Theoretical Study of Electronic Properties and Spectral Properties for Coumarone and Derivatives molecules

دراسة نظرية للخواص الألكترونية والخواص الطيفية لجزيئات الكومارين ومشتقاتها

Rajaa Khedir Al-Yasari

University of Karbala, College of Science, Physics Department, Karbala, Iraq

ABSTRACT

Density functional theory (DFT), using the B3LYP(Lee-Yang-Parr) with the 6-31Gbasis set was utilized to study the effect of different substitution sites on the molecular properties of the Coumarin , Umbelliferone and Coumarin 522 *or* ($C14H12NO2F3$)molecules. the optimization structure, electronic properties such as energy gap (Eg), electron affinity(EA) , symmetry , ionization potential(IP), dipole moment(μ), IR spectra, Raman spectrum and UV-VIS spectra. This properties are coumputed by using Gaussian09 program and Gaussian view 5.08 program using (DFT) method, except UV-VIS computed by using TD-DFT method.

Keywords: DFT calculation, Electronic properties, IR spectra, Raman and UV-VIS spectrum, coumarin.

الخلاصة

نظرية دوال الكثافة (DFT) ، و باستخدام أنموذج الدالة B3LYP(Lee-Yang-Parr) مع عنصر القاعدة (6-31G)تم استخدامها لدراسة تأثير الاستبدال وبمواقع مختلفة على الخواص الجزيئية للجزيئات (الكومارين(Coumarin)، وألامبلفيرون (Umbelliferone) والكومارين 522 أو (C14H12NO2F3)) تم حساب كل من البنية الفراغية, الخواص الالكترونية مثل, فجوة الطاقة (Eg), الألفة الالكترونية (EA),التماثل,طاقة التأين (IP)عزم ثنائي القطب (μ),طيف الأشعة تحت الحمراء (IR), طيف رامان ,طيف الأشعة فوق البنفسجية(UV) والطيف المرئي(VIS). هذه الخواص تم حسابها باستخدام برنامج (Gaussian09) مع برنامج واجهة المستخدم بالرسوم (Gaussian view 5.08) وباستخدام طريقة (DFT) باستثناء طيف الأشعة فوق البنفسجية والطيف المرئي(UV - VIS) تم حسابها بطريقة (TD-DFT).

INTRODUCTION

Coumarin is one important organic chemical compounds In the field of medicine and optics science , has molecular formula $C_9H_6C_2$, in standard state is a colorless crystalline substance, Coumarin has density (0.935 g/cm^3) and molar mass(146.14 g·mol^{-1}),metiling point in (71 °C) and boling point in (301.71 °C), solubility in water in point (0.17 g/100 mL) . Coumarin is used in fabric conditioners and certain perfumes. Coumarin has been used in general it is banned as a flavorant food additive and certain alcoholic drinks, although a gain medium in some dye lasers.Coumarins they are approved for few medical uses as pharmaceuticals therefore have shown some evidence of biological activity[1]. It is used in lymphedema and the treatment of asthma [2] .

Many studies have been carried out to calculate electron properties, IR spectra, and NMR spectroscopy. Ionization potential, The DFT / B3LYP computed vibrational frequencies wavenumbers including IR and Raman spectra activities for 4-hydroxy-3[1-(4-nitrophenyl)-3-oxobutyl]-2H-1-benzopyran-2-one (Acenocoumarol) ,and the values this spectra were in good agreement compared with the experimental data[3].

The geometry optimization,energy gap ,HOMO,LOUMO, IR, UV-VIS spectra computed by using DFT method with the 6-311G** bases set   for coumarin derivatives [4]. Study the hardness, chemical potential ,electronegativity , ionization potential, electrophilicity index ,electron affinity, IR and Raman spectral for the 4,6-Dichloro-3-formyl coumarin by using (DFT)method with the hybrid functional B3LYP using the basis sets 6-31G (d,p) and 6-311++G(d,p) [5]. Hartree Fock (HF) and DFT methods with 6-31G(d,p) basis set to calculate the geometries optemazation, electronics   structure and IR spectral of 7-amino-4-tri°uoromethyl coumarin[6]. Study the derivatives of coumarin substituted at its 6 or 7 nucleus position. The structures of the final compounds and their intermediates were confirmed by their infrared spectroscopy , elemental microanalysis(CHN) , and melting points [7].

