THEORETICAL AND EXPERIMENTAL STUDY OF THE VIBRATIONAL SPECTRUM OF PHENOL BASED ON THE DENSITY FUNCTIONAL

Truong Tan Trung[1*✉,] Lai Thi Hien[2✉], Nguyen Ngoc Huong[2],
Nguyen Thanh Si[3], Tran Anh Tu[2]
[1]Institute of Research and Applied Technological Science (IRATS),
Dong Nai Technology University, Dong Nai, 760000, Vietnam
[2]Faculty of Applied Sciences – Health, Dong Nai Technology University, Dong Nai, 760000,
Vietnam
[3]College of Natural Sciences, Can Tho University, Can Tho, 940000, Vietnam

ABSTRACT

In this paper, vibrational characteristics of phenol have been investigated using experimental IR and computational data using DFT (density functional theory) method employing the 6-311++G(2df,2p) basis set available on quantum computational software Gaussian 09W was used. The optimized geometrical parameters suggest that the overall symmetry of the most stable molecule is Cs. The charge transfer occurring in the molecule has been show by HOMO – LUMO energy orbitals the energy gap of HOMO – LUMO orbitals have been found 0.215 84 eV. The mapping of electron density iso-surface with the molecular electrostatic potential (MEP), has been carried out to get the information about the shape, size and charge density distribution of phenol. Some essential vibrational characteristics, namely, O–H stretch/bend/torsion, aromatic C–H stretch, C–O stretch, C=C ring stretch/bend of the molecule have also been analyzed and compared with the previously reported ab initio data and with the experimental.

Keywords: Density functional theory, infrared spectrum, HOMO – LUMO analysis, phenol

1. Introduction

Phenol, also referred to as carbolic acid or monohydroxy benzene, is a versatile industrial organic chemical. It is used to produce a wise variety of chemical intermediated, including bisphenol-A, phenolic resins, cyclohexanone and aniline. Major applications of phenol involves adhesives, agro chemiscal, automotive, cleaning, coatings, construction, cosmetics and packaging. Their characteristic group is the OH group joining to a $C = C – C$ part of the aromatic ring. The vibrational spectroscopic study of phenol is restricted mainly to the benzene derivatives. However, during the last decade, considerable efforts have been devoted to the understanding of the vibrational spectra of phenol. It has been shown that the experimentally observed frequencies of phenol are reasonably well reproced by quantum chemical calculations at moderate computational levels [1], [2].

The evolution of Density Functional Theory (DFT) that includes electron correlation in an alternative way has affording opportunities of performing vibrational analysis of organic molecules. Systematic comparison of the results from DFT theory with results of experiments has shown that the methods using Becke's theory parameter hybrid functional (B3) with

correlation functions such as one proposed by Lee, Yang and Parr (LYP) are the most promising in providing correct vibrational wave numbers [3]. Hence, a systematic study on the vibrational spectra of phenol and some of its derivatives with DFT calculations using Gaussian program has been carried out [1], [2], [4], [5]. However, the basis sets used is low. Therefore, the calculated value is different so that the experimental value.

In the present paper, we report calculated geometric and vibrational spectroscopic data of phenol, along with corresponding experimental data as far as available. The calculations with density functional theory methods using B3LYP/6-311++G (2df,2p) level. The experimental parameters are compared with the calculated ones. We are going to reveal the information about the shape, size and charge density distribution of phenol, hope to provide insight into the nature of the vibrations of molecule have been analysed.

2. Computational methods

The optimized molecular geometries, vibrational spectroscopic data (bond distances and angles, vibrational frequencies, infrared intensities) and HOMO – LUMO analysis of phenol is calculated by DFT with the hybrid B3LYP [6], [7], [8] exchange correlation functionals and the 6-311++G(2df, 2p) [9] basis functions. The Gaussian 09 program package [10] was used for all the calculations. The calculated results were visualized via Gauss View 5.0 program [11].

