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Concentrations and [pH] Effects on Spectral Shifts of C_6H_6 and CCl_4 Compounds

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Abstract:

The electronic spectra within UV-Vis region for benzene (C_6H_6) and Carbone tetrachloride (CCl_4) molecules have been studied. Since Benzene molecule belongs to D_6h point group, with very high symmetry elements, therefore it may be expected for its internal vibrations to be either infrared or Raman active only. The spectral properties of (CCl_4) are also have been studied. This (CCl_4) belongs to T_d point group, where its fundamental internal vibrations will be also, infrared or Raman actives. These aspects will be considered and discussed in this work.

Keywords: CCl_4 molecules, FTIR, Raman spectroscopy.

خصائص الإزاحة الطيفية عند تراكيز وقيم مختلفة للاس الهيدروجيني لمحاليل البنزين ورابع كلوريد الكاربون

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الخلاصة

تمت دراسة الاطياف الالكترونية ضمن منطقة الأشعة فوق البنفسجية والمرئية لجزيء البنزين ورابع كلوريد الكاربون. نظرا لان جزيء البنزين ينتمي الى المجموعة النقطية D_{6h}، ويمتلك عناصر تناظر عالية جدا، لذلك فمن المتوقع ان تكون الاهتزازات الداخلية الأساسية إما نشطة بالأشعة تحت الحمراء او الرامان فقط.

كما تمت دراسة الاطياف الاهتزازية لرابع كلوريد الكاربون، ينتمى هذا الجزيء (CCl_4) الى مجموعة النقطية T_d حيث تكون اهتزازاتها الداخلية الأساسية هي أيضا نشطة في الاشعة تحت الحمراء او رامان.

الكلمات المفتاحية: جزيئات CCl_4، FTIR ، طيف رامان.

1. Introduction

The benzene is an aromatic molecule which consists of six carbon atoms to form the hexagonal ring where each Carbon atoms is linked to hydrogen atom. All these twelve atoms are located within a plane, therefor the benzene molecule belongs to the point group D_{6h} ,which possesses the followings symmetry elements : - One axis of rotation at an angle 60° ($1C_6$) perpendicular to the plane of the molecule ,Six axis of rotations at 180° ($6C_2$), located at the molecular plane and vertical on axis C_6, six planes of reflection (σ_v) perpendicular to the molecule plane ,one plane of reflection ($1\ \sigma_h$) applies perpendicular on the plane of the molecule, and one axis of rotation of an angle of 180° ($1C_2$) per level the molecule, and one axis of rotation by angle of 120° ($1C_3$) is also perpendicular to the level of the molecule and one analog element for a rotational axis - reflective (S_6) and finally one inversion element, C_6H_6 is considered to be a non-polar solvent [1,2].

CCl_4 is also considered to be a non-polar solvent as it doesn't express any permanent molecular dipole moment. This feature is very important in the spectral studies in the cases of using carbon tetrachloride as a dilute solvent for some polar substances such as methanol and acetone [3-6].

The carbon tetrachloride belongs to T_d point group, which has the following symmetry elements, eight axes of rotations by 120 ° ($3C_2$), six planes of reflection, three axes of rotation by 180 °, and four of rotation by 180 ° + 6 planes of reflections [1].

The internal vibrations are equal (3N-6) where N represents the number of atoms, within the molecule.

Accordingly, the internal vibrations for C_6H_6 molecule would be thirty vibrations (some of them are single and double degenerates), either infrared Or Raman actives depending on changing of dipole moment or polarizability tenser respectively.

However, for CCl_4 molecules, the internal vibrations are nine (some of them are single and triple degenerates).

These internal vibrations are either infrared or Raman actives depending on changing of dipole moment or polarizability tenser respectively.

It should be noted that the external vibrations of the nonlinear molecules (including C_6H_6 and CCl_4) are; which are beyond six vibrations, three translational and three rotational vibrations [6,7].

