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Electronic Properties of NaOH Experimental and Theoretical Fluorescence Study

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ABSTRACT

The study of spectral of multi molecules by theoretical and experimental, parts, Where the theoretical parth studies using Gaussian 09 program of NaOH molecules using semiempirical quantum programs but experimental part which studies by tacking solution of this molecular and studying absorption and fluorescence spectrum also we calculate quantum efficiency and oscillation parameters .By using semi-empirical (PM6) HF and DFT methods this by using different bases sets so this methods gives approximant results with experimental result.

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INTRODUCTION

Sodium hydroxide (NaOH)is an inorganic compound. It is a white solid and highly caustics metallic base and alkalis salt which is available in pellets, flakes, granules, and as prepared solutions at a number of different concentrations. Sodium hydroxide forms an approximately 50% (by weight) saturated solution with water Physical properties (Safarikova, 2002)

Pure sodium hydroxide is a whitish solid, sold in pellets, flakes, and granular form, as well as in solution. It is highly soluble in water, with a lower solubility in ethanol and methanol, but is insoluble in non-polar solvents.

Similar to the hydration of sulfuric acid, dissolution of solid sodium hydroxide in water is a highly exothermic reaction in which a large amount of heat is liberated, posing a threat to safety through the possibility of splashing. The resulting solution is usually colorless and odorless with slippery feeling upon contact in common with other alkalis (Okudaira, 2004; Jeyakodi Moses, 2015).

Fluorescent (FL) that is a highly fluorescent molecule and a type of xanthenes dyes was firstly synthesized by Von Bayer in 1871

So quantum efficiency for fluorescence. In fact that's only a select number of species fluoresce can be used to our advantage by using fluorescence as a selective technique**.**

Table 1: The main parameters of NaOH

Parameters	molecules
Chemical formula	NaOH
Molecular weight (g/mol)	40
Refractive index	1.4220
Density (g/cm^3)	1.034
Melting point (degrees Celsius)	11.8
Boiling point (°C)	80

MATERIAL AND METHODS

Experiment part:

NaOH is a plane molecule consisting of linear particle At the centre of the molecule is a hydrogen atoms. As shown in figure (1).

The solvent preparation:

The solvent was prepare using sodium hydroxide (NaOH) have molecular weight (40 gm/mol). With pointing degree 318 ^{o} C In the present investigation we use pure Dioxane 99.99 % (spectra Grade) as shown in table (1) (Mustafa Arık, 2005).

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Solution preparation:

Solution of concentration for solvent is prepared by weighting an appropriate amount of the material by using a mettler balance having a sensitivity of 10^{-4} gm. Different concentrations are prepared according to the following equation:

$$W = \frac{M_W \times V \times C}{1000} \quad (1)$$

Where W weight of the dissolved NaOH (gm)
M_W Molecular weight of NaOH(gm/mol)
V the volume of the solvent (ml)
C the SOLVENT concentration (mol/l)

The prepared solutions are diluted according to the following equation:-

$C_1 V_1 = C_2 V_2$ (2)

Where
C_1 primary concentration
C_2 new concentration
V_1 the volume before dilution
V_2 the volume after dilution

Three concentrations are prepared for concentrations are$1x10^{-3}$ M.

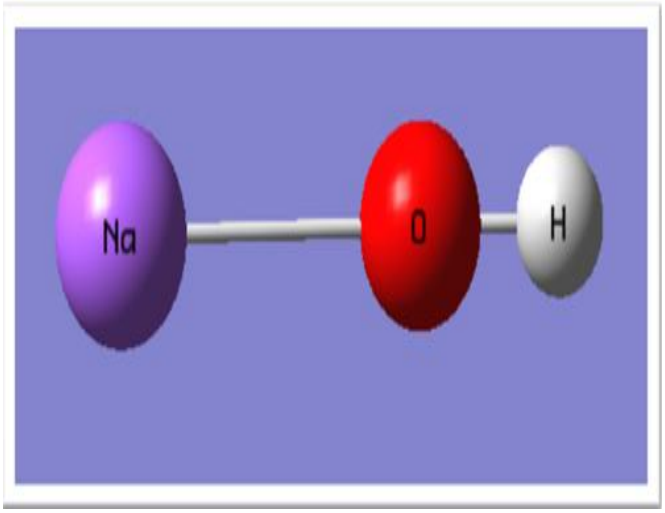


Fig. 1: The NaOH molecule.