3. Results and discussion

3.1. Molecular structure analysis

The optimized molecular structure of phenol was give in Figure 1 with numbering of the atoms. Although the theoretical geometries (i.e., minimum energy geometries) for phenol isn't the main focus of this investigation, we should like to comment briefly on these result. The bond lenghts and angles optimized at the same leve of theory is displayed in Table 1 along with the available experimental data, were calculated using B3LYP/6-311++G (2df,2p) theoretical methods.
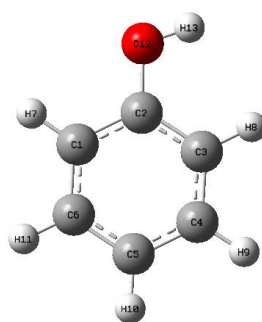

Figure1. The optimized molecular structure and atom numbering scheme adopted in this study for phenol at the B3LYP/6-311++G (2df,2p) level

The calculated molecular geometric parameters were compared with the experimental and theoretical geometric parameters of similar structures in the literature [12]. C2 – C3, C3 – H8, C4 – H9, C5 – H10 and C2 – O12 bond lengths of phenol were computed as 1.392 Å, 1.084 Å, 1.082 Å, 1.081 Å, 1.367 Å respectively. Likewise, H13O12C2 bond angles were computed as 109.940 for B3LYP/6-311++G (2df,2p), 108.50 for MP2/6-31G(d,p) [12], whereas their experimental values were reported as 109.90 [13].

Table 1: B3LYP/6-311++G (2df,2p) optimized and experimental geometric parameters of phenol

| Parameters	B3LYP	MP2[a]	Exper.[b]
r(C2–C3)	1.392	1.396	1.398 Å
r(C3–H8)	1.084	1.084	1.084 Å
r(C4–H9)	1.082	1.082	1.076 Å
r(C5–H10)	1.081	1.081	1.082 Å
r(C2–O12)	1.367	1.372	1.364 Å
r(O12–H13)	0.962	0.965	0.956 Å
α(H13O12C2)	109.94^0	108.5^0	109^0

Note: Bond lengths in Å, angles in degrees
[a] From Ref. [12]
[b] From Ref. [13]

The agreement between the DFT/B3LYP-calculated structure of phenol and experiment would have better. It is interesting that, the DFT/B3LYP/6-311++G (2df,2p) level overestimates both the O – H, C – O, C = C bond length, it produces frequencies of the corresponding O – H, C – O, and C = C stretching vibrations in excellent agreement with experiment, as we will show in the next section.

3.2. Vibrational frequency analysis
Phenol molecule has 13 atoms and 33 fundamental vibrational modes. The three normal modes of OH-group are: O – H stretching, O – H bend and O – H torsion. The two normal modes of C = C group are: C = C ring stretch and out-of-plane ring C = C bend. The calculated harmonic frequencies and infrared intensities are shown in Table 2 and compared to the available experimental data. The calculated and experimental IR are reproduced in Figure 2.
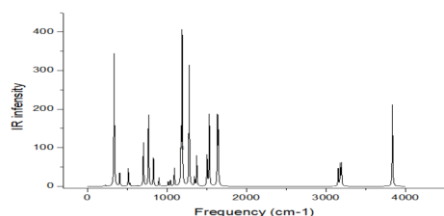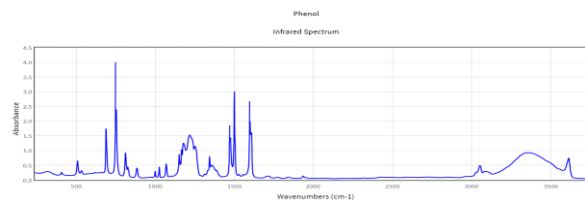
NIST webpage: http://webbook.nist.gov/chemistry
[Error! Bookmark not defined.]