The aims of this work are to study the vibrational prop and electronic spectral properties by using infrared and Raman techniques, as well as electronic properties as function of concentration and [pH] values of solution of C_6H_6 and CCl_4 molecules.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Chemicals and reagents

1. Different chemicals and reagents which have been used in this study are listed in table (I). The table is also listed the chemical purities, and manufacture compunies and counteries.

Table I: Chemical and regents, which have been used in this study.

Number of Sample	**C_2(M)**	**V_1 (Volume of C_6H_6) ml**	**V_2 (Volume of C_6H_6+CCl_4) ml**
1.	0.1	0.224	25
2.	0.2	0.449	25
3.	0.3	0.674	25
4.	0.4	0.899	25
5.	0.5	1.12	25
6.	0.5	1.12	25+drops (HCl)
7.	0.5	1.12	25+drops of (NaOH)
8.	0.6	1.3	25
9.	0.01	0.022	25

2.2. Benzene diluted in carbon tetrachloride

The concentration of Benzene in carbon tetrachloride solvent in unit of molarity has been measured by using equation (1);

M =sp.sr x purity % x 1000/ Mw **…** (1)

C_6H_6 (purity %) = 99.8 %

And the Benzene specific density (Sp.sr) = 0.87 gm/cm^3

Mw= 78.11 (gm/mole)

Different concentrations, which have been used in this work, where calculated by using equation (2);

$[M_1]\ V_1 = [M_2]\ V_2$ **…** (2)

where, $[M_1]$ is the high concentricity, V_1 is the volume before diluted, $[M_2]$ is the low concentration, and V_2 is the the volume after diluted. Table (II) is listed nine concentrations of C_6H_6, which have been used in this work.

Table II: Different concentrations of Benzene in carbon tetrachloride solvents

Chemical	**Company**	**Country**	**purity**
Benzene	BDH	England	98.4%
Carbon tetrachloride	Fluka .Ga	Switzerland	99.5%
Ethanol	sigma Aldrich	USA	99.9%
NaOH	BDH	England	99.9%
HCl	Romil	UK	99.9%

2.3. Carbon tetrachloride to diluted in Benzene

Equation (1) has been used to dilute the benzene in carbon tetrachloride solvents, where M_1 is equal to ten molarity as listed in table (III).

M =sp.sr x % x 1000/ Mw … (1)

CCl_4 (purity %) = 99.5

And the Carbon Tetrachloride specific density (Sp.sr) = 1.586 gm/cm^3

Mw= 153.81 (gm/mole)

$[M_1]\ V_1 = [M_2]\ V_2$ … (2)

Where, $[M_1]$ is the high concentricity, v_1 is the volume before dilution, $[M_2]$ is the low concentricity, and V_2 is the total magnitude after dilution.

Table III: Different concentrations of carbon tetrachloride in Benzene Solvents.

Number of samples	**C_2(M)**	**V_1 (Volume of CCl_4) Ml**	**V_2 (Volume of CCl_4+C_6H_6) ml**
1.	0.1	0.29	25
2.	0.2	0.58	25
3.	0.3	0.88	25
4.	0.4	1.17	25
5.	0.5	1.46	25
6.	0.6	1.75	25
7.	0.01	0.03	25

2.4. The UV-Visible spectra have been measured by using Perkin -Elmer lambda 750, (Germany).

2.5. Fourier Transform Infrared Spectroscopy (FTIR) Measurements:

Fourier transform infrared spectrometer (SHIMADZO IRAFFINITY- Japan) has been used. To measure Infrared spectra of, C_6H_6 solution and CCl_4 compound.

2.6 The Raman Spectroscopy:

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.

2.7 [pH] value measurments

[pH] value measurments have been recorded by using pH meter type Hana, (Mauritius) .

3. Results and discussions

3.1. The results of C_6H_6 molecule

3.1.1. Infrared spectrum

The chemical structures and nomenclature for mono- and disubstituted benzene rings, show how the presence or absence of the ring bend, and the position of the out-of-plane aryl C-H wag together can be used to distinguish mono-, ortho-, meta-, and para-isomers from each other. These peak positions are summarized, both mono- and meta-isomers have the ring bend present and have C-H wagging peaks [8].

