined by $i-j-k$ and $j-k-l$ meeting at the line $j-k$, $\phi(i,j,k,l)$.

The structure of the acetone was optimized at the restricted Hartree-Fock level of theory using the slater-type orbital (STO-3G) basis sets . The geometry optimization of the acetone studied is shown in Fig(1) .



Fig(1) Geometry optimization of Acetone

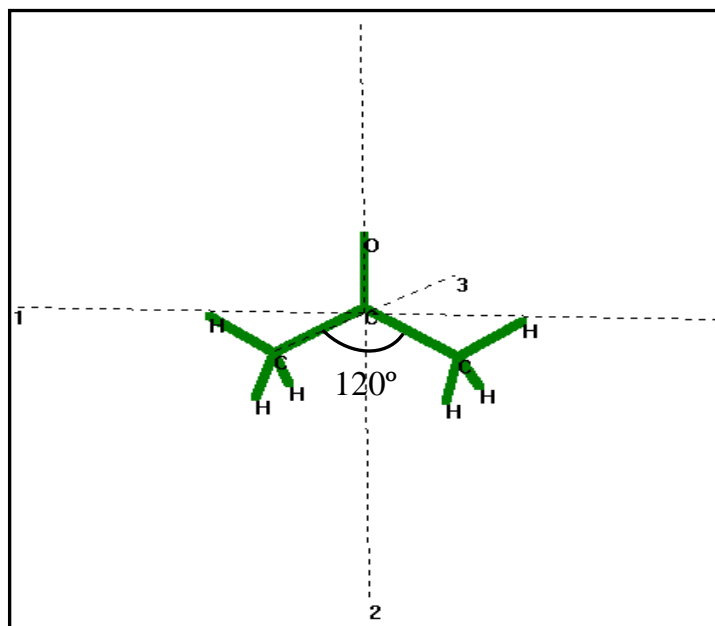
Table (1) shows the geometry of Acetone molecule as follow .

Table(1) Geometry parameters of $\text{CH}_3\text{-CO-CH}_3$

Bond	Bond length(\AA)	Bond angle(degree)
C-O	1.21	——
C-C	1.51	——
O-C-C	——	120

Using the coordinate system shown in Fig (2) , one can describe the molecular orbitals of the studied compound in terms of basis orbital derived from ;

- (i) The 2s,2p orbitals of the oxygen ion .
- (ii) The carbon ion 2s,2p orbitals .
- (iii)The hydrogen ion is orbitals .



Fig(2) Coordinates system diagram of the Acetone $\text{CH}_3\text{-CO-CH}_3$ molecule .

Table (2) shows the net charges and coordinates of the geometry more stable of actone molecule.

Table(2) Net charge and coordinates of acetone molecule.

Atom	Z	Charge (Mulliken)	Coordinates(Angstrom)			Mass
			X	Y	Z	
O	8	-0.226373	0.33914959	2.12955750	0.20987620	15.99900
C	6	0.211679	0.01538874	0.96251474	0.07441182	12.01100
C	6	-0.208437	1.04451581	-0.15065639	-0.21331462	12.01100
C	6	-0.208498	-1.4517617	0.49616026	0.17677388	12.01100
H	1	0.075463	2.04022678	0.27193775	-0.30005968	1.00800
H	1	0.070324	1.03831604	-0.88183252	0.59042114	1.00800
H	1	0.069976	0.79303379	-0.66218500	-1.13821755	1.00800
H	1	0.075496	-2.09844456	1.33794260	0.40150144	1.00800
H	1	0.070295	-1.7666580	0.04725224	-0.76129007	1.00800
H	1	0.070075	-1.55376548	-0.24985053	0.95989747	1.00800

Ab-initio calculation of the acetone total energy is the sum of the electronic energy plus core-core repulsion and ionization potential as well as dipole moment compare with different semi-empirical methods as presented in table (3) .