Apparatus used in work laboratory:

Absorption spectral of the samples were recorded with ShimadzuUV-3101PCUV-VIS-NIR spectrophotometer. (Robert Sjoback, 1995)

Fluorescence spectra were taken with Shimadzu RF- 5301PC spectrofluorophotometer to meter by using a cuvette of 1.0 cm optical path length

Absorption:

Bouguer and Lambert have measured the fractional part of the energy absorbed in a thin layer of solution. They have found that it depends upon the substance itself and hence directly proportional to the concentration of the absorption species in solution. The Combination of these results gives the relationship, now commonly, is known as Beer-Lambert law (Andreas, 2012). In general:

Where:

$I = I_0 10^{-\varepsilon cL}$ (3)

Where:
I_0, I: incident and transmitted intensity, respectively.
L: is the cell thickness (cm)
C: is the molar concentration (mol/ lit)
ε: is the molar extinction coefficient (lit / mol.cm), which depends on the nature of the absorption material and the energy of the incident photon (hν).
The absorption cross section σ is simply related to ε by the expression

$\sigma = 2.303\varepsilon / N_A$ (cm^2) (4)

Where:
N_A: is the Avogadro's number.
Eq. (2) is usually represented in logarithmic form:

$A = \log (I_0/I) = \varepsilon cL$ (5)

A: is called the absorbance (optical density) of the sample.
The absorption spectra in the visible and ultraviolet are preferably plotted of ε as a function of wave number ($\bar{\upsilon}$) .The total area under the curve gives the integrated absorption intensity (Yakuphanoglu, 2010)

$$\int \varepsilon(\bar{\nu})\, d\bar{\nu} = \frac{1}{cL} \int \log \frac{I_\circ}{I}\, d\bar{\nu} = A \quad (6)$$

The total energy ($E_{tot.}$) of a molecule in its electronic ground state is given as

$E_{tot.} = E_{ele.} + E_{vib} + E_{rot}$ (7)

Where:
E_{ele}: is the electronic energy.
E_{vib}: is the vibartional energy.
$E_{rot.}$ is the rotational energy.

And the total energy $\bar{E}$tot in an excited electronic state :

$\bar{E}_{tot} = \bar{E}_{ele} + \bar{E}_{vib} + \bar{E}_{rot}$ (8)

Where E_{ele}, E_{vib}, and E_{rot}, are electronic, vibrational, and rotational energy in the ground state and excited state, respectively.

Spectrophotometer:

Absorption spectrum is measured by a CARY 100 Conc. UV-visible spectrophotometer) by the processor (Varian Company) is made off . This device operates within the range of the visible and ultraviolet region, where contains lamp of exaction are:

Spectrofluorophotometer:

Fluorescence emission and excitation are measured for the samples prepared using a (SHIMADZU Recording Spectrofluorophotometer-Model RF-510), the main parts that make up the device or Spectrofluorophotometer.

Fluorescence Spectrum:

Molecular fluorescence is the optical emission that has been excited to higher energy levels by absorption of electromagnetic radiation compared to absorption measurements is the greater sensitivity achieve because the fluorescence signal has in principle a zero background . Also the fluorescence spectrum yields

data about the vibrational levels of the ground electronic state. Both the absorption and fluorescence spectra display similarly structured intensity patterns which are said to process "mirror symmetry". A symmetry that exists between absorption and fluorescence spectra of certain molecules is not rigorously correct with the development of a theoretical understanding of the luminescence process. It is believed that the best approximation to mirror symmetry should exist between the absorption curve versus and the fluorescence curve versus where is the relative rate of photon emission $\varepsilon(\bar{\upsilon})$per unit wave number. $(\bar{\upsilon})$.