The FTIR spectrum of benzene has absorption peaks caused by vibrations of aromatic C-C, C=C and C-H bonds.

Fig (1) shows the infrared spectrum of benzene, it also shows the assignments of most of the shown bands. The strong absorption band at the range (3600-3300) cm^{-1} is due to the stretching C-H bond while, the absorption bands belongs to the stretching and bending vibrations of the functional groups of the benzene molecule, where a similar bands have been observed by many researchers [9-13].

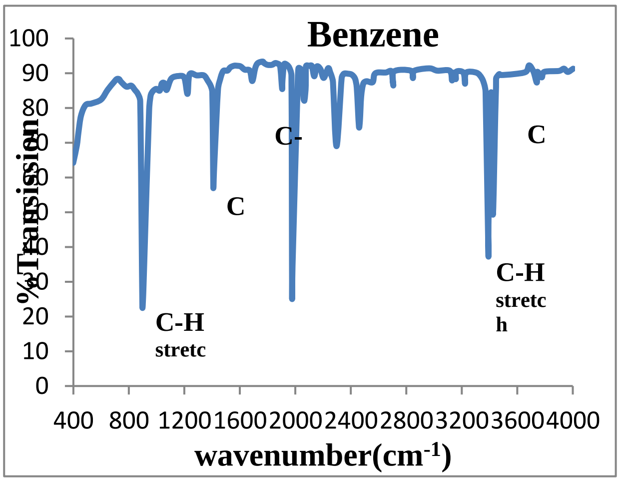

Figure 1: FTIR spectra for (C_6H_6).

The IR spectra of Benzene molecule show pieces between 800-3600 cm^{-1}, as shown in figure (1). These observed bands are due to active fundamental and combination bands [10]. The infrared spectrum of the molecule shows only the active infrared fundamental and combination bands. However, no overtone bands have been detected within this region because of the high symmetry of this molecule [1].

3.1.2. Raman spectrum of Benzene

The growth in Raman last year continues, with ongoing improvements in the tools and a number of new systems being launched. New generations of small Raman spectrometers continue to appear. Both commercial and academic users of Raman are seeing more laser, detector, and optical options [14].

Fig (2) shows the Raman spectrum of benzene. This spectrum shows about five bands centered at 606, 996, 1177, 2950 and 3063cm^{-1} for the vibrations of the above-mentioned bonds. Usually the vibration bands at 2950, and 3063cm^{-1} due to stretching vibration of C-H, while the bands center at 1177, 996, due to C=C and C-C stretching vibrations. The band centered at 606 cm^{-1} is due to out of plain rocking vibration of C-H [15-16].

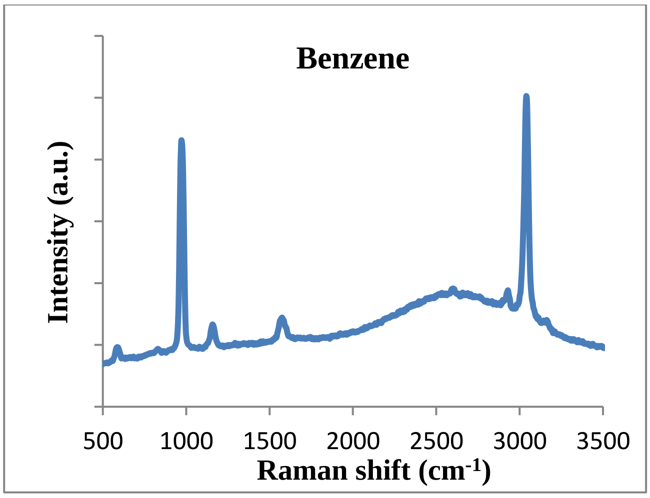

Figure 2: Raman Spectrum of (C_6H_6).