(a)   (b)

Figure 2. (a) The calculated and (b) experimental IR spectrum of phenol

OH Vibrations. The most indicative frequency shifts, due to compexation of phenol, are associated with the O – H stretching, O – H bending and the torsion vibration about the C – O axis. The OH stretching (Q33) mode corresponds to the frequency 3834.9 cm-1 (Table 2). The O – H stretching vibration is pure and highly localized mode. The frequency of this mode obtained at the DFT level is overestimated by about 6% than the experiental value, 3656.7 cm^{-1}.

The OH in-plane bending vibration is still controversial in the ab intro calculated spectra. Therefore, the OH in-plane bending vibration contributes mainly to the fundamental at 1193.1 cm^{-1} (Q20) and also to the mode at 1374.8 cm^{-1} (Q23) in the spectrum of phenol.

CO Group modes. These modes are labeled (Q1), (Q3), (Q5), (Q6), (Q11), and (Q21). Six modes involve considerable motion of both the phenyl ring and CO group. The computed B3LYB frequencies of these modes is quite close to the corresponding experimental values. According to the Potential Energy Distribution (PED) obtained at the theory levels, the C – O stretching vibration contributes mainly to the band observes at 1280.6 cm^{-1} (Q21) and also to the band at 830.8 cm^{-1} (Q11).

Phenyl Ring. The phenyl ring modes are due to the CH in-plane bending, CH out-of-plane bending, and ring deformation vibrations. In phenol there are five modes associated with the CH in-plane bending vibrations: Q16, Q17, Q18, Q19, Q22 (Table 2). The infrared intensities of these modes computed at the DFT when compared with the ralative experimental data are quite similar; however, a large discrepanct is noted for mode Q19. This mode is observed in the infrared spectrum of phenol at 1191.4 cm^{-1}, very close to the mode at 1193.1 cm^{-1} (Q20) of OH bending vibration. Assignment of the out-of-plane CH vibrations in phenol: Q9, Q10, Q12, Q13, and Q14 are associated with the out-of-plane γCH vibrations.

Table 2: The results of vibrational frequencies (ν, cm^{-1}) for experimental and calculated.

Mode no.	Assignment	B3LYP/6-311++G(2df,2p)	Experiment*
Q1		229.6	244.5
Q2	O – H torsion	338.0	309.2
Q3		406.5	403.1
Q4		422.0	408.5
Q5		515.4	502.8
Q6		537.4	526.6
Q7	Out-of-plane ring C = C bend	634.3	618.7
Q8		705.1	685.9
Q9	Out-of-plane C – H bend	769.5	750.6
Q10	Out-of-plane C – H bend	826.6	817.2
Q11		830.8	823.2
Q12	Out-of-plane C – H bend	900.3	881.0
Q13	Out-of-plane C – H bend	972.0	958.0

Q14	Out-of-plane C – H bend	998.7	972.5
Q15		1017.6	999.3
Q16	in-plane C – H bend	1044.9	1026.1
Q17	in-plane C – H bend	1094.5	1072.4
Q18	in-plane C – H bend	1177.5	1150.7
Q19	in-plane C – H bend	1191.4	1168.9
Q20	O – H bend	1193.1	1176.5
Q21		1280.6	1261.7
Q22	in-plane C – H bend	1347.2	1277.4
Q23		1374.8	1343.0
Q24		1505.0	1472.0
Q25		1533.0	1501.0
Q26		1635.9	1603.0
Q27	C = C ring stretch	1646.6	1610.0
Q28	Aromatic C – H stretch	3153.2	3027.0
Q29	Aromatic C – H stretch	3170.6	3049.0
Q30	Aromatic C – H stretch	3178.9	3074.5
Q31	Aromatic C – H stretch	3193.1	3070.0
Q32	Aromatic C – H stretch	3199.4	3086.6
Q33	O – H stretch	3834.9	3656.7

 *From Ref. [12]

HOMO-LUMO energy gap. The molecular orbital (MO) is a very important concept in quantum chemistry, being extensively employed to describe the chemical behavior. The highest occupied molecular orbital HOMO and lower unoccupied molecular orbital LUMO are the two most important molecular orbitals in a molecule as both are used to describe various chemical properties such as reactivity and kinetics [14]. These orbitals are known by the name frontier orbitals, they lie at the outermost boundaries of the electrons of the molecules. Both the HOMO

and LUMO are the main orbitals that take part in the chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The difference of the energies of the HOMO and LUMO is a measure of the excitability of the molecule, the smaller the energy, more easily it can be excited and vice versa [15]. The atomic orbital compositions of the frontier molecular orbital are sketched in Figure 3.