Fluorescence Quantum Efficiency:

We define the molecular fluorescence quantum efficiency q_{FM} as the ratio of the number of fluorescence photons emitted by a system of molecules in dilute solution to the number of molecules excited into S1(the number of absorbed photons). The molecular fluorescence spectrum is then defined as the relative fluorescence quantum intensity at frequency , normalized by the relation (Andreas, 2012)

$$q_{FM} = \int_0^\infty F(\upsilon)d\upsilon \qquad (10)$$

Or

$$q_{FM} = \frac{\text{number of quantum emitted}}{\text{number of quantum absorbed}} \qquad (11)$$

$$= \frac{K_{FM}[M^*]}{I_a} \qquad (12)$$

Where:

K_{FM}: is the rate of fluorescence emission the unit (sec^{-1}).

M^*: is the molar concentration of excited molecules.

I_a: is the intensity of light absorbed.

Quantum efficiency for most important parameter of molecular and its values between (1-0) it depends on the nature, concentration, viscosity, temperature and natural of molecular structure of the solvent. Quantum efficiency in higher concentration for solvent is called (Quantum yield) q_{FM} . We can calculate quantum efficiency by using the relation:

$$q_{FM} = \frac{\tau_F}{\tau_{FM}} \qquad (13)$$

Where:

$\tau_{FM:}$ The radiative lifetime

τ_F: The fluorescence lifetime

Calculation for parameters of the NaOH:

By observing the results obtained for some parameters compared with the literature it has been noticed that those results are an approach for mechanism of action, we have found that the impact of solvent on the Molar coefficient (ε) is inversely proportional with the increase of the concentration. The values of these parameters for the molecular used at $1x10^{-3}$ M .

Therotical Part:

This part consist many steps to study molecules using Gaussian 09 program

a. Geometrical parameters:

The optimization of molecular structures for NaOH molecules group, as shown in figure (3) have been done by employing B3LYP density functional theory (DFT) with 6-31G(d,p), Hartree – Fock (HF) calculations and Austin Model (AM1) using Gaussian 09 Package of programs.

b. HOMO/LUMO:

These acronyms stand for the highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO). The HOMO is the molecular orbital of highest energy that is occupied by electrons. The LUMO is the molecular orbital of lowest energy that is not occupied by electrons**.** The HOMO and LUMO are important in determining such properties as molecular reactivity and the ability of a molecule to absorb light

c. Reduce Mass and zero potentional energy:

The energy gap and zero potentional energy for NaOH molecules group is a linear . The result total energy of the product is the collection of energy of all small molecules means.

d. Resulte and Conclusions:

By studying the results and discussion of the absorption and fluorescence spectra and the relation between the Molar extinction coefficient with wave number, and calculating the parameters, the following conclusions have been reached.

e. Absorption spectra in UV:

The absorption spectrum of the dioxane solvent as shown in figure(2) indicates that no absorption spectrum shows the absorption spectrum of NaOH .

Table 2: Shows the flourescence parameter which studies.

Band Width Δλ (nm)	λ_{max}flu(nm)	Relative Intensity (a.u.)	Width
44.379	421	0.506	13spc
352.36	365	1.65	53spc
353.26	357	7.176	55spc
352.37	356	25.64	33spc