3.1.3. UV-Visible spectra of Benzene

The UV-Vis spectrum of C_6H_6 is shown in Fig (3) the band center at 270 nm is assigned to $\pi\rightarrow\pi^*$ electronic transition of C=C. 270 nm is assigned to $\pi\rightarrow\pi^*$ electronic transition of C=C [17].

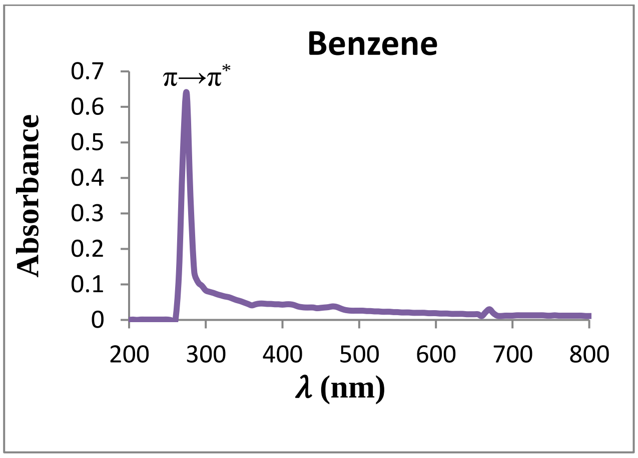

Figure 3: The UV-Visible Spectrum of pure C_6H_6 compound.

the absorption peak wavelength tends to be shifted toward the long wavelength region and the absorption peaks tend to be larger. The absorption peak of Benzene at 275nm. The ultra-violet region shows only bands belong to $\pi\rightarrow\pi^*$ electronic transitions single bands C-H and C-C and also $\pi\rightarrow\pi^*$ electronic transitions of type electronic double bounded C=C.

However, no absorption has been observed within visible region (200-800) nm which is confirmed since pure benzene liquid has colorless [18].

3.1.4. Changing of the [pH] values of the solvent with Benzene

In Figure (4) a few changes in the spectra of C6H6 compound have been obsorved when NaOH is added. However, no change was observed when HCl was add. The absorption spectrum exhibits a broad band centered at 270 nm.

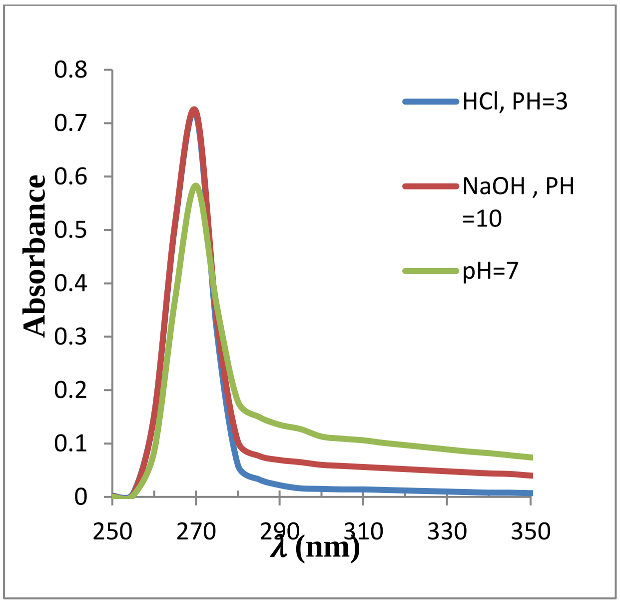

Figure 4: The UV-Visible spectra of C_6H_6 at different pH values.

On changing [pH] values of the solution, it should be noted that there is no wavelength shift has been observed for the $\pi \rightarrow \pi^*$ band of C_6H_6 Compound, as shown in figure (5).