Table(3) Some physical properties calculated by Ab-initio method of acetone molecule.compare with different semi-empirical methods

Quantity	Ab-initio (present work)	Semi-empirical methods			
		MNDO- PM3	MNDO- AM1	MIND O/3	MNDO [7]
Total Energy (eV)	-5157.258583	-742.15	-787.41	-781.19	-791.31
Electronic Energy(eV)	-8375.019121	-2293.6	-2350.5	-2290.9	-2347.1
Core-Core Repulsion(eV)	3217.760538	1551.50	1562.86	1509.7 18	1555.7
Ionization Potential(eV)	8.757333	10.7706	10.6335	9.9527	10.734
Dipole Moment(Deby)	1.9182	2.77	2.8	3.2	2.4
No. of Filled Levels	16	12	12	12	12
Molecular Weight(g/mole)	58.08	58.08	58.08	58.08	58.08
Zero Point Energy(eV)	2.7126	2.277	2.3	2.279	2.407

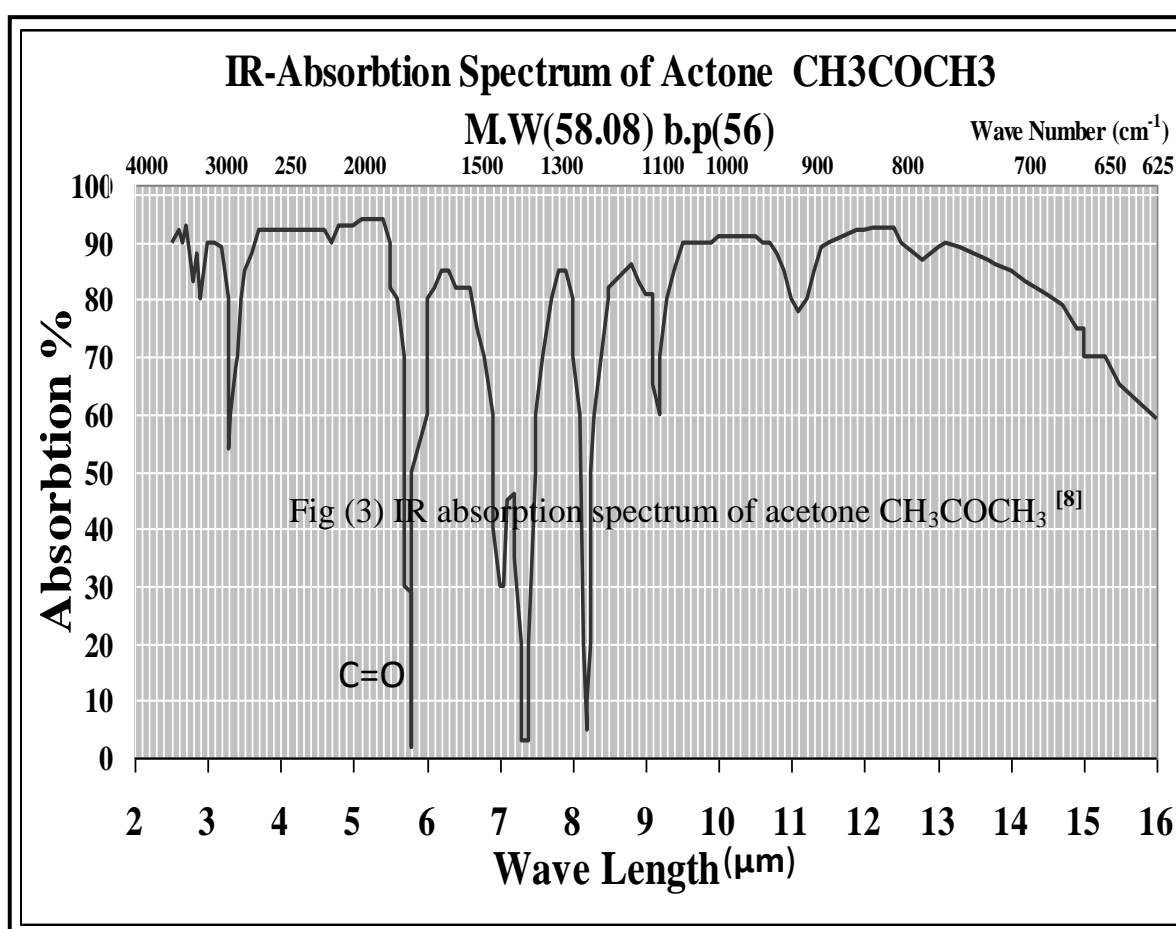
The normal modes of vibration of acetone nonlinear molecule are calculated which indicate 24 modes of vibration , 9 of these modes are stretching and the rest 15 is bending , are presented with frequency, intensity and symmetry for each modes as shown in table (4) .

