IRAQI Academic Scientific Journals
العراقية المجلات الأكاديمية العلمية
Al-Kut University College Journal
ISSN (E) : 2616 - 7808 II ISSN (P) : 2414 - 7419
www.kutcollegejournal.alkutcollege.edu.iq
Vol. 6 , Issue 2 , Dec. 2021

The Spectral Properties of C_6H_5Cl and C_6H_5OH Compounds

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Abstract

The electronic spectra within UV-Vis region for chlorobenzene (C_6H_5Cl) and phenol (C_6H_5OH) and, have been studied. The bands, centered at 260nm and 240nm are assigned to electronic transitions $\pi\rightarrow\pi^*$ type for C6H5Cl and C_6H_5OH respectively. However, an electronic transition of type $n\rightarrow\sigma^*$ has been absorbed, at 265nm only for C_6H_5OH compound .The spectral shifts of these electronic bands were studied under various [pH] values. The vibrational bands of these two compounds have been studied by using Infrared and Raman scattering techniques. In the fact, these two compounds may be regarded as benzene C_6H_6 which belongs to D6h point group with one of the hydrogen atom is substituted by Cl- and OH- ions for C_6H_5Cl, and C_6H_5OH respectively .These substitutions will reduce the symmetry of point group to C_2V, and hence will activate all the vibrational modes to be allowed in both infrared and Raman techniques. These aspects will be studied and discussed in this work.

Keywords: vibration, FTIR, Raman spectroscopy

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Paper Info.
Published: Dec. 2021

الخصائص الطيفية لمركبات الكلوروبنزين والفينول

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الخلاصة :

تم دراســة الأطياف الإلكترونية في منطقة فوق البنفســجية والمرئية (UV_Visble) للكلوروبنزين (C_6H_5Cl) والفينول (C_6H_5OH). يتم تعيين النطاقات المتمركزة في 260 نانومتر و 240 نانومتر على التحولات الإلكترونية $\pi \rightarrow \pi^*$ من النوع C6H5Cl و C_6H_5OH بشكل ملحوظ. ومع ذلك، تم امتصاص الانتقال الإلكترونية لنوع $n \rightarrow \sigma^*$ ، عند 265 نانومتر فقط لمركب C_6H_5OH. تم دراسة التحولات الطيفية لهذه النطاقات الإلكترونية تحت قيم [pH] مختلفة . وقد تمت دراسة الحزم الاهتزازية لهذين المركبين باستخدام تقنيات الانتشار بالأشعة تحت الحمراء والرامان. في الواقع ، يمكن النظر إلى هذين المركبين على أنه يتم اســتبدال البنزين C_6H_6 الذي ينتمي إلى مجموعة نقطة D_6h مع واحدة من ذرة الهيدروجين بواسطة -Cl- and OH أيونات C_6H_5Cl ، و C_6H_5OH على التوالي. هذه البدائل سوف تقلل من تناظر مجموعة النقاط لـــ C_2V، وبالتالي سيتم تفعيل جميع وسائط الاهتزاز ليتم السماح في تقنيات الأشعة تحت الحمراء ورامان. سيتم دراسة هذه الجوانب ومناقشتها في هذا العمل.

الكلمات المفتاحية : الاهتزازية، الأشعة تحت الحمراء، الرامان

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معلومات البحث
تأريخ النشر : كانون الأول 2021