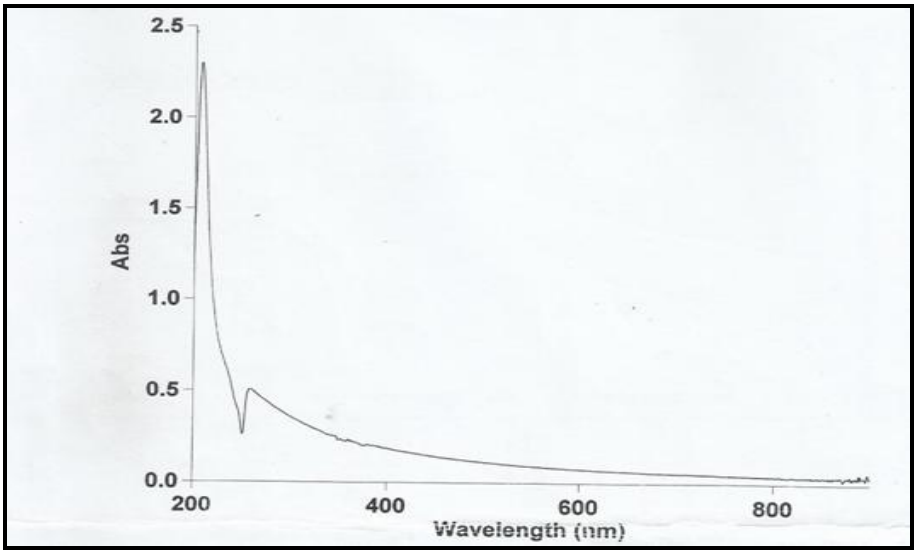


Fig. 2: The relation between absorbance and wavelength Fluorescence spectra in UV region we notice from fluorescence spectrum of the NaOH as shown in figure (3)

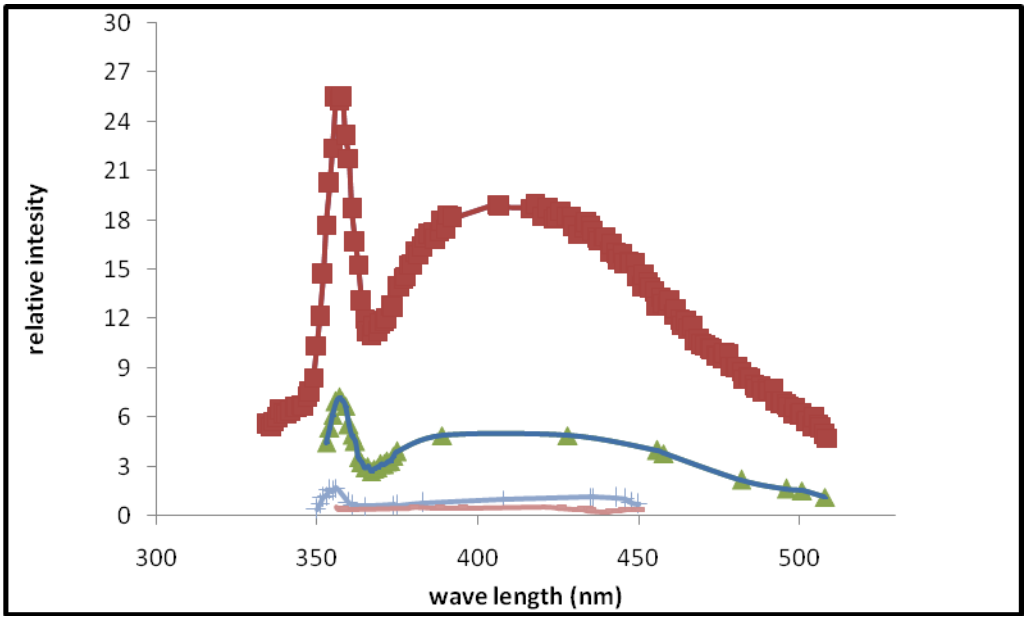


Fig. 3: The relation between fluorescence and wavelength.

So the table 2 shows the flourescence parameter which studied. That peaks of fluorescence shifted (Red Shift) with increasing concentration. Also the fluorescence spectrum was shifted to the longest wavelengths (Red shift) with increase the concentration because of the loss of energy due to non-Radiatve transitions like, internal conversion (IC) and inters system crossing (ISC)

.f. Calculation the Fluorescence Quantum Efficiency:

Quantum efficiency is calculated of the molecular used as an approximation by calculating areas under the curves of the relative absorption and fluorescence spectra using the relation below and software (MATLAB 6.5) so the table 3 explain this results

By using the equation (14) for calculating the quantum efficiency of NaOH solvent, as follow:

$$q_{FM} = \frac{\text{Area under the Curve of the relative Fluorescence}}{\text{Area under the Curve of the relative Absorption}} \quad (14)$$

Table 3: Shows the quantum efficiency and flourescence parameter.