Table(4)Rrepresents the normal modes of vibration with frequency,intensity,symmetry and types of modes

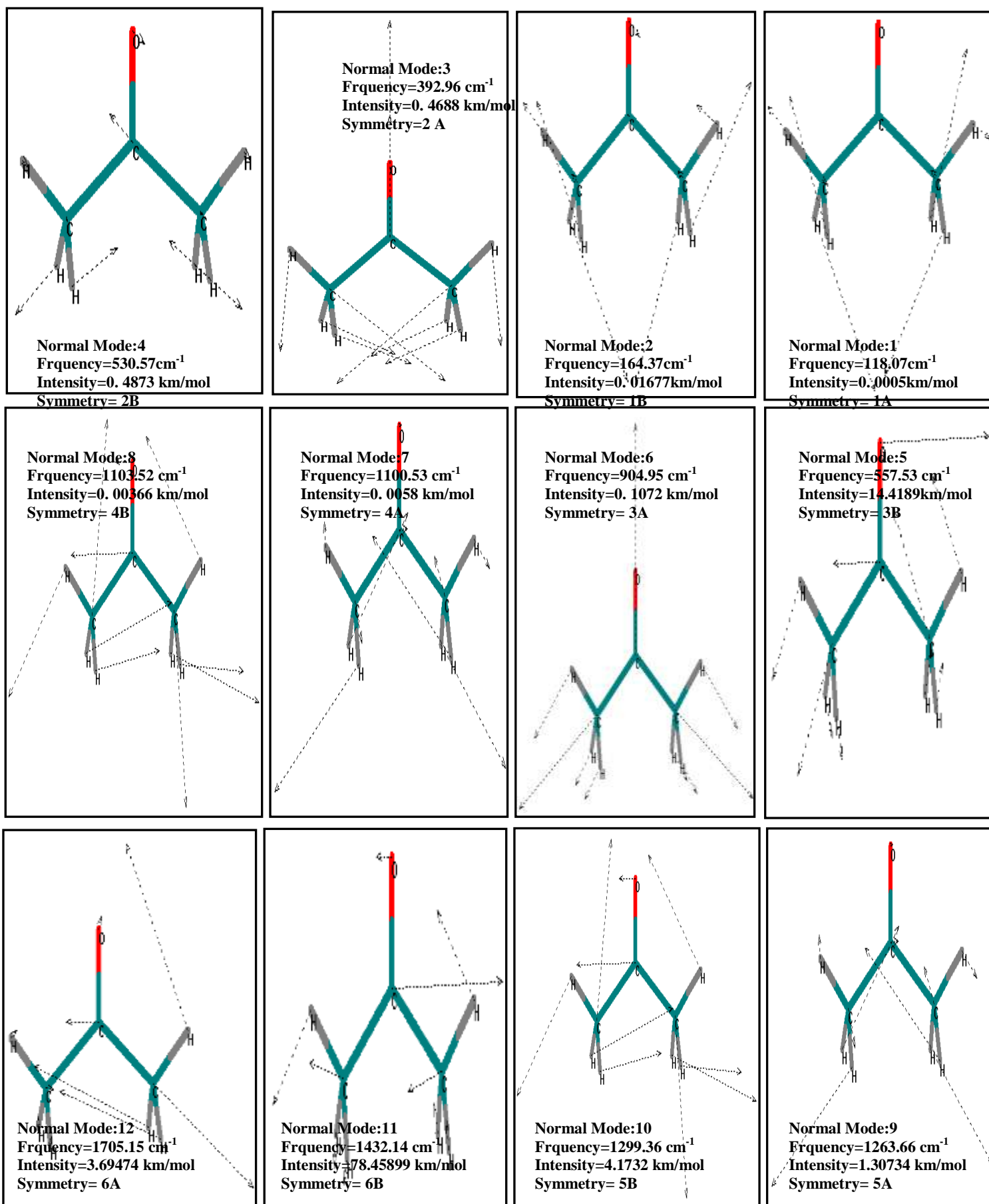
No.	Intensity km/mol	ν^- (cm ⁻¹)	(λ)/ μ m	Types of modes	Symmetry
1	0.00005	118.07	84.69	bending	1A
2	0.01677	164.37	60.83	bending	1B
3	0.46886	392.96	25.44	bending	2A
4	0.48739	530.57	18.84	bending	2B
5	14.41895	557.53	17.93	bending	3B
6	0.10720	904.95	11.05	bending	3A
7	0.00582	1100.53	15.11	bending	4A
8	0.00366	1103.52	9.08	bending	4B
9	1.30734	1263.66	7.91	bending	5A
10	4.17325	1299.36	7.69	bending	5B
11	78.45899	1432.14	6.98	bending	6B
12	3.69474	1705.15	5.864	bending	6A
13	3.61665	1705.69	5.86	bending	7B
14	0.09335	1805.52	5.53	bending	7A
15	7.39688	1809.36	5.526	bending	8B
16	0.19766	1809.94	5.525	stretching	8A
17	8.00098	1813.77	5.51	stretching	9B