Figure 3 shows mapped is odensity surface plots of molecular orbitals from HOMO-2 to LUMO+2 of phenol in which all the LUMO surfaces are well localized within the benzen ring.

HOMO energy (B3LYP) = -0.240 05 eV

LUMO energy (B3LYP) = - 0.024 21 eV
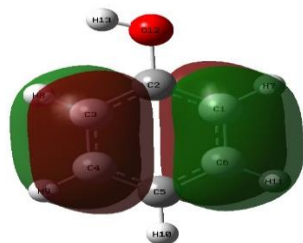
HOMO-LUMO energy gap (B3LYP) = 0.215 84 eV

As seen in Figure 4, the HOMO-LUMO gap energy value (0.215 84 eV) indicates a good reactivity. This electron trasition corresponds to the transition from the ground to the first excited state and is mainly described by an electron excitation from HOMO to LUMO.
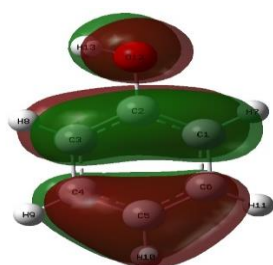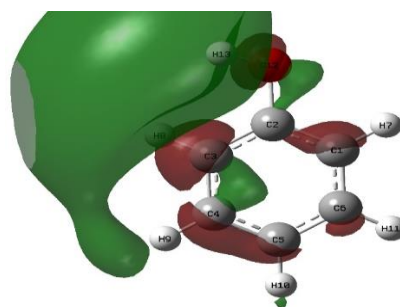

(a)   HOMO
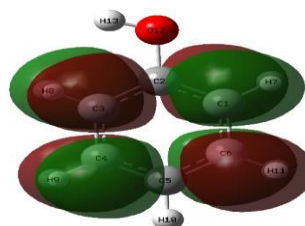
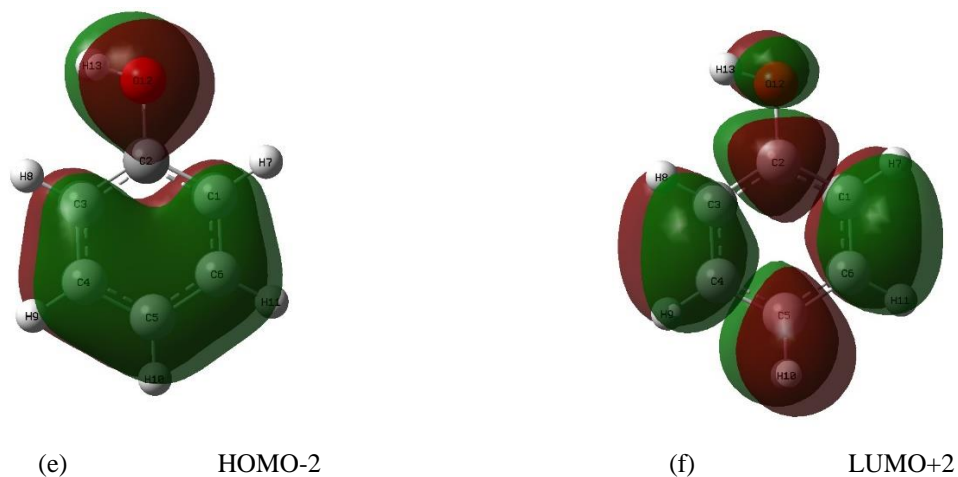(b)   LUMO

(c)   HOMO-1

(d)   LUMO+1

<div align="center">(e)   HOMO-2   (f)   LUMO+2</div>

Figure 3: Isodensity plots of the frontier molecular orbitals of phenol.