CALCULATIONS

The Density functional (DFT) methods has been carried out using the Gaussian 09 programs [8]. For the electronics properties of the Coumarin and derivatives molecules by using the 6-31G) basis set . The lowest energy structures of the species conformational analysis of the molecules had been performed using . The vibrational wave number assignments were used by combining the results in the Gauss view 5.08 programs [8]. In this investigation , energy gap(Eg) , electronegative (X) ,electronic potential (IP) , dipole moment(μ) and electron affinities (EA), were computed. The(HOMO) is the   highest occupied molecular orbital and(LUMO)is   the lowest Unoccupied Molecular Orbital energy were also used to estimate the IP and EA in the framework of Koopmans, theorem: IP=- EHOMO and EA=- ELUMO [9]. In quantum chemical the Energy gap (ΔEgap =ELUMO-EHOMO) is one of the important parameters calculations that considered as a function of reactivity of the inhibitor molecule towards adsorption on to the metal surface[10].

Ionization potential (IP) and electron affinity (EA) have been calculated by using equations[9].

IP= - EHOMO ... (1)

EA= - ELUMO ... (2)

While the electronegative (X)has been calculated by using the following equation[11].

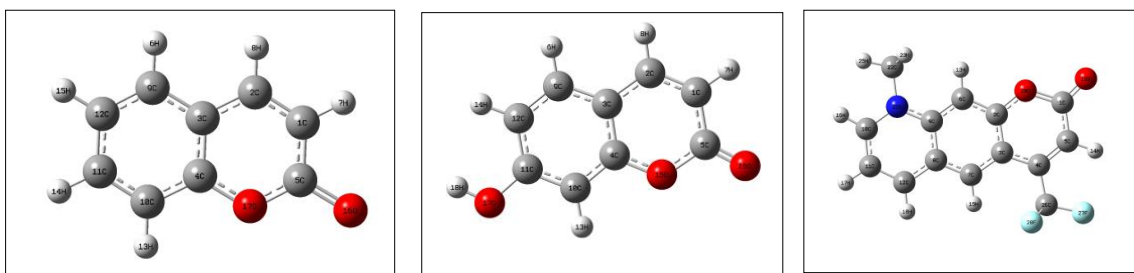 X = -1/2 (EHOMO + ELUMO)………………….(3)

The dipole moment   (μ) has been calculated by using the following equation[12].

$$< \mu >= \left(\mu^2{}_x + \mu^2{}_y + \mu^2{}_z \right)^{1/2} \dots\dots\dots\dots\dots\dots (4)$$

RESULT AND DISCUSSION

   1.Molecular geometry: Figure (1) shows the gas phase optimized structure computed by using DFTB3LYP method with the basis set 6-31G .

   1Coumarin

                              2Umbelliferone   **3Coumarin 522**

Figure(1) : The structures of coumarin and depravities molecules .

   The values of the calculated quantum chemical parameters such as (EHOMO) isthe highest occupied molecular orbital, (ELUMO)is the lowest unoccupied molecular orbital, dipolar moment (μ) and energy gap, (ELUMO-EHOMO)= ΔEgap, are presented in Table 1.From this table the values of HOMO, LOUMO and energy gap are decreasing ,while the values of dipole moment are increasing, the high values of dipole moment is indicated higher reactivity to accept the electron, the 2(Umbelliferone) has high values of HOMO, LOUMO and energy gap compared with 1(Coumarin) and 3(Coumarin 522), while all molecules have the same symmetry(C_1),because this molecules has symmetry. (360 ^{o} angle of rotation around the axis of symmetry).