Width	f	q_{fm}
13spc	0.99	0.02
33spc	2.9	0.2
53spc	0.115	0.31
55spc	1.7	0.7

The steady-state interpretation of Stern–Volmer equation shows a linear relationship between *Io/I* and quencher concentration values for the studied system. continuous irradiation with polarized light of

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

Where

P: molecules in solutionPolarization

$I_{\parallel}$ and I_{λ} are time-independent steady state values for fluorescent intensity polarized parallel and perpendicular.

P_o is the maximum P which occurs when the rotational motion is very slow compared to the singlet excited state lifetime.

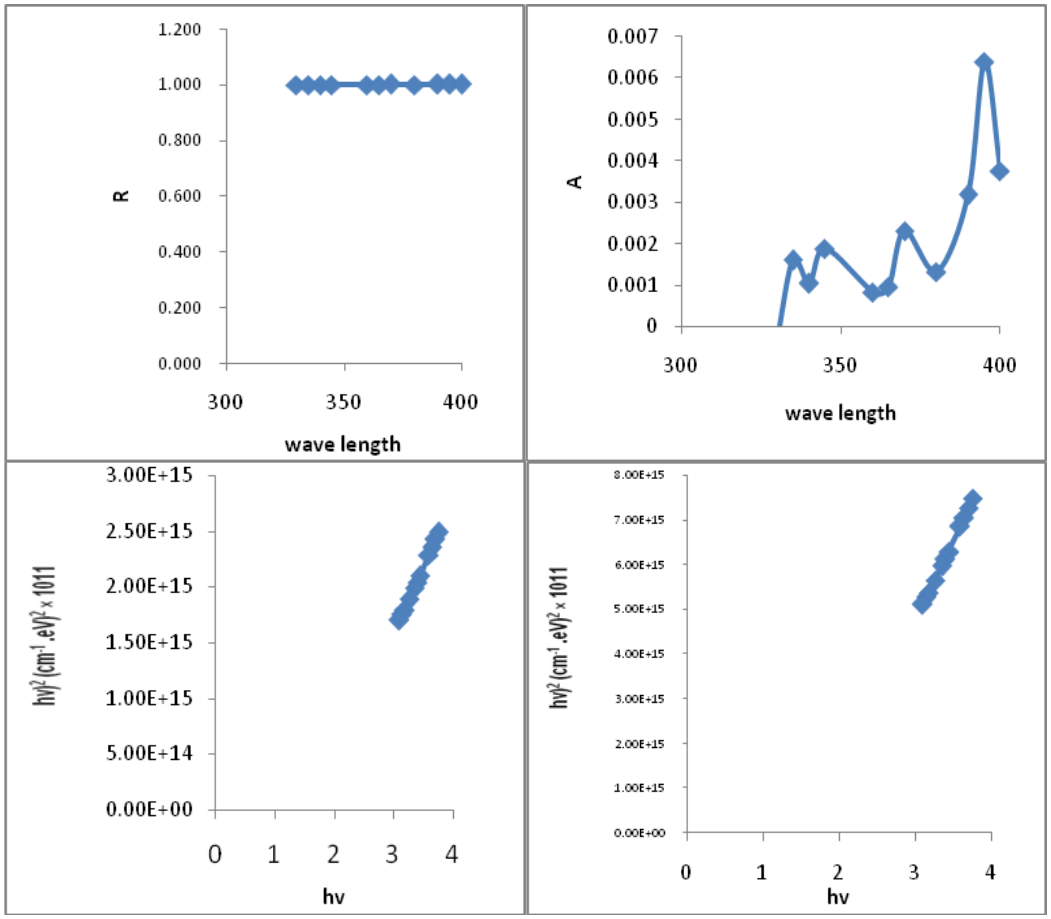
t_{rot} = rotational correlation time = the characteristic lifetime of rotational diffusion. For large proteins t_{rot} is large.

