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Ab-initio-rhf methods calculation to study the fundamental vibrational frequency of Acetophenone ($C_6H_5COCH_3$)

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Abstract

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

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

The modes of vibrationes 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 = 7.628904 eV, while the low electron affinity is equal to =5.897452 eV. The total energy of acetophenone equal to (-10277.43266 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 into a ccount all electrons internal and external orbital but need a long time for calculation with a large process capacity .

Keywords: Ab-initio rhf methods for acetone modes .

الخلاصة

تم دراسة التوزيع الالكتروني وطاقة المستوي كذلك انماط الاهتزاز لجزيئة الاسيتوفينون نظريا باستخدام طريقة المبادئ الاساسية المحددة لهارتري- فوك (ab-initio) . ان افضل شكل هندسي جزيئي مستقر لجزيئة الأسيتوفينون حصل على الإعتماد على معادلة هارتري – فوك للنظام المقيد باستعمال مجموعة القواعد STO-3G .

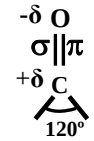
تم حساب انماط الاهتزاز الاساسية للجزيئة تحت شروط الاستقرار الجزيئي الهندسي وتمثيلها بشكل تخطيطي مع التردد والشدة والتماثل لكل نمط . كما تم تمثيل المدارات الجزيئية ومستويات الطاقة بشكل تخطيطي يظهر فيها المزدوج الالكتروني . كما تم حساب طاقة جهد التاين والتي كانت يساوي (7.628904 eV) , بينما الالفة الالكترونية تساوي (5.897452 eV) .

ان الطاقة الكلية المحسوبة لجزيئة الاسيتوفينون المحسوبة بطريقة المبادئ الاساسيةAb-initio فكانت **(**-10277.43266**eV)** مقارنةً بطرائق شبه 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 depandant 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 electronic 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 acetophenone as an example of non-linear molecule theoretically according to group theory using the linear combination of benzophenone orbitals (LCAO) .

Methods:

I- Hartree - Fock theory .

In Hartree Fock HF theory , the wave function is represented by a single N-dimentional slater determinant $\phi(x_1,x_2,\ldots\ldots x_N)$ 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 :

$X_i(x) = \psi_i^{\alpha}(r)\,\alpha(\omega) + \psi_i^{\beta}(r)\,\beta(\omega)$ ……..(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 $C_{\mu i}^{\alpha}$, $C_{\mu i}^{\beta}$

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

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) :

$$E_e = \sum_{i=1}^{N}\langle X_i\left|-\frac{1}{2}V_I + \sum_{I=1}^{N}V_I(r_i,R_I)\right|X_i\rangle + \sum_{i=1}^{N}\sum_{j<i}\left[\langle X_iX_j\left|X_iX_j\right.\rangle - \langle X_iX_j\left|X_iX_j\right.\rangle\right]\ldots\ldots\ldots\ldots(3)$$

Where :

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

The Born-oppenheimer (Sherrill,2000;klienert,1999) 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 :

$$E(\{C_{\mu i}^{\alpha}, C_{\mu i}^{\beta}\},\{R_i\}) = E_{ele}\ E(\{C_{\mu i}^{\alpha}, C_{\mu i}^{\beta}\},\{R_i\}) + \sum_{I,J<1}^{M}\frac{Z_IZ_J}{|R_IR_J|}\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

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 evalution of E [Ψ] (szabo,and ostlund 1982) .

E [Ψ] = < Ψ|H| Ψ > / < Ψ|Ψ > …… …….. …….. …….. …… …. (5)

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

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 term of electrons 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 ϕi that are called

$$\psi = \sum_I C_I \phi_I \quad \text{.....7}$$

molecular orbitals , and this leads to the general properties :

$$\phi_I = [\phi_{iI} \text{.....} \phi_{in}] \quad \text{.....(8)}$$

$$\langle \phi_i | \phi_j \rangle = s_{ij} \quad \text{.....(9)}$$

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 .