18	32.09822	2129.73	4.69	stretching	9A
19	0.56062	3563.90	2.805	stretching	10A
20	0.05633	3565.60	2.80	stretching	10B
21	0.00178	3741.15	2.673	stretching	11B
22	0.04549	3743.33	2.67	stretching	11A
23	0.00469	3761.55	2.658	stretching	12A
24	0.05470	3763.79	2.656	stretching	12B

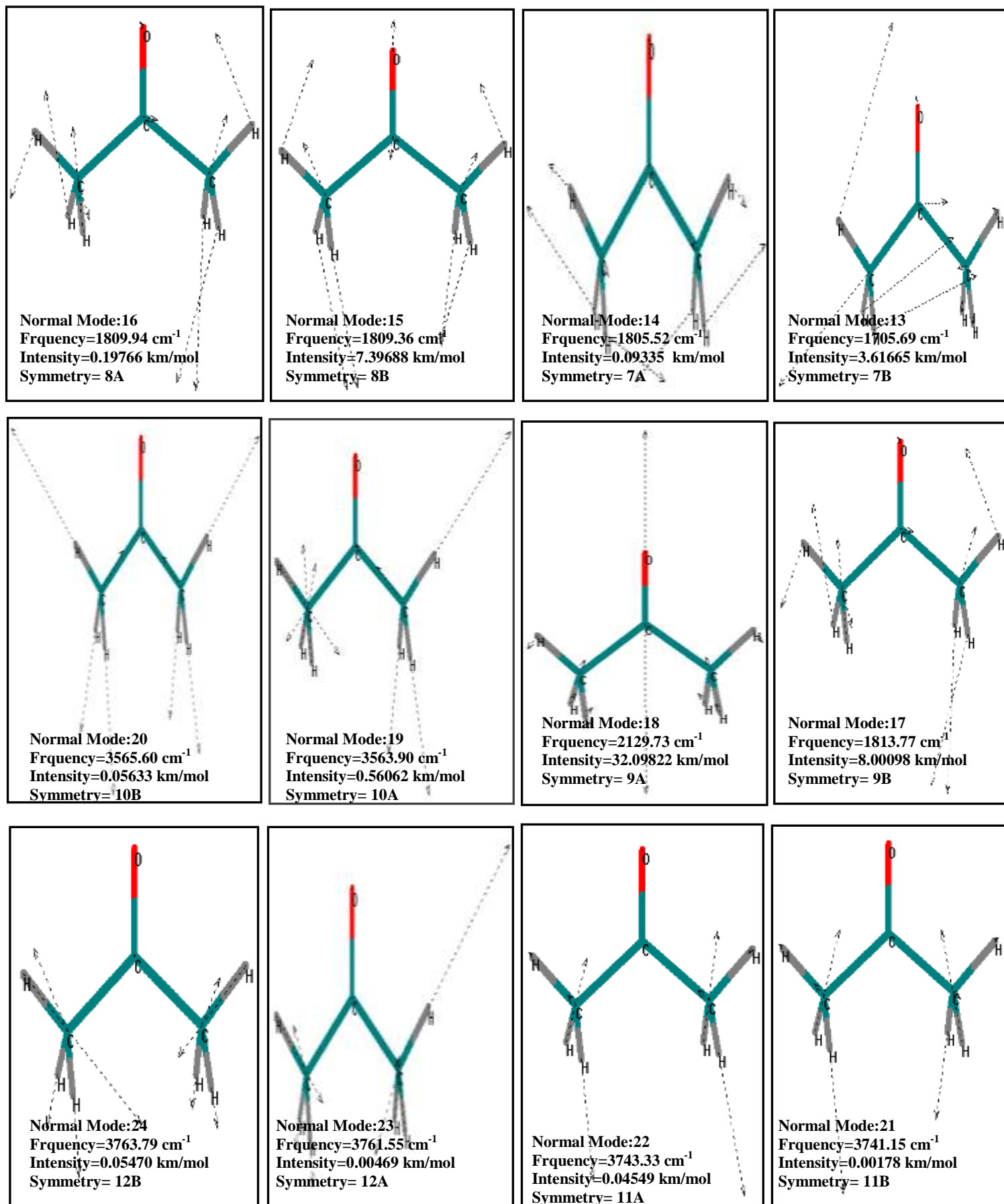
The vibrational frequencies and its corresponding intensities compare with experimental IR absorption spectrum as shown in Fig (3) ^[8].