Table 1 : HOMO, LUMO, and Eg measured in eV units , while the dipole moment measured in debye for (1-3) coumaren molecules using DFT with B3LYP/6-31G basis set.

molecules	HOMO (eV)	LUMO(eV)	Eg (eV)	Symmetry	Dipole Moment (Debye)
1 Coumaren	-6.63785	-2.08572	4.552128	C1	5.5200
2Umbelliferone	-2.08572	-1.96518	4.406277	C1	7.2119
3 Coumarin 522	-4.15022	-2.32382	1.826402	C1	8.8485

The electric properties are shown in table 2. From this table the coumarin molecules has high values for IP and X, compeered with other molecule ,while 2 (Umbelliferone) and 3 (Coumarin 522) have small values of IP and X respectively. The 2 (Umbelliferone) has small value of EA compeered with other molecule.   The reason of that for the substitution atoms that have high electronegative.

Table-2: IP,EA and X are   measured in eV units for (1-3)coumaren molecules using DFT with B3LYP/6-31G basis set.

molecules	IP(eV)	EA(eV)	X(eV)
1 Coumarin	6.637851	2.085723	4.361787
2 Umbelliferone	6.371456	1.965178	4.168317
3 Coumarin 522	4.150222	2.323819	3.237021

2. IR Spectra

The IR spectra of coumarin and derivetives molecules are shown in the figure (2). The vibrational modes were computed for study of coumarin and derivetives molecules by using B3LYP level with 6-31G basis set. It is clear from table(3)and figure (2) that the coumarin has stretching vibrational modes of (C- H) had been observed with the region (3094.74)cm^{-1},and (O=C) in region (854.138) cm^{-1} ,while the (C=C) stretching mode observed within the region (1697. 09) cm^{-1} and the stretching mode of (C-O) bond shown in the region (1346.79) cm^{-1} is weak, while in region (1142.56)cm^{-1} is strong and the (O=C) in region (667.771)cm^{-1} is medium. The stretching mode bond (O=C-O)had been observed with the region(1045.21)cm^{-1}is strong.

In 2Umbelliferone and 3Coumarin 522 the (C-H) had been observed with the region(3215.6)cm^{-1} and (3279.48) cm^{-1} are strong ,but the stretching mode bond (O=C-O),(C-O) and the   (O=C) in region(1141. 57and 1684.87)cm^{-1},(1765.72)cm^{-1} and the (1108.92and 1746.34)cm^{-1} are strong, also in 2Umbelliferone and 3Coumarin 522 found new modes such as (O-H) and (C-OH) had been stretching observed in region (3669.26 and 1610.54)cm^{-1} for 2Umbelliferone ,while in 3Coumarin 522 found (C-H2 stretching and C-H2 rocking) had been observed in the region(3125.02 and 3057.52)cm^{-1}, also (N -C and C-N-C) had been observed in the region (1439.32 and 1421.64)cm^{-1}, and found (C-F2 rocking and   F-C-F stretching) had been observed in the region(1121.02 and 1108.92) cm^{-1}. From this figure and table (3) found the values of stretching vibration (C-H and O=C) for derivatives are higher than coumarin. This difference in the values of vibrational frequencies due to several factors, including the number and the longest bond, the nature and size of atoms, electronegativity, bond hydrogen and the most important influential factor is an electronic influences.

Table-3: Vabrational modes (IR spectra and Raman spectra)   measured in (cm^{-1})units for (1-3)coumaren molecules using DFT with B3LYP/6-31G basis set.