$E_{LUMO} = -0.024\ 21\ eV$

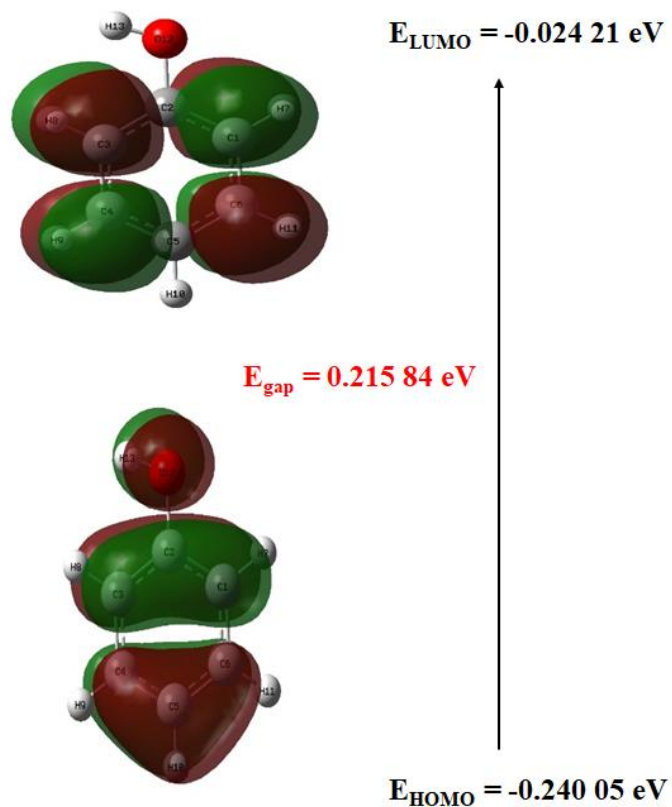$E_{gap} = 0.215\ 84\ eV$

$E_{HOMO} = -0.240\ 05\ eV$

Figure 4. The molecular orbitals and energies for the HOMO and LUMO of the title compound

Molecular electrostatic potential surface. In the present study, molecular electrostatic potential (MEP) and contour map for phenol illustrated in Figure 5. The MEP which is a plot of electrostatic potential mapped into the constant electron density surface. The importance of MEP lies in the fact that it simultaneously display molecuar size, shape as well as positive, negative and neutral electrotatic potential regions in terms of color grading and is very useful in research of molecular structure with its physiochemical property relationship.
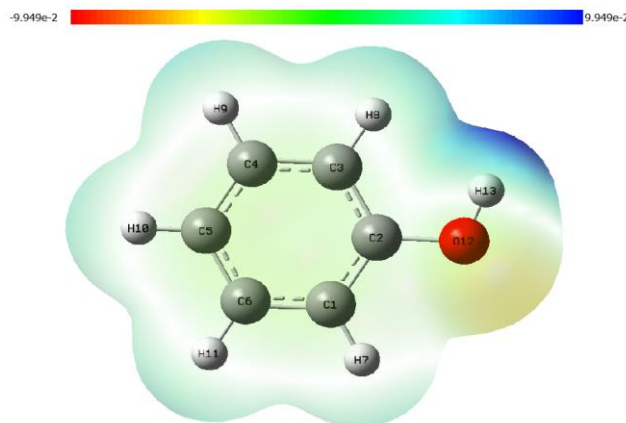

Figure 5. Molecular Electrostatic Potential (MEP) map calculated at the B3LYP/6-311++G(2df,2p) level.

The Figure 5 to shows the electrostatic potential for phenol. The more red an area is, the higher the electron density and the more blue an area is, the lower the electron density. The hydroxyl O atom is a region of high eletron density (red) due to the lone pairs. The hydorxyl O atom can function as a nucleophile or Lewis base. There is low electron density (blue) on H atom of the hydroxyl group, i.e. H+ character, therefore phenols are acidic. Due to conjugation with the ring, phenols are more acidic than alcohols.