1. Introduction

The C_6H_6 molecule posses D_{6h} point group , with $6C_2$, C_3 , and C_6 (axes of rotations) , $6\sigma_v$, and σ_h (planes of reflections) , and S_6 (plane of reflection + axis of rotation) symmetry operations . However when one of hydrogen atom at corner is substituted by Cl^- and OH^- , the point group of the new molecule will be reduced to C_{2V} point group [1]. These two organic compounds are colorless, and flammable usually used as intermediate solvents in manufacturing of some pesticide [2]. The impress of the hydroxyl group on the electronic spectra of Benzene derivatives (for example C_6H_5OH) is of interest for a number of reasons [3]. Firstly phenol is known to give rise to hydrogen bonding form, and secondly, phenol may be regarded as substation compound of Benzene (derivative). The Chlorobenzene compound is also an aromatic organic compound with one hydrogen atom is substituted by Cl- [2]. The bond lengths of the ring have also shown characteristic variation but these changes have been small and less well determined than the changes of angles between bonds [4]. Due to the high symmetry of the hexagonal unsubstituted benzene framework and its relative rigidity, the substituted benzene derivatives are well suited for accurate geometrical studies [4,5]. The following work will deal with the electronic spectra, and vibrational spectra by using IR and Raman techniques for these two compounds.

2. Experimental details

2.1 Chemicals and reagents

Different chemicals and reagents which have been used in present study, are listed in table(1) . The purities, companies, and manufacture countries of the used chemical are show in table (1).

Table (1): Chemical and regents, which have been used in this study

Chemical	Company	Country	Purity
Chlorobenzene	Schuchardt	Germany	99.8%
Phenol	Fluka	Switzerland	98.6%
Ethanol	sigma Aldrich	USA	99.9%
NaOH	BDH	England	99.9%
HCl	Romil	UK	99.98%

Derivatives are well suited for accurate geometrical studies [4,5].

The following work will deal with the electronic spectra, and vibrational spectra by using IR and Raman techniques for these two compounds.

2.2 The UV-Visible spectra:

The UV-Visible spectra have been measured by using Perkin – Elmer lambda 750.

2.3 Fourier Transform Infrared Spectroscopy (FTIR) Measurements:

Fourier transform infrared spectrometer (SHIMADZO IRAFFINITY- Japan) has been used.to measure Infrared spectra of, C_6H_5Cl solution and C6H5OH compounds.

2.4 The Raman spectra:

Have been measured by using ventana spectrophotometer which is used the second

harmonic generation laser (532nm) of the Nd-Yag laser as an excitation source.

3. Results and discussions

The UV-Vis spectrum of C_6H_5Cl is shown in figure (1). The band centered at 240nm is assigned to $\pi \rightarrow \pi^*$ electronic transition of C=C band. It should be mentioned that there is no bands have been observed within visible region (400-800nm) which indicates that this compound is colorless substance [6].

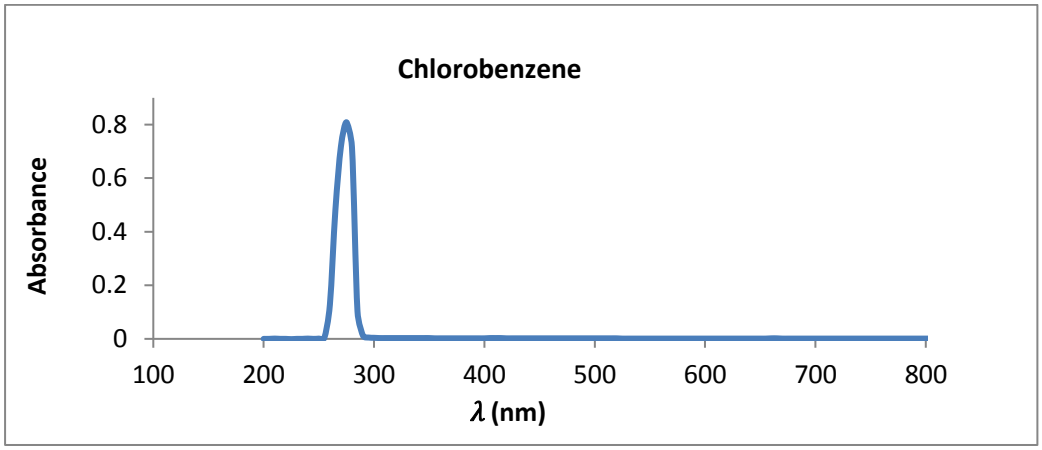

Figure 1: Shows; the UV-Visible Spectrum of pure C6H5Cl compound

However, one may expect bands within vaccum Ultra-Violet region (λ < 200nm) for $\sigma \rightarrow \sigma^*$ electronic transitions of C-H , C-C and C-Cl bonds , where the used UV-Vis spectrometer does not cover this wavelength range.