| Molecules	Vabrational modes	IR (cm^{-1})	Raman (cm^{-1})
1 Coumarin	(C-H)	3094.74	(3253.72-3279.51)
	(O=C)	854.138,667.771medium	
	(C=C)	1697. 09	(1597.5-1697.07)
	(C-O)	1346.79week, 1142.56 strong	(1746.34-1765.72)
	(O=C-O)	1045.21	(632.575-1098.17)
2Umbelliferone	(C-H)	3215.6	
	(C-O)	1684.87	(1746.34-1765.72)
	(O=C)	1765.72	
	(O=C-O)	1141. 57	(632.575-1098.17)
	(O-H)	3669.26	
	(C-OH)	1610.54	1141.57
3 Coumarin 522	(C-H)	3279.48	
	(O=C)	1746.34	
	(O=C-O)	1108.92	(632.575-1098.17)
	(C-H2)	3125.02	
	(C-H2)	3057.52	
	(N-C)	1439.32	1597.5
	(C-N-C)	1421.64	
	(C-F2)	1121.02	483.407
	(F-C-F)	1108.92	
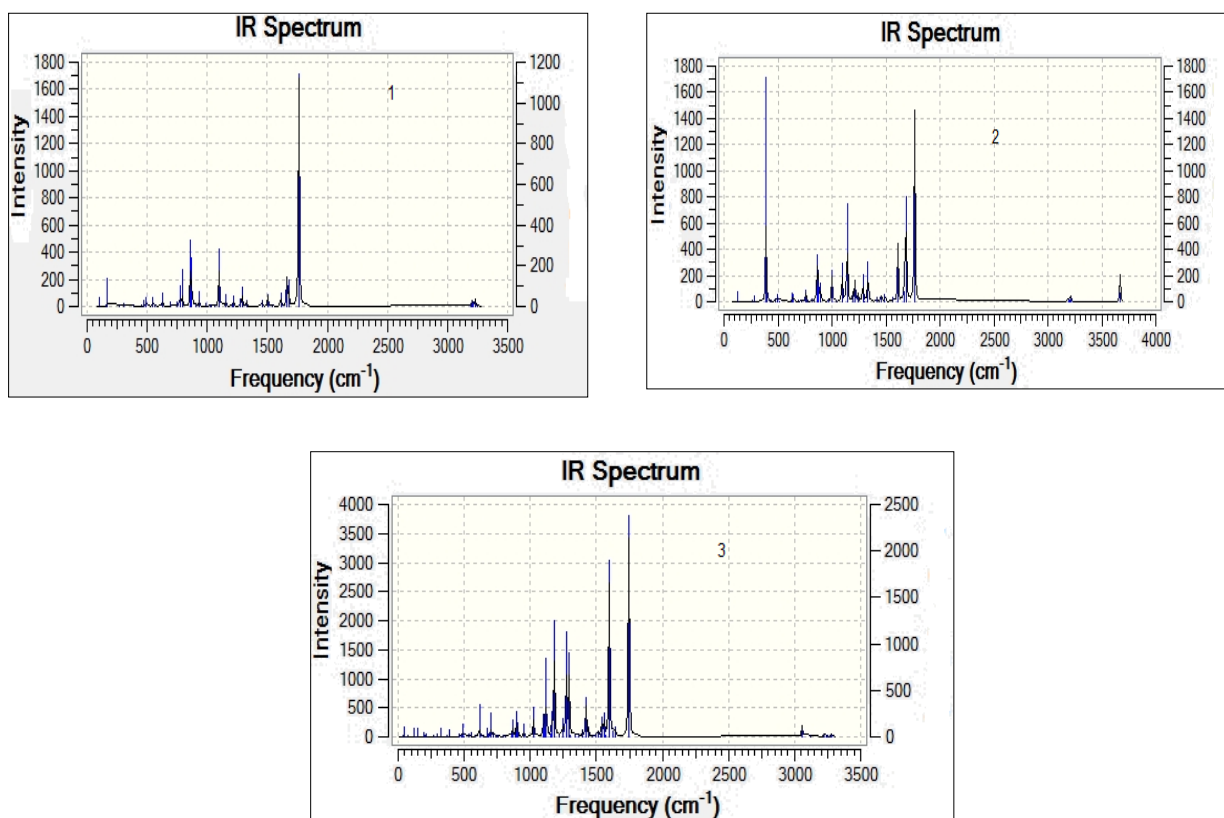
Figure 2: Calculated IR spectra of coumarain and derivatives usingDFT/ B3LYB /6-31G method.

3. Raman Spectra

From table(3) and figure (3)shown the Raman spectra of coumarin and derivetives molecules. The vibrational modes frequencies were calculated for study of molecules by using B3LYP level with 6-31G basis set. the (C − H) stretching mode studied in the region (3253.72-3279.51) cm^{-1}. The (C=C),(C - O) and (C-O =O) stretching vibrations for coumarin and derivatives molecules occur in the region (1597.5-1697.07) cm^{-1},(1746.34-1765.72)cm^{-1} and (632.575-1098.17)cm^{-1}.