If $t_{rot} << t_F$ than the polarization, approaches to zero (i.e., the steady-state fluorescence is completely depolarized so that by the time the fluorescence occurs, the direction of oscillation of the emission dipole is completely random).

The relationship between P and t_{rot} is:

$$\frac{[(1/P)+(1/3)]}{[(1/P_o)+(1/3)]} = 1+3\left(\frac{\tau}{\tau_{rot}}\right)$$

Using the excel program to evaluate some optical parameter using uv-results to calculate the R,n,E $_g$ real and emaginary and K valuose of NaOH solution as in fig.(4)



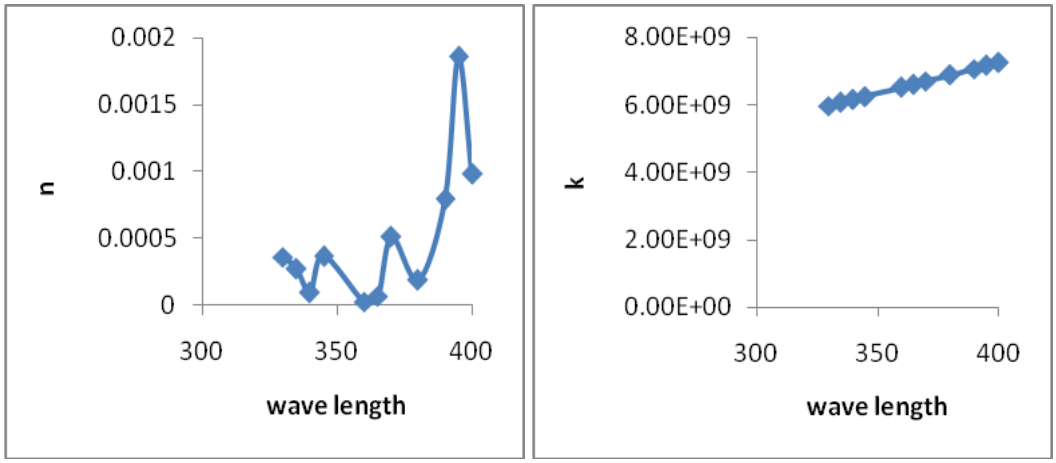


Fig. 4: Optical parameter of NaOH Molecular.

Therotical Resuls:

This parts includes many parameter an methods which calculate to solution which studies in research as show in point below

Used methods:

Three methods have been used. Density function theory, Hartree – Fock and Austin model PM6. The three methods are used Semi empirical method to study the electronic properties for NaOH molecules .. Density functional theory and Hartree – Fock are efficient to study the geometrical optimization and total energies for studied molecules group. And DFT is the best method to calculate the electronic variables and IR spectra for these molecule. The basis sets [6-311 G**, aug-cc-pVQZ ,SDD] are a large description of these molecules and it is more suitable to get a best results and provides economic method for best time with required accuracy. The PM6 semi empirical method gives good results for geometrical parameter for organic molecules but it is poor to calculate the physical properties compared with DFT and HF methods

Geometry optimization:

…The geometry optimization for NaOH in Both base sets [6-311 G**, aug-cc-pVQZ ,SDD]density functional theory and Hartree – Fock method have been found in a good agreement with experimental data. While for other studied Sodium hydroxide molecules, it has not been found a reference data, 6-311G*therefore, this work supplies new results for these molecules as shown in table 4.

Table 4: Shows the Geometry optimization of NaOH .