The [pH] value measurements have been recorded by using pH meter Hana, (Mauritius), different values of [pH] for C_6H_5Cl compound as shown Table [2]. However, on going from $[pH^-] = 7 \rightarrow 12$, blue shift (shifting toward shorter wavelenght) has been absorved.

Table 2: wave length shifts of $\pi \rightarrow \pi^*$ band at different values of [pH] , for C_6H_5Cl compound.

[pH] values	**λ (nm)**
2	235
4	240
7	260
10	240
12	235

On changing the values of [pH] by adding drops of HCl and NaOH , the centre of $\pi \rightarrow \pi^*$ band shows red shift (shifting toward higher wavelenght on going from [pH] = $2 \rightarrow 7$, as shown in figure [2].

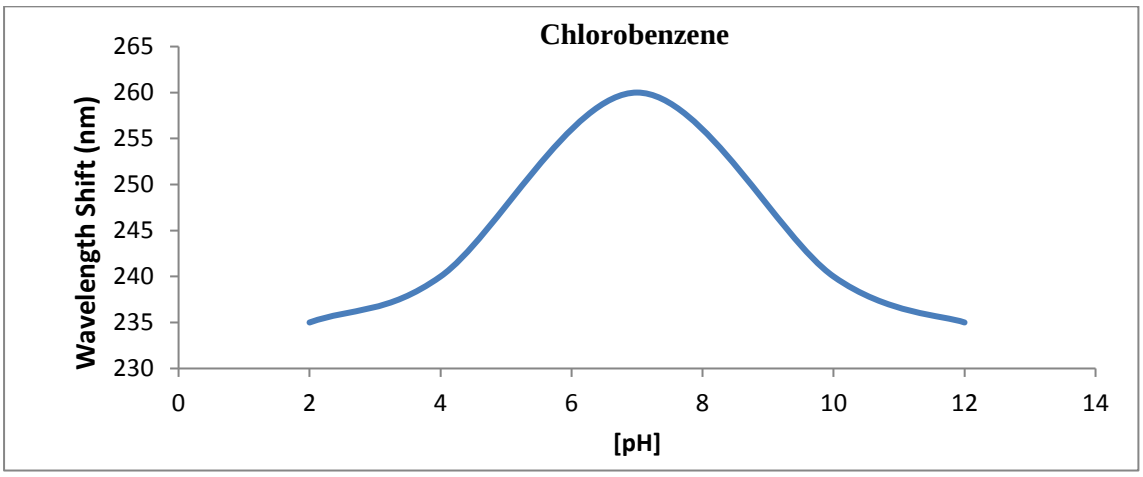

Figure2: Shows; the wavelength Shifts of $\pi \rightarrow \pi^*$ band with various [pH], for C_6H_5Cl compound.

For C_6H_5OH compound the UV-Vis spectrum shows two bands center at 240nm and 262nm as has been shown in figure (3). These two bands are assigned as $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ electronic transitions, respectively [6].