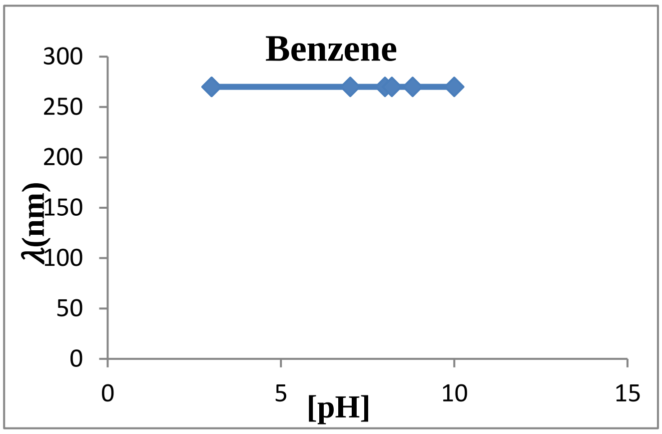

Figure 5: The wavelength Shift of $\pi \rightarrow \pi^*$ band for C_6H_6 compound.

3.1.5. Changing of concentrations of benzene

Fig (6) shows the UV-Visible Spectra of (C_6H_6) at different concentrations. The $\pi \rightarrow \pi^*$ broad band has been seen at 275 nm at high concentrations (0.5M), while at the low concentration (0.01 M), the broad band has been shifted to 270 nm, which means blue shift on diluting of the solution [19].

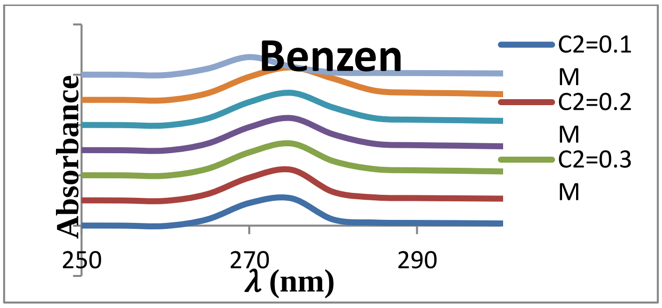

Figure 6: The UV-Visible Spectra of different concentrations of C_6H_6.

3.2.1. Infrared Spectra of Carbon tetrachloride.

The infrared spectrum of CCl_4 compound is shown in Fig (7). The point group of CCl_4 is T_d with high symmetry, therefore one would expect the vibrations of this molecule to be either IR or Raman active. The IR of figure **7** is in good agreement with that previously reported [20]. However, the strong band centered at 1028 cm^{-1} is the anti-symmetric stretching vibration of CCl_4.

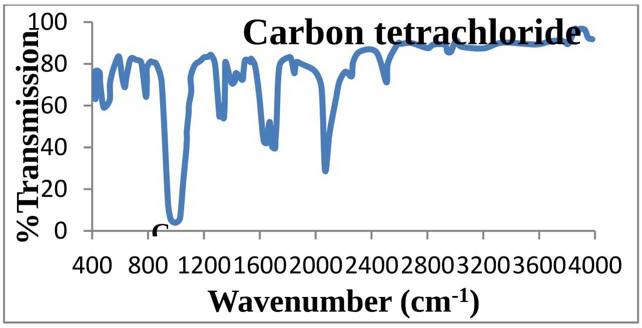

Figure 7: FTIR spectraum of CCl_4.

3.2.2. Raman spectra of Carbon Tetrachloride

Fig (8) Shows the Raman spectrum of CCl_4 which shows only the symmetric stretching and bending only, since these modes of vibrations produce change in magnitude of polarizability tenser [21-22].

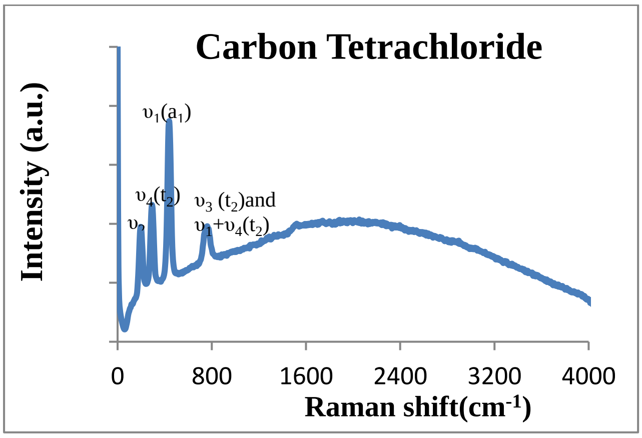

Figure 8: Raman Spectrum of CCl_4.