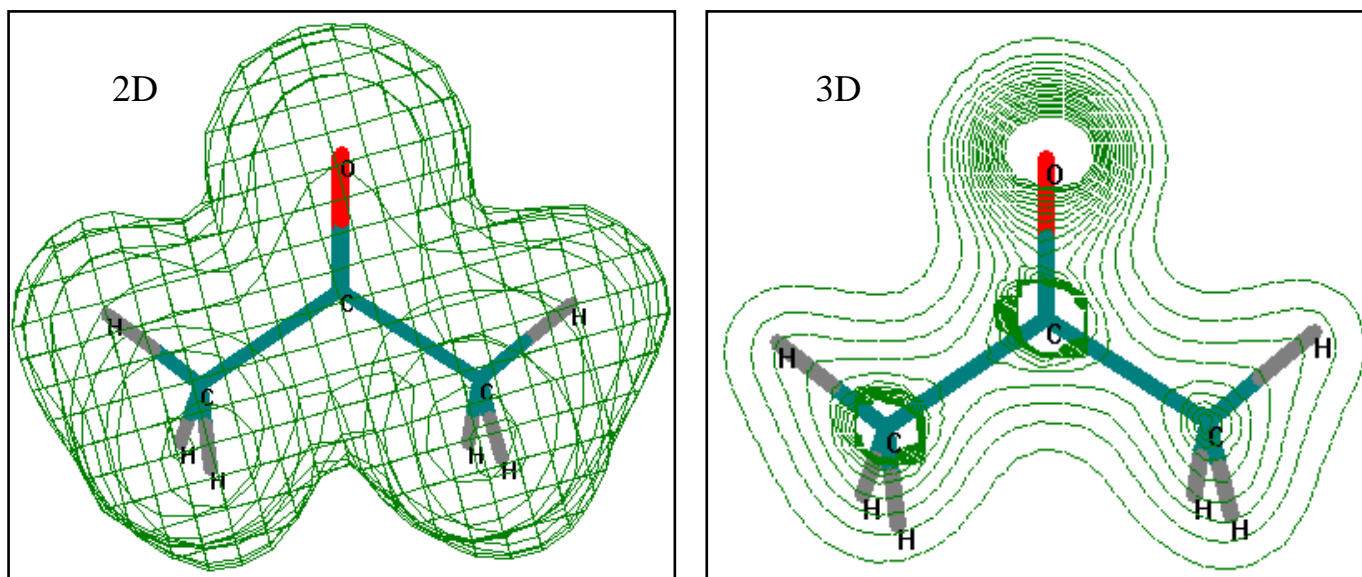
The types of the modes of vibration can be describe as shown in Fig (4)