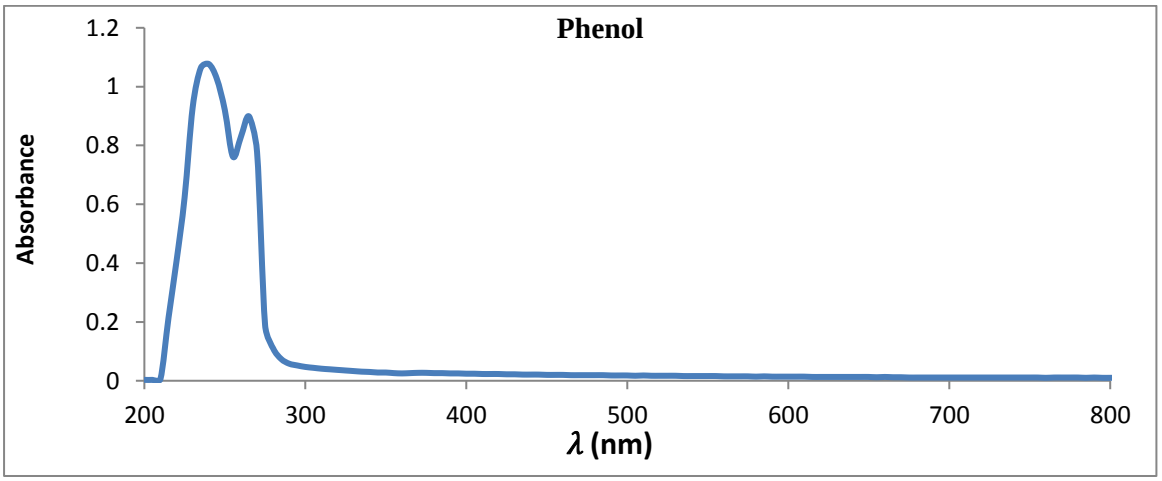

Figure3: Shows; the UV-Visible Spectrum of pure C_6H_5OH compound .

The [pH] value measurements have been recorded by using pH meter Hana, (Mauritius), different values of [pH] for C_6H_5OH compound as shown Table [3].

Table 3: listed the wave length shift of n →σ* band center at different values of [pH] for C_6H_5OH compound

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[pH]	λ(nm)
2	290
4	270
7	265
10	280
12	295

However, blue shift has been absorbed for n→σ* band, on increasing the value from [pH] = 2→ 7, and red shift has been recorded on changing [pH] = 7→12, as shown in figure (4).These wave length shifts, of the electronic bands for the two compounds, are expected because of the environmental existences of H^+ and OH^- ions by adding HCl and NaOH respectively