The vibration ν_1(symmetric stretching vibration), and the vibration ν_2(symmetric bending) are Raman active only, while ν_3 (anti-symmetric stretching vibration), and ν_4 (anti-symmetric bending) are Infrared active only.

3.2.3. UV-Visible spectra of Carbon Tetrachloride

The UV-Vis spectrum of CCl_4 is shown in Fig (9). The only band centered at 280nm is assigned to $\sigma\rightarrow\sigma^*$ electronic transition of C-Cl. This indicates that this compound is colorless since there is no band is observed within visible region. It should be mentioned that there is no wavelength shift is observed, for this band on changing [pH] values.

So, the behaver of $\sigma\rightarrow\sigma^*$ electronic transition of CCl_4 is similar to $\pi\rightarrow\pi^*$ of C_6H_6 which has been mentioned earl ear [23].

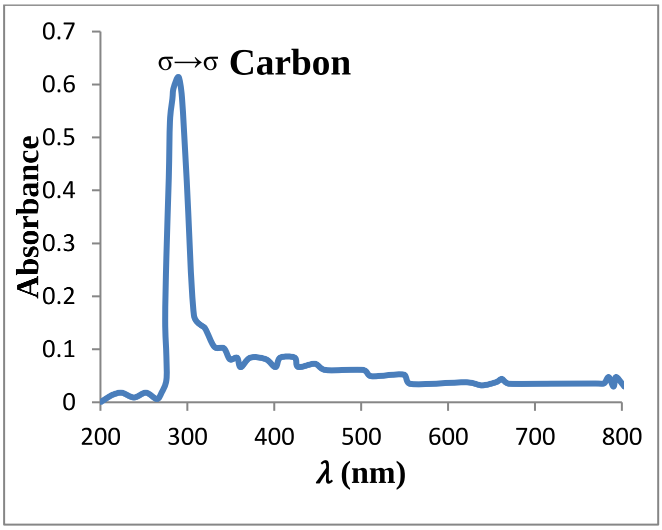

Figure 9: The UV-Visible Spectrum of pure CCl_4 compound.

3.2.4. Changing of concentration of Carbontetrachloride.

Fig (10) shows the UV-Visible Spectra of (CCl_4) at different concentrations. The $\sigma\rightarrow\sigma^*$ broad band has been seen at 280 nm for all concentrations, which means that there is no wavelength shifts were observed on change the concentrations [23].

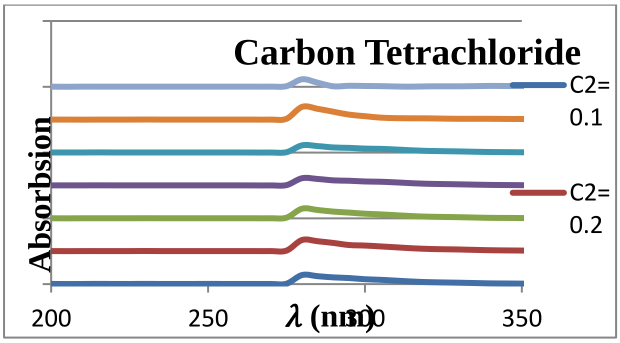

Figure 10: The UV-Visible Spectra at different concentrations of Carbon Tetrachloride (CCl_4).

4. Conclusions

The spectral properties of C_6H_6 and CCl_4 shows similarity, in activities of the vibrational transitions, where each fundamental band of both molecules is either IR or Raman active. However, the electronic spectral properties show an $\pi\rightarrow\pi^*$ electronic transition band for C_6H_6 molecule, while it shows $\sigma\rightarrow\sigma^*$ band for CCl_4 molecule.

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