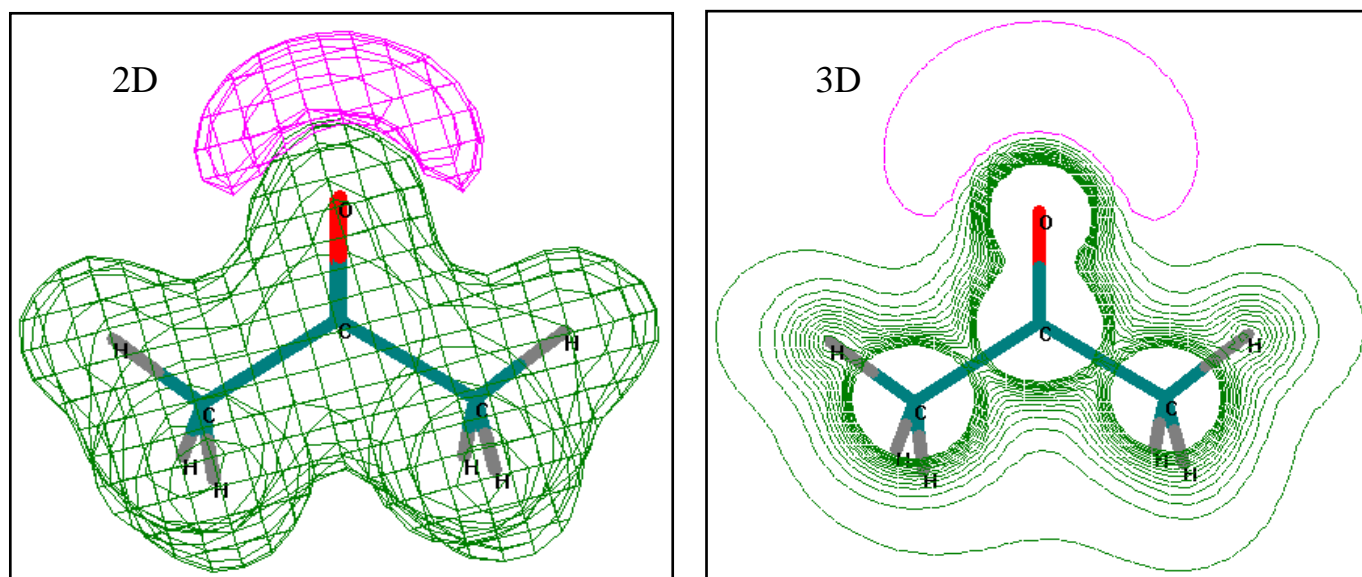
Fig(4) Schematic view of vibrational modes of acetone molecule



The total charge density distribution and electrostatic potential of acetone molecule in two and three dimension as shown in Fig (5) and Fig (6) respectively .



Fig(5) Illustrated total charge distribution for acetone molecule in 2D and 3D



Fig(6) Illustrated electrostatic potential for acetone molecule in 2D and 3D

Fig (7) shows an act final level HOMO and energy value $E_{\text{HOMO}} = -8.75733$ eV while symmetry of this level was 2B, and the first LUMO with energy value $E_{\text{LUMO}} = 8.075379$ eV with symmetry 3B. The absolute value of the final level HOMO gives the Ionization potential which is equal to (8.75733) eV, while the first level LUMO represent electron affinity which is equal to (8.075379) eV .They determined the Fermi level as the center of the HOMO and LUMO energies and calculated the gap between them to be 16.73270 eV according to Fischer and Herriksson^[9] is defined as $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$.

No.Level	Symmetry	Energy (eV)
10	8A	27.39115
9	7B	21.524239
8	6B	20.297749
7	5B	19.793493
6	7A	19.681839
5	6A	19.105013
4	4B	18.245502
3	5A	18.016109
2	4A	16.353270
1	3B	LUMO 8.075379
	0
1	2B	HOMO -8.757333
2	1B	-10.816548
3	3A	-13.184724
4	13A	-13.491787
5	12A	-14.306868
6	11B	-15.551773
7	10B	-15.773011
8	9A	-15.947606
9	8B	-18.548069
10	7A	-24.932789
11	6A	-26.669682
12	5A	-35.950657
13	4B	-300.659546
14	3A	-300.661438
15	2A	-302.605621
16	1A	-551.641113

Fig(7) Schematic diagram for energy levels values for acetone shows E_{HOMO} , E_{LUMO} and symmetry .

Conclusion :

Acetone is non-linear molecule has $3N-6$ mode of vibration .24 modes are the total number of fundamental modes, 9 of these modes are stretching according to rule $(N-1)$ is the number of stretching and 15 is the number of bending according to the rule $(2N-5)$ is the number of bending . The Ab-initio calculation of total energy compare with different semi-empirical methods is given too low value , indicate the geometry more stable .

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