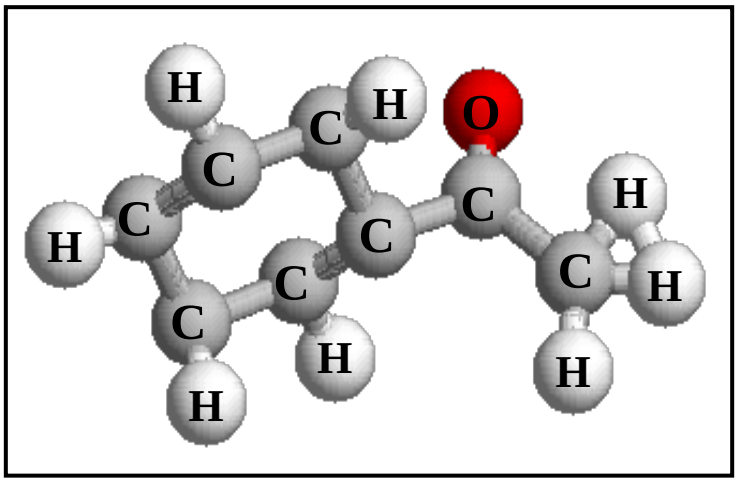
In quantum mechanics computer programs, such as Mopac 7.21 and hyperchem 6.01, the form of geometry in put called z-matrix . This matrix specifies the positions of an atom(n) by three geometric parameters :

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 , θ(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 , φ (i,j,k, **l**) .

The structure of the acetophenone was optimized at the restricted Hartree-Fock level of theory using the slater-type orbital (STO-3G) basis sets . The geometry optimization of the acetophenone studied is shown in fig(1) ,contain on two group ,benzene ring(C_6H_5) and methyl group(CH_3) connection with carbonal group .



Fig(1) Geometry optimization of Acetophenone

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

Table(1) Geometry parameters of C_6H_5-CO-CH_3

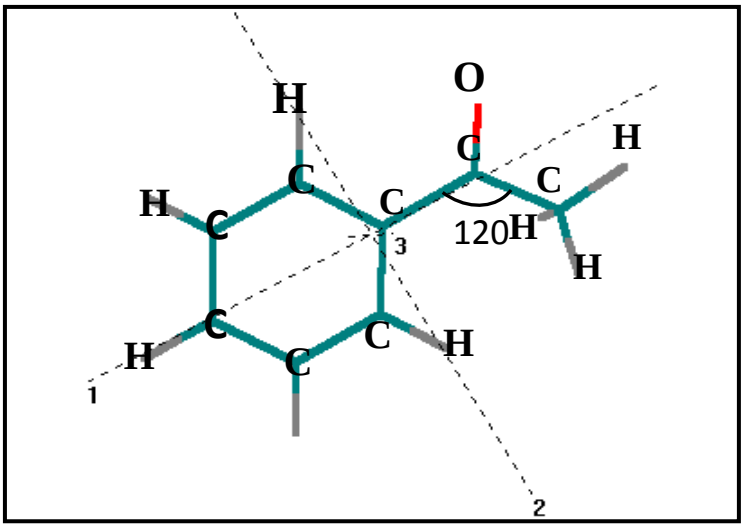
Bond	Bond length(A^o)	Bond angle(degree)
C-O	1.21	———
C-C	1.52	———
O-C-C	———	116.8

Using the coordinate system shown in fig (2) , the describing of the molecular orbitals of the studied compound in terms of basis orbital can be derived from ;

(i) The 2s,2p orbitals of the oxigyen ion .

(ii) The carbon ion 2s,2p orbitals .

(iii) The hydrogen ion is orbitals .



Fig(2) Coordinates system diagram of the Acetophenone C_6H_5-CO-CH_3 molecule .