From this figure and table(3) we see the substitution hydrogen for OH in Umbelliferone and the substitution hydrogen for CF3 and N in place of carbon atoms in coumarin 522 lead to multiply vibrational modes, such as (C-O-H)rocking , (C-N) stretching vibrations and (C-F2)rocking in the region(1141.57)cm^{-1},(1597.5)cm^{-1} and(483.407)cm^{-1}. Of the same shape we note the emergence of severe intensity lines largely due to vibrations similar in the molecule. Also, The molecular polarization, which is accompanied by change is moment when the vibration in addition to the type and number and locations of atoms substituted factors play a role important in influencing the vibrational frequencies .
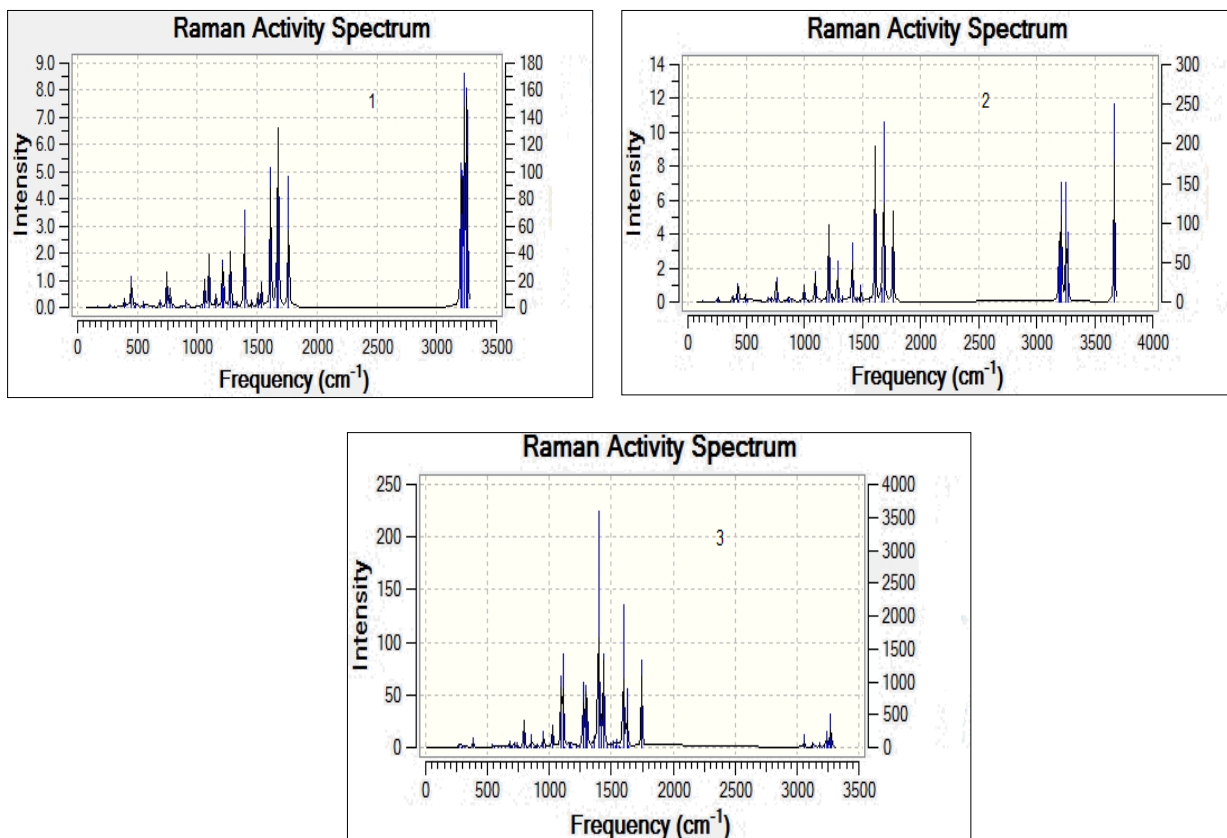
Figure 3: Calculated Raman spectra of coumarain and derivatives usingDFT/ B3LYB /6-31G method.