Parameters (Å)	Calculation methods				
	semi	HF	Density Functional Theory/B3LYP		
	PM6	6-311G*	6-311G**	aug-cc-pVQZ	SDD
Na1 ─ O2	1.9605	1.9236	1.9523	1.9487	1.9158
O2 ─ H3	0.8743	0.9346	0.9588	0.9525	0.9700
Na1 ─ H3	2.8348	2.8582	2.8012	2.9012	2.8857
∠Na1O2H3	180.000	180.000	180.000	180.000	180.000

Computed total energy and symmetry:

By using mode AM1 semiempirical method has not given acceptable results for total energy. While in a good agreement with other studies, Thus this study also supplies a new result in this aspect. The the total energies calculated by [6-311 G**, aug-cc-pVQZ ,SDD] DFT and HF methods have been found results showed in table 5, where the decreasing in total.

Table 5: Shows results of reduce mass and zero point energy

ZPE cm^{-1}	reduced mass(amu) symstreth	reduced mass(amu) bend	reduced mass(amu) asym stretch	Calculation Method	
1963	12.1992	1.1395	1.0624	PM6	Semi empirical
2722	11.3922	1.1479	1.069	6-311*	Hartree Fock
2270	8.2307	1.1926	1.0687	6-311G**	Density functional
2426	11.4094	1.1485	1.0688	aug-cc-pVQZ	
2521	11.2878	1.1523	1.0699	SDD	

Electronic states and energy gap:

The electronic states (HOMO and LUMO) for NaOH molecule using B3LYP / 6-31 G (d,p) have found in good agreement with previous studies, but AM1 / calculations have showed a difference in values of the mentioned properties.

Table 6: Shows results of Electronic states and energy gap.

Energy gap(ev)	Lumo(ev)	Homo(ev)	Calculation Method	
9.3639	0.5867	-8.7772	MP3	Semi-empirical
8.6938	-0.0620	-8.7558	HF/6-311G*	Hartree Fock
3.0107	-1.6063	-4.6170	6-311G**	Density function theory/ B3LYP
3.4205	-1.6158	-5.0363	aug-cc-pVQZ	
2.9127	-1.6076	-4.5204	SDD	

Electronic properties:

B3LYP / 6-31 G (d,p) is a suitable method for calculating the ionization potential, electron affinity, electronegativity chemical hardness, softness and electrophilic index for the studied molecules. Hartree – Fock method The electron affinity, electronegativity, electrophilic index for NaOH These results refer to new species are more .

Dipole moment and polarizability:

The three methods used in this study showed a good result of electric dipole moment of NaOH. As we know that the dipole moment Describes the properties of whole molecules, therefore, it has no effects which may be related to the adding of the substituents as shown in table 7.

Table 7: Shows results of a. Dipole moment b. polarizability.

μ_{total}(Debye)	μ_z(Debye)	μ_y(Debye)	μ_x(Debye)	Calculation Method	
6.356	6.356	0.000	0.000	PM3	Semi empirical
6.344	6.344	0.000	0.000	HF/6-311*	Hartree Fock
5.661	0.000	-5.656	-0.235	6-311G**	Density function theory / B3LYP
6.717	6.717	0.000	0.000	aug-cc-pVQZ	
5.577	5.577	0.000	0.000	SDD	

$<\alpha>$ Å^3	α_{yz} Å^3	α_{xz} Å^3	α_{xy} Å^3	α_{zz} Å^3	α_{yy} Å^3	α_{xx} Å^3	Calculation Method	
0.6223	0.000	0.000	0.000	1.209	0.329	0.329	PM3	Semi empirical
1.6585	0.000	0.000	0.000	2.197	1.428	1.428	HF/6-311*	Hartree Fock
2.751	0.000	0.000	0.752	3.192	4.153	2.907	6-311G**	Density function theory/ B3LYP
1.7611	0.000	0.000	0.000	3.257	3.655	3.655	aug-cc-pVQZ	
1.5411	0.001	-0.001	0.000	3.659	2.793	2.795	SDD	

Table 8: Shows vibration mods of IR spectra of NaOH.