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

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

Atom	Z	Charge (Mulliken)	Coordinates(Angstrom)			Mass
			X	Y	Z	
O	8	-0.237152	0.56171005	3.23257701	0.28751001	15.99900
C	6	0.146812	0.69691921	2.01696856	0.19852569	12.01100
C	6	0.020308	2.06717023	1.32355999	0.23251564	12.01100
C	6	-0.024942	-0.48515298	1.05806022	0.11368611	12.01100
C	6	-0.052318	-1.76800016	1.58204405	-0.01312783	12.01100
C	6	-0.061952	-2.86264768	0.73820220	-0.10155643	12.01100
C	6	-0.054270	-2.68074142	-0.63711122	-0.06518870	12.01100
C	6	-0.063628	-0.30983743	-0.32285274	0.15172508	12.01100
C	6	-0.061162	-1.40463322	-1.16650920	0.06215207	12.01100
H	1	-0.003278	4.15696709	-2.34365314	-0.13674395	1.00800
H	1	0.003248	4.15609173	-1.68321689	0.13060434	1.00800
H	1	0.035917	2.38820743	1.28036199	-0.84158501	1.00800
H	1	0.080814	-1.89354389	2.65803605	-0.04059538	1.00800
H	1	0.069156	-3.85897787	1.15099416	-0.19796241	1.00800
H	1	0.069151	-3.53567496	-1.29830795	-0.13468043	1.00800
H	1	0.068790	-1.26281697	-2.23905489	0.09360393	1.00800
H	1	0.064504	0.68201959	-0.74505617	0.26111726	1.00800

Ab-initio calculation of the acetophenone total energy is the sum of the electronic energy and 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 acetophenone molecule,compare with different semi-empirical methods

Quantity	Ab-initio (present work)	Semi-empirical methods			
		MNDO-PM3	MNDO-AM_1	MINDO/3 [7]	MNDO [7]
Total Energy (eV)	-10277.43266	-1364.4960	-1454.3512	-1443.4235	-1457.790
Electronic Energy (eV)	-21177.97869	-6229.5220	-6386.2202	-6181.4882	-6346.423
Core-Core Repulsion (eV)	10900.54603	4865.0259	4932.8044	4738.0647	4888.633
Ionization Potential (eV)	7.628904	9.99367	9.92248	9.30643	9.66154
Dipole Moment (Deby)	1.8886	2.785	2.817	3.316	2.636
No. of Filled Levels	32	23	23	23	23
Molecular Weight(amu)	120.151	120.151	120.151	120.151	120.151
Zero Point Energy(eV)	4.36492	3.7157	3.83877	3.80265	3.93559

We see from above table , the total energy by Ab-initio method is minimum magnitude from other methods , so this method(ab-initio) make acetophenone molecule more stable . And in this method(ab-initio)No.of filled levels 32 orbital ,because it take all electrons in calculations, while the other methods deals with external orbital electrons .

The normal modes of vibration of acetophenone nonlinear molecule are calculated which indicate 45 modes of vibration under rule (3N-6),16 of these modes are stretching and the rest 29 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	$\bar{\nu}$ (cm^{-1})	(λ)/µm	Types of modes	symmetry	No	Intensity km/mol	$\bar{\nu}$ (cm^{-1})	(λ)/µm	Types of modes	symmetry
1	1.55226	49.15	203.458	bending	1A	24	17.659	1264.33	7.90302	bending	24A
2	0.08462	176.81	56.5578	bending	2A	25	0.5014	1275.76	7.83846	bending	25A
3	0.38732	211.63	47.2522	bending	3A	26	3.0218	1367.58	7.31218	bending	26A
4	1.70026	221.70	45.1059	bending	4A	27	1.1771	1377.83	7.25779	bending	27A
5	0.68511	383.96	26.0443	bending	5A	28	2.5965	1484.43	6.73659	bending	28A
6	0.00096	477.01	20.9639	bending	6A	29	6.3172	1546.12	6.46781	bending	29A
7	0.10713	484.23	20.6513	bending	7A	30	116.44	1703.42	5.87054	Stretchi	30A
8	0.90002	515.15	19.4118	bending	8A	31	23.252	1723.94	5.80066	Stretchi	31A
9	24.1474	644.15	15.5243	bending	9A	32	2.7419	1788.72	5.59058	Stretchi	32A
10	4.61971	670.66	14.9106	bending	10A	33	2.6119	1811.61	5.51995	Stretchi	33A
11	0.18868	712.05	14.0439	bending	11A	34	3.7621	1814.45	5.51131	Stretchi	34A
12	8.34632	831.16	12.0313	bending	12A	35	2.2391	1914.72	5.22269	Stretchi	35A
13	0.58988	841.07	11.8896	bending	13A	36	3.5055	1938.00	5.15996	Stretchi	36A
14	10.0181	907.40	11.0204	bending	14A	37	29.394	2084.13	4.79816	Stretchi	37A
15	0.02742	1035.0	9.66142	bending	15A	38	0.8821	3566.81	2.80362	Stretchi	38A
16	0.92505	1122.1	8.91178	bending	16A	39	0.0976	3711.64	2.69423	Stretchi	39A
17	9.51331	1138.9	8.77986	bending	17A	40	1.3508	3726.70	2.68333	Stretchi	40A
18	0.87434	1157.9	8.63587	bending	18A	41	9.2520	3733.31	2.67858	Stretchi	41A
19	1.41660	1178.3	8.48680	bending	19A	42	11.731	3742.05	2.67233	Stretchi	42A
20	0.05177	1193.0	8.38194	bending	20A	43	0.0044	3744.77	2.67039	Stretchi	43A
21	0.00426	1206.1	8.29098	bending	21A	44	1.4126	3747.76	2.66826	Stretchi	44A
22	0.03942	1207.2	8.28335	bending	22A	45	0.3032	3762.01	2.65815	Stretchi	45A
23	1.95593	1225.0	8.16319	bending	23A						