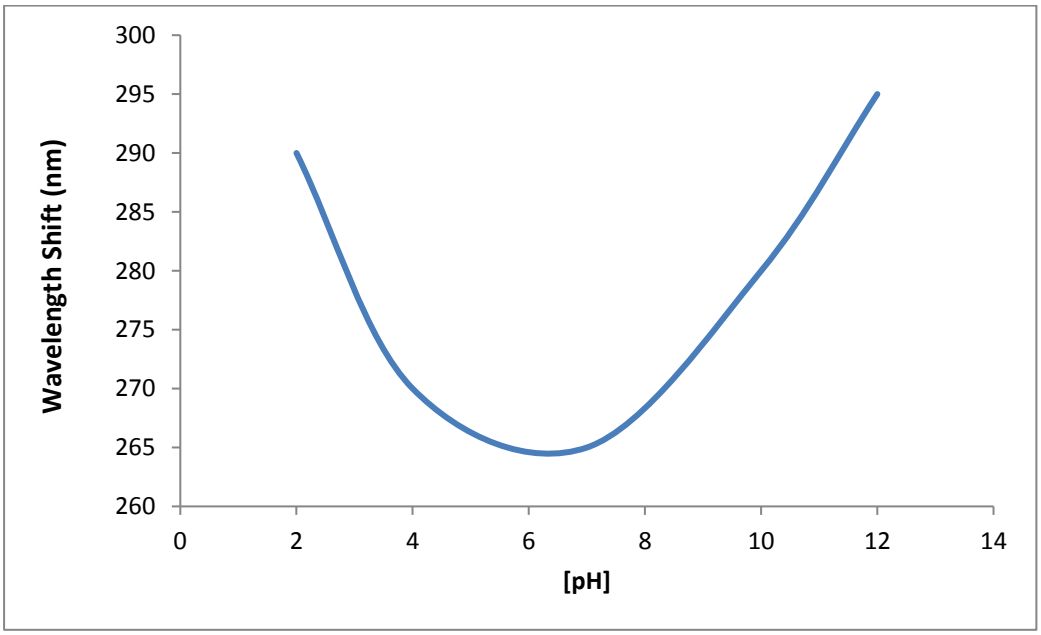
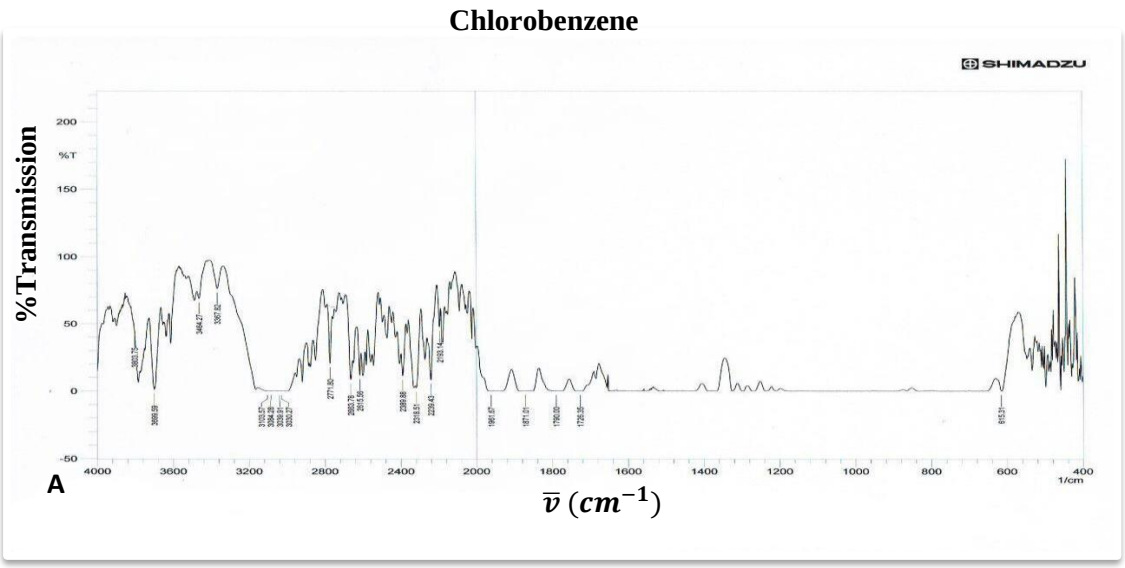


Figure 4 : Shows; the wavelength Shift of n →σ* band for C_6H_5OH compound .

Therefore ,when the point group of C_6H_5Cl and C_6H_5OH molecules have been reduced to C_{2v} [12] , on substuting one H-atom at covner by Cl^- and OH^- , respectively , Accordingly , all modes of vibrations will be active in both techniquce Figure (5) (A) the FTIR Spectrum, and (B) the Raman spectrum of C_6H_5Cl compound.