4. Conclusions

From the above studies on the (geometric, vibrational spectroscopic, HOMO-LUMO, MEP) of phenol at the B3LYP/6-311++G(2df,2p) level, we can draw the following conclusions.

(1) For geometric data, agreement between theory and experiment. For vibrational spectroscopic data, DFT calculations excellently agree with experimental results, although most frequencies are higher than the experimental fundamentals.

(2) The charge transfer occurring in the molecule has been show by HOMO – LUMO energy orbitals the energy gap of HOMO – LUMO orbitals have been found 0.215 84 eV. The resulting surface displays molecular size, shape and electrostatic potential value when molecular electrostatic potential is analyzed.

ACKNOWLEDGMENTS

REFERENCES

H. Lampert, W. Mikenda, A. Karpfen (1997), Molecular geometries and vibrational spectra of phenol, benzaldehyde, and salicyladehyde: Experimental versus quantum chemicak data, *J. Phys. Chem. A* **101**, pp 2254-2263.

I. Mohammed-Ziegler, F. Billes (1997), Vibrational spectrpscopy of phenols and phenolic polymers. Theory, experiment, and applications, *Applied Spectroscopy Review*, **42**, pp.369-441.

A. Sirvastava, V. B. Singh (2007), Theoretical and experimental studies of vibrational spectra of naphthalene and its cation, *Indian Journal of Pure & Applied Physics*, **45**, pp.714-720.

G. X. Waang, X. D. Gong, Y. Liu, H. M. Xiao (2009), A theoretical study on the vibrational spectra and thermodynamic properties for the nitro derivatives of phenol, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **74**, pp.569-574.

D. Mahadevan, S. Periandy, S. Ramalingam (2011), Vibrational spectroscopy (FTIR and FTRaman) investigation using ab initio (HF) and DFT (B3LYP) caculations on the structure of 3-Bromo phenol, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **78**, pp.575-581.

A. D. Becke (1993), Density-functional exchange-energy approximation with correct asymptotic behavior, *J. Chem. Phys.* **98**, pp.5648-5652.

A. D. Becke (1996), A new mixing of Hartree-Fock and local density-functional theories, *J. Chem. Phys.* **104**, pp. 1040-1046.

C. T. Lee, W. T. Yang, R. G. Parr (1988), Development of the Coll-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B,* **37**, pp. 785-789.

(a) A. D. McLean, G. S. Chandler (1980), Contracted Gaussian basis sets for molecular calculation. I. Second raw atoms, Z = 11 – 18, *J. Chem. Phys.* **72**, pp.5639-5649; (b) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople (1980), Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions, *J. Chem. Phys.* **72**, pp.650-655; (c) T. Clark, J. Chandrasekhar, G. W. Spitzagel, P. V. R. Schleyer (1983), Efficient diffuse funcion-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li-F**,** *J. Comp. Chem.,* **4,** pp. 294-301.

M. J. Frisch et al. (2009), *Gaussian 09 (Rversion-A.02)*; Gaussian, Inc., Wallingford, CT.

R. Dennington, T. Keith, J. Millam (Eds). (2009), Gauss View, Version 5, Semichem Inc., Shawnee Mission KS.

D. Michalska, D. C. Bienko (1996), Density functional, Hartree-Fock, and MP2 studies on the Vibrational spectrum of Phenol, *J. Phys. Chem.* **100**, pp.17786-17790.

NIST webpage: http://webbook.nist.gov/chemistry

G. Zhang, C. B. Musgrave (2007), Comparison of DFT methods for molecular orbital eigenvalue calculations, *J. Phys. Chem.*, **111**, pp.1554-1561.

V. Dixit, RA. Yadav (2015), Experimental IR and Raman Spectroscopy and DFT methods bases material characterization and data analysis of 2-Nitrophenol, *Biochem Phamacol, an open access journal,* volume 4, Issue 4.