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

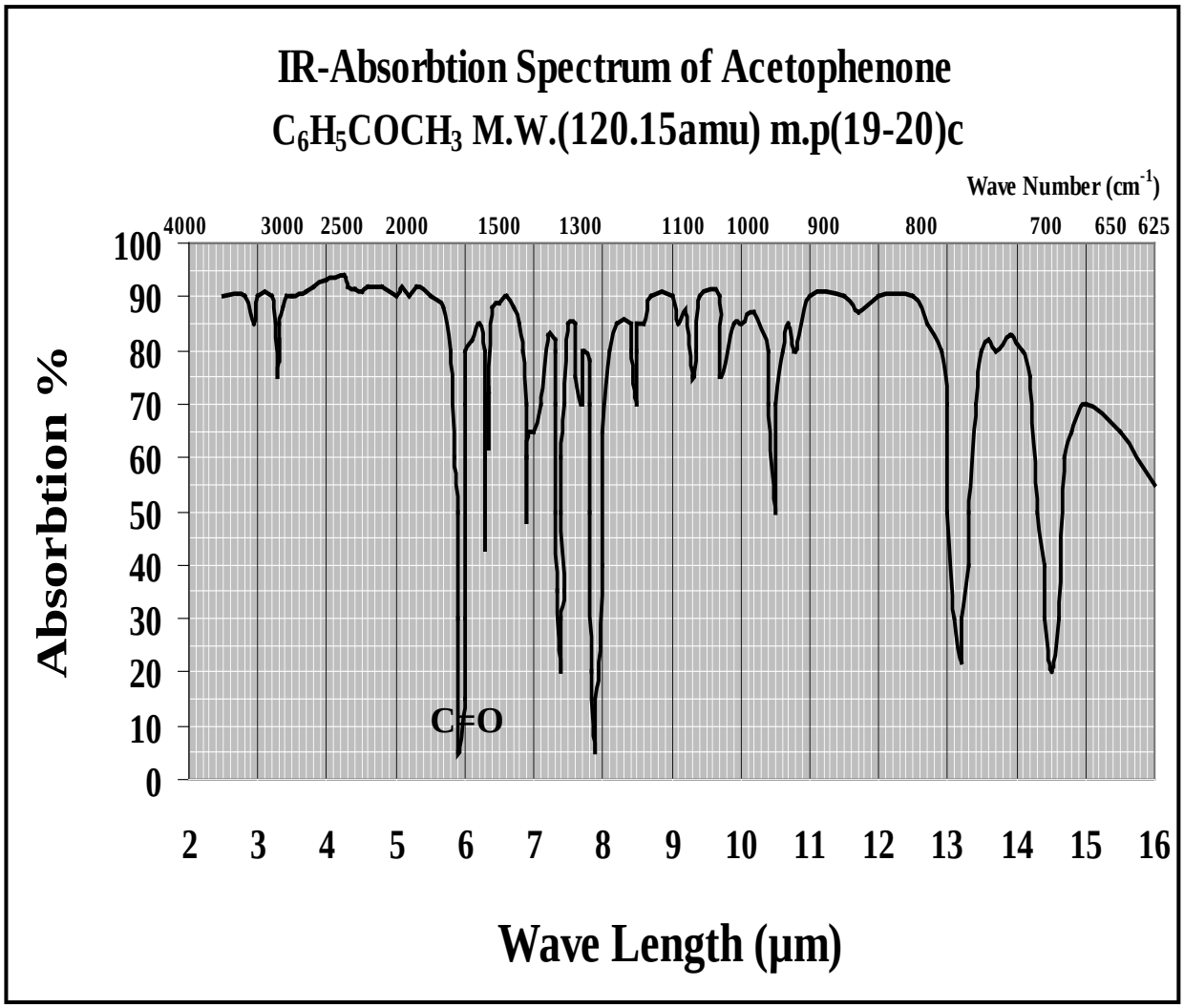
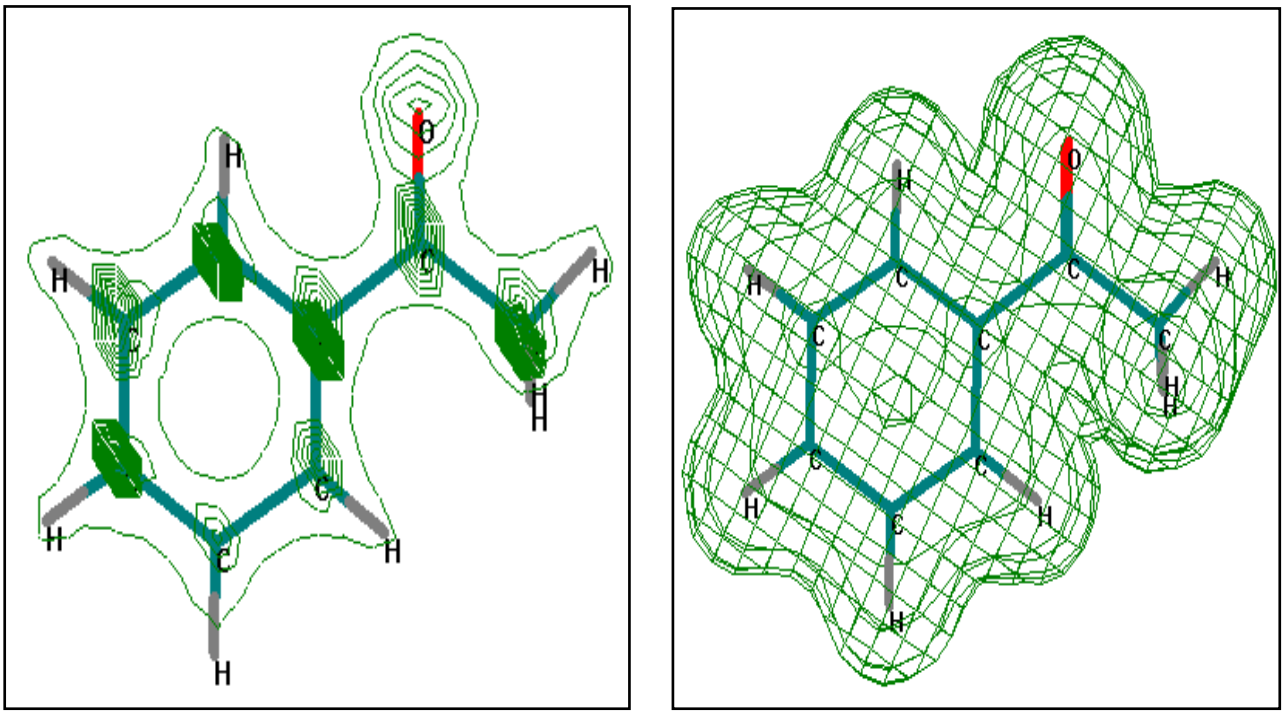