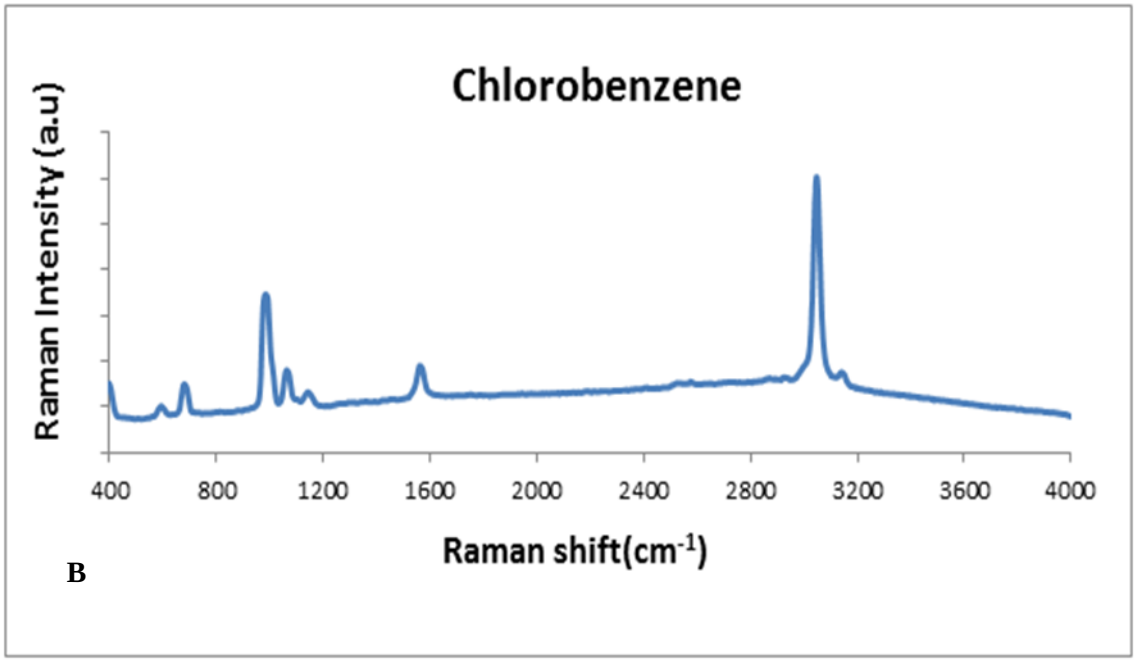
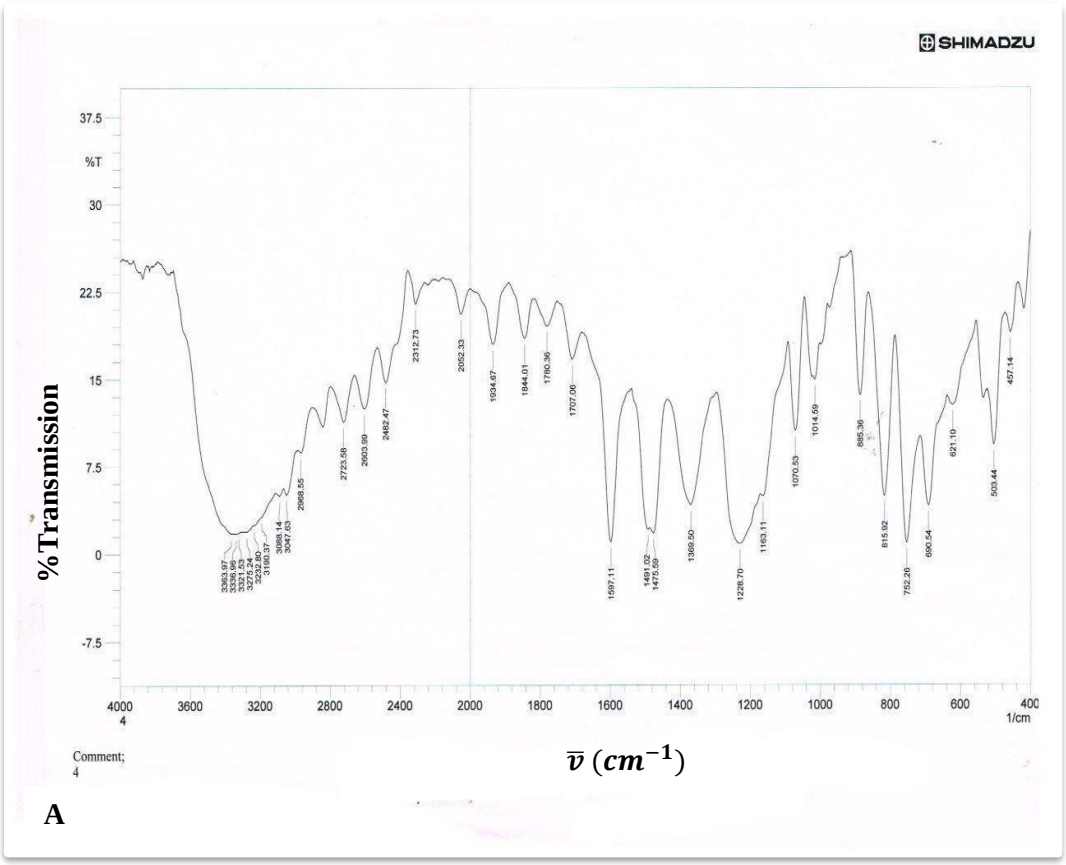