4. UV - VIS Spectra

Figure (4):Shown   The vibrational frequencies were calculated for study coumarain and derivatives by using TD-DFT/ B3LYP level with 6-31G basis set. has been used to study the first three low excited states for investigate the spectral UVandVIS absorption spectra of the coumarain and derivatives in gas phase .From coumarain found the bond in (323.95)nm and for Umbelliferone in(430.53)nm, while in coumarin 522 we see tow bonds in(1059.7 and 611.12)nm, The reason for this goes back to the substituent groups (NH3 and CF3) and their locations in the molecule because it affects the lengths of the bonds , the values of angles and geometry optemazation, which in turn affect the spectral values in excited states.
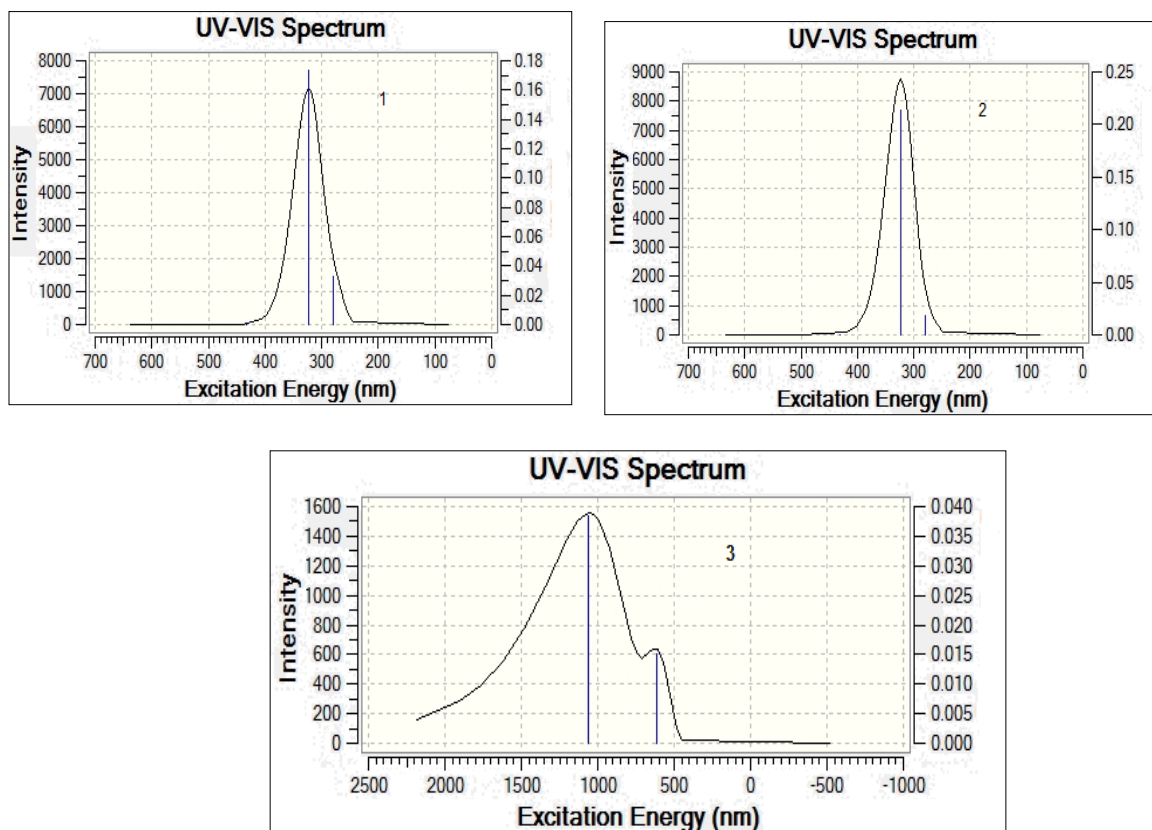
Figure 4: Calculated UV-VIS spectrum of coumarain and derivatives using TD-DFT/ B3LYB /6-31G method.