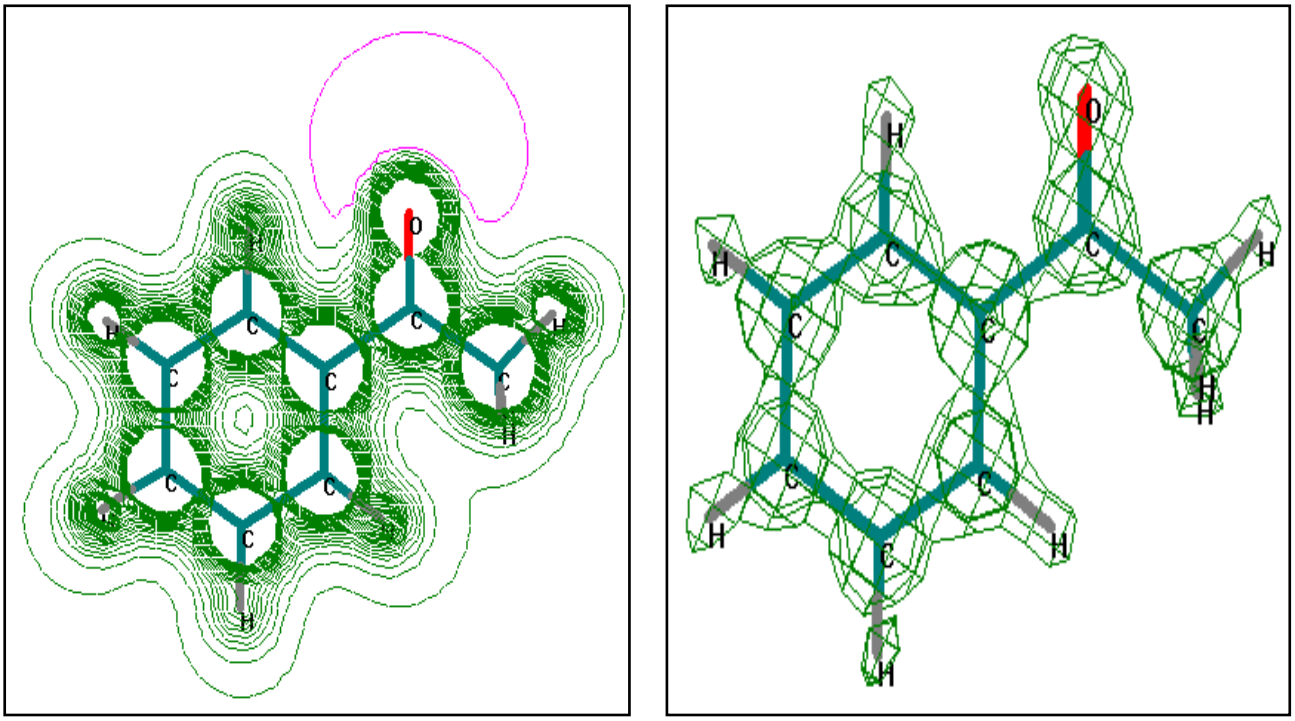
Fig (3) IR absorption spectrum of acetophenone C_6H_5-CO-CH_3 [8]

The wave length wich calculate by ab-initio method(table 4) and intensities are nearest to value of IR absorption fig(3) , and we see the best absorption happen at wave length (5.87 µm) and wave number(1703.42 cm^{-1}) which its stretching frequency for the carbonal group **C=O** .

The total charge density distribution and electrostatic potential of acetophenone molecule in two and three dimension as shown in Fig (4) and Fig (5) respectively .