Figure (5) : Shows, (A) the FTIR Spectrum, and (B) the Raman spectrum of C_6H_5Cl compound.

When the intensities of vibrational modes depend on the strength, of dipole moments , and polarizability tensors [16-18].

the point groups of Phenol C_2v symmetry according to the activities of the vibrational bands, techniquce Figure (6) Shows (A) the FTIR Spectrum, and (B) the Raman spectrum of C_6H_5OH compound.

Phenol



Similar spectra have been reported by many workers for both compounds C_6H_5Cl and C_6H_5OH . [13-15].

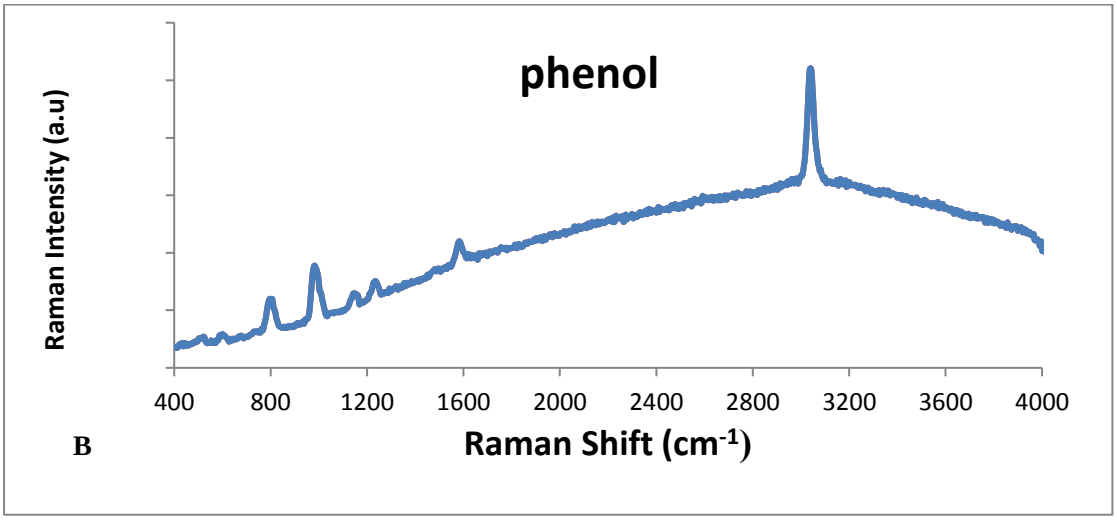


Figure (6) Shows , (A) the FTIR Spectrum, and (B) the Raman spectrum of C_6H_5OH.

4. Conclusions

The spectral bands for the C_6H_5OH and C_6H_5Cl, which have been observed within UV- region, have been assigned as $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ electronic transitions. The wavelength shifts of these bands were studied.

The modes of vibrations have been studied by using IR and Raman techniques where the point groups of these two compounds revealed C_2v symmetry according to the activities of the vibrational bands.

Acknowledgments

Authors wish to thank Applied Sciences Department - University of Technology, for encarging to achieve the following research.

References

[1] Gerhard Herzberg, van Nostrand Reinhold Co (USA) 1945.