sym stretch Σ_g		Bend π_u		asym stretch Σ_u		Calculation Method	
IR Intensity (km/mol)	Frequency (cm^{-1})	IR Intensity (km/mol)	Frequency (cm^{-1})	IR Intensity (km/mol)	Frequency (cm^{-1})		
98.919	511	461.032	489	195.670	2436	MP6	Semi-empirical
73.310	610	328.004	303	0.719	4230	6-311G*	Hartree Fock
43.972	600	58.706	19	1.764	3928	6-311G**	Density functional theory / B3LYP
80.016	560	110.122	176	8.112	3951	aug-cc-pVQZ	
45.034	600	212.184	303	0.082	3842	SDD	

IR spectra:

In IR spectrum calculations, B3LYP / 6-31 G (d,p) method has been used. For NaOH, the used method gives a large approach of observed peaks with computed experimentally. For other molecules this study supplies new data for IR spectrum table 8 and fig 5 shows this results

Physical properties:

In this section we calculate some electronic properties for NaOH molecules group using DFT, HF and AM1 methods. These properties included the ionization potential IP, electron affinity EA, electronegativity χ, chemical hardness η, softness S and electrophilic index ω the table 9 shows results.

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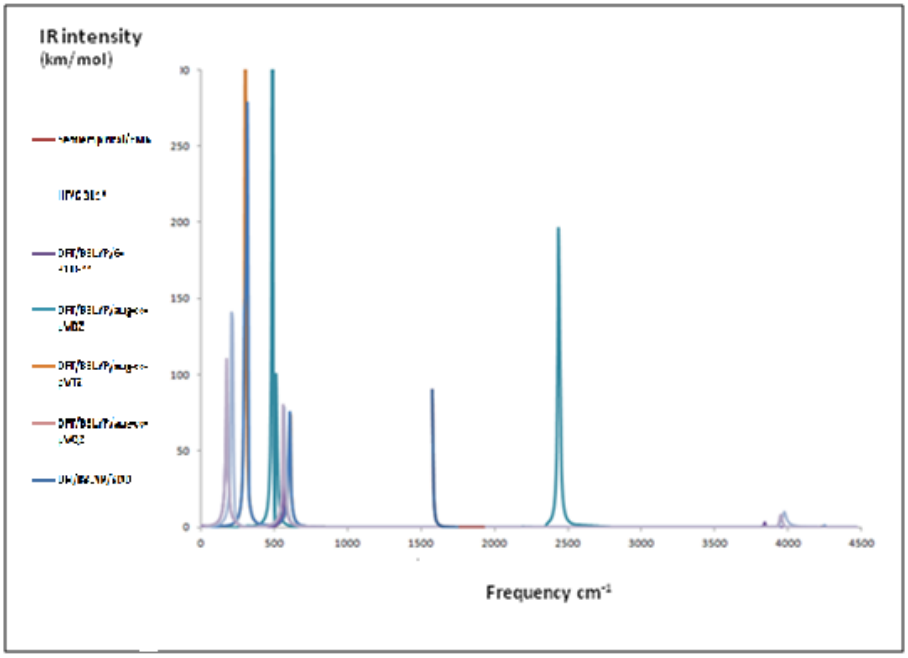

Fig. 5: The IR spectrum by calculation methods.

Physical properties	Calculation Method				
	semi	HF	Density functional theory / B3LYP		
	PM6	6-311G*	6-311G**	aug-cc-pVQZ	SDD
IP	8.7772	8.7558	4.617	5.0363	4.5204
EA	-0.5867	0.062	1.6063	1.6158	1.6076
κ	4.09525	4.4089	3.11165	3.32605	3.064
η	4.68195	4.3469	1.50535	1.71025	1.4564
S	0.106793	0.115025	0.332149	0.292355	0.343312
ω	1.791035	2.235892	3.215985	3.234208	3.223049

Conclusion:

A study of experimental and theoretical study of NaOH solution using Gaussian 09 program gives agood approximation methods which development of science to get results agreement with expermental results and it simplest .So it gives a good indecator of effect on band gap of light which exited the solution and effect on quantum effeciency which results to reduce a quenching effect on flourescence quantum efficiency.

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