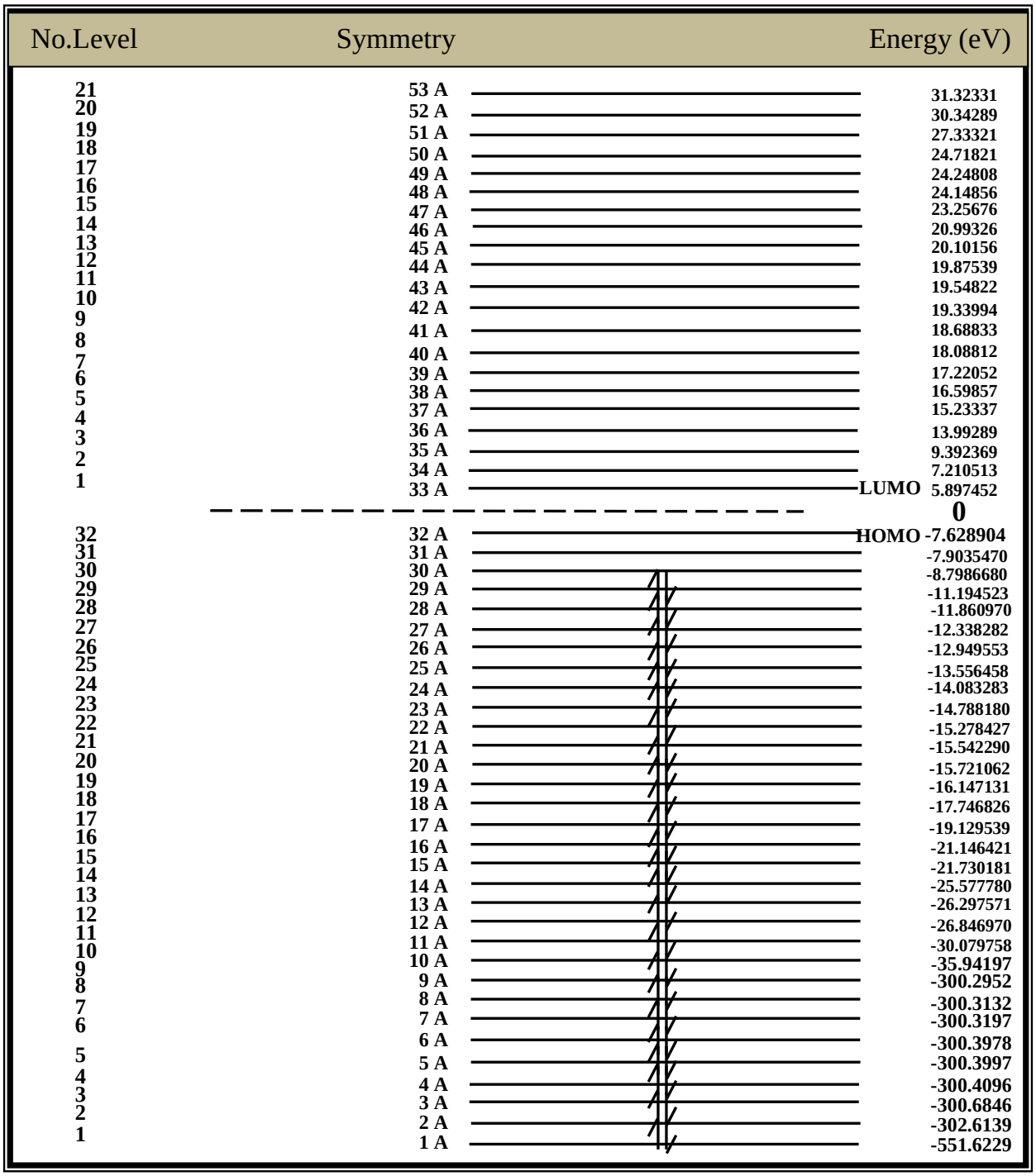


Fig(4) Illustrated total charge distribution for acetophenone molecule in 2D and 3D



Fig(5) Illustrated electrostatic potential for acetophenone molecule in 2D and 3D

Fig (6) shows an act final level HOMO and energy value E_{HOMO} = -7.628904 eV while symmetry of this level was 32A ,and the first LUMO with energy value E_{LUMO} = 5.897452 eV with symmetry 33A. The absolute value of the final level HOMO gives the Ionization potential which is equal to (7.628904) eV, while the first level LUMO represnt electron affinity which is equal to (5.897452) eV .They determined the Fermi level as the center of the HOMO and LUMO energies and calculated the gap between them to be (13.526356) eV according to Fischer and Herriksson[9] is defined as $\Delta E=E_{LUMO}-E_{HOMO}$.



Fig(6) Schematic diagram for energy levels values for acetophenone shows E_{HOMO} , E_{LUMO} and symmetry .

Conclusions :

Acetophenone is non-linear molecule has 3N-6 mode of vibration .45 modes are the total number of fundamental modes, 16 of these modes are stretching according to rule (N-1) is the number of stretching , and 29 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 .

Ab-initio method given a data more accuracy , but it taken long time because it take all electrons .

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