[2] Xiaoyan Zhao., Xiaolan Zeng, Yu Qin, Xiang Li, Tianle Zhu, Xiaolong Tang , " An experimental and theoretical study of the adsorption removal of toluene and chlorobenzene on coconut shell derived carbon " , (Pertain) ,18, 2018 , 18, 30775-6 .

[3] J.C.DEARDEN AND W. F. FORBES," LIGHT ABSORPTION STUDIES PART XIV THE ULTRAVIOLET ABSORPTION SPECTRA OF PHENOLS", (Can. J. Chem), 37, 1959, 1294-1304.

[4] M. Govindarajana, M. Karabacakb, V. Udayakumarc, and S. Periandyd, " FT-IR, FT-Raman and UV spectral investigation: Computed frequency estimation analysis and electronic structure calculations on chlorobenzene using HF and DFT ", 2012, (Spectrochimica Acta Part A.), 88, 2012, 37–48.

[5] Sieghard Spectroscopy, Albert a,b, Karen Keppler a, Philippe Lerch b, Martin Quack a, Alexander Wokaun c, " Synchrotron-based highest resolution FTIR spectroscopy of Chlorobenzene ", (Journal of Molecular) , 03, 2015, 004 .

[6] Banwell C N 1983 3rd e. London: McGraw-Hill.

[7] R.M. Silverstein., G.C. Bassler, T.C. Morrill, "Spectrometric Identification of Organic Compounds", John Wiley, (Chichester) 1991.

[8] Bernhard Schrader Raman / infrared atlas of organic compounds (Wiley-VCH publisher), New York (USA) 1989.

[9] E. A. Nothnagel, and R. N. Zitter, The pH dependence of the ultraviolet and visible absorption and the resonance Raman spectra of 4-nitro-1, 2-benzenediol in aqueous solution, (J. Phys. Chem), 80 (7), 1976, 722–727.

[10] V. Krishnakumar, R. John Xavier, Normal coordinate analysis of vibrational spectra of 2-methylindoline and 5-hydroxyindane, (Indian J. Pure Appl. Phys). 41, 2003, 597.

[11] F.R. Dollish, W.G. Fateley, F.F. Bentley, (Characteristic Raman Frequencies of Organic Compounds), Wiley, New York 1997.

[12] S. Albert, P. Lerch, R. Prentner, M. Quack, Angew, Synchrotron-based rotationally resolved high-resolution FTIR spectroscopy of azulene and the unidentified infrared bands of astronomy, (Chem. Int. Ed). (Engl.) 52, 2013, 346–349.

[13] V.S. Madhavana, H.T. Vargheseb, S. Mathewc, J. Vinsovad, C.Y. Panicker, FT-IR, FT-Raman and DFT calculations of 4-chloro-2-(3,4-dichlorophenylcarbamoyl) phenyl acetate, (Spectrochim. Acta A Mol Biomol Spectrosc) 72, 2008, 547–553.

[14] V. Sortur, J. Yenagi, J. Tonannavar, V.B. Jadhav, M.V. Kulkarni, Vibrational assignments for 7-methyl-4-bromomethylcoumarin, as aided by RHF and B3LYP/6-31G* calculations , (Spectrochim Acta A Mol Biomol Spectrosc.) , 71, 2008, 688–694.

[15] G. Varsanyi, Vibrational Spectra of Benzene Derivatives, (Academic Press), 1969, NewYork.

[16] Buchner, D., Jin, B., Ebert, K., Rolle, M., Elsner, M. and Haderlein, S.B., Experimental determination of isotope enrichment factors Bias from mass removal by repetitive sampling. Environmental Science & Technology , (Environmental Science & Technology) 51(3), 2017, 1527-1536.

[17] Collins, J. and Bolton, J.R. , "The Advanced Oxidation Handbook", 2016 , (Denver), CO, USA.

[18] Ternes, T.A. and Elsner, M., Exploring trends of C and N isotope fractionation to trace transformation reactions of diclofenac in natural and engineered systems , (Environmental Science 614 & Technology) 50(20), 2016, 10933-10942.