COUNCLUSION

1- Values of HOMO, LOUMO and energy gap are decreasing ,while the values of dipole moment are increasing, the high values of dipole moment is indicated higher reactivity to accept the electron. While all molecules have the same symmetry .

2- Electronic properties   IP   and   EA are increasing, while the values are   X decreasing with substitution hydrogen for OH and N,CF3 in place of hydrogen and carbon atoms.

3- It was found that for IR spectra that the substitution hydrogen for OH and N,CF3 in place of hydrogen and carbon atoms cusses to increasing the vibrational modes .And   found the values of stretching vibration mode (C-H and O=C) for derivatives are higher than Coumarim.

4- For Raman spectra also the substitution cusses to increasing the vibrational frequencies modes, and highest wave numbers of stretching vibration mode .

5- For UV-VIS used TD-DFT and B3LYP level with 6-31G basis set, has been to determine the first three low-lying excited states for investigate the UV-VIS absorption spectra of the coumarain and derivatives in gas phase. From the coumarain and Umbelliferone found one bond, while in coumarin 522   we see tow bonds ,because the groups substitution   NH3 and CF3 are effect on the values of spectrums in the excited states, and depend on the position of the substitution atoms.

REFERENCES

1- H. Liu, *Extraction and Isolation of Compounds from Herbal Medicines*. In: Willow, J. and H. Liu (Eds.) *Traditional Herbal Medicine Research Methods*. John Wiley and Sons, Inc., 2011.

2- N .Farinola and N.Piller, *Pharmacogenomics: Its role in re-establishing coumarin as treatment for lymphedema*, Lymphatic Research and Biology,3(2):81-86, 2005.

3- I. kostovaA, I. hubertjoe, and S. Cintapinzaru, *Vibrational spectral characterization of new La(III) and Dy(III) complexes*, J.Opto. Biom.l Mate.,1(2):188-199, 2009.

4- M.Mudaasir and Rajeev, *Vabrational spectral and Electronic Structure Studeis of Coumarain*, Int.j.Res. Eng.Scie.,11(3):1-15,2013.

5- R.K.Raj, S.Gunasekaran, T.Gnanasambandan and S.Seshadri, *Structural, Spectroscopic (FT-IR, FT-Raman & UV-Vis) and theoretical studies of 4,6-Dichloro-3-formylcoumarin*, Int.Curr.Res.Aca.Rev.,3(3):130-149,2015.

6- M. Subramanian, P . Anbarasan and S. M.animegalai,*Molecular structure, vibrational spectroscopic studies and natural bond orbital analysis of 7-amino-4-tri°uoromethyl coumarin*, PRA.J.Physi. Indian Academy of Sciences,74(5):845-860, 2010.

7- A.Rouaa , Y.Kawkab and A.Ammar , *Synthesis and Antimicrobial Evaluation of New 6 and7 Substituted Derivatives of Coumarin*, Iraqi J Pharm Sci,23(1):35-41, 2014.

8- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L.Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T.Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E.Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N.Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B.Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev,A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V.G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, revision A. 02 Gaussian, Inc., Wallingford CT. 2009.

9- A.Vektariene, G.Vektaris and J. Svoboda , *A Theoretical Approach to the Nucleophilic Behavior of Benzofused Thieno[3,2-b]Furans Using DFT and HF Based Reactivity Descriptors,* ARKIVOC ,USA,Inc.,5(2):311-329, 2009.

10- E. Bundgaard and F. Krebs ,*Solar Energy. Materials and solar cells,*91:954-985, 2007.

11- H.Kampen, *Energy Level Alignment at Molecular Semiconductor/GaAs(100) Interaces*: *Where is the LUMO,* University of Chemnitz, Institut fur,Germany, 1999.

12- J.Pipek and P.Mezey, *A fast intrinsic localization procedure applicable for abnitio and semiempirical linear combination of atomic orbital wave functions*, The Journal of Chemical Physics,90(9):4916-4926, 1989.