Interpretation & studies of the visible spectra and to exploit properties of polyenes and to develop a new method for classroom experimental studies by use of one dimensional box Model.

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ABSTRACT

Polyenes are the long chain molecules derived from the polymerization of acetylene. These are linear conjugated oligomers, which posses alternate double bonds. The π - electrons are completely delocalized over the entire molecule which can be considered as a one dimensional box. We have applied particle in one dimensional box model to interpret the electronic spectra and to study other properties of few of the synthetic and natural polyenes. We have also made an effort to predict λmax and other properties of few of the hypothetical polyenes. Furthermore we have carried out a detailed study of conducting polymers. In addition, this paper describes an experiment in which Lycophene compound which is present in Tomato is used to model the particle in one dimensional box system. This idea may expose students to the chemistry of natural substances. The results of the quantum mechanical model indicates less error for small length polyenes where as error increases as the chain length increases.

Key words: Polyenes, PIB model, delocalization, conjugation, absorbance.
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INTRODUCTION

Polyacetylene is a polymer which is obtained by the polymerization of acetylene. Earlier it was known as a black powder. It was first prepared as a silvery film by Shirakawa [1] and co-workers, using Ziegler-Natta[2] catalyst. Polyacetylenes are the simple linear conjugated molecules which are characterized by alternate double and single bonds. The molecules can be named as 1, 3 butadiene, 1, 3, 5 – hexatriene, 1, 3, 5, 7 – octatetraene and so on. These polymers range from C_2H_6 to $C_{26}H_{28}$ and $C_{28}H_{30}$. Every alternate double bond contains a π – bond. The electrons from the unsaturated π – system are delocalized along the polymer chain. Due to the delocalization, each carbon atom is linked with other carbon atom by a partial double bond. Thus we may predict that these molecules are rich source of electrons or free electrons, even though these polymers do not conduct electric current. The conductive organic polymers were synthesized by C.K. Chiang and M.A. Druy[3, 4]. In simple words they are prepared as follows. The electrons from the polymer is removed i.e. oxidation or electrons are inserted into the chain i.e. reduction is carried out. This process is known as doping. The oxidation is carried out by halogen, known as p-doping or by reduction with alkali metal, known as n-doping. Thus, polymers show conductivity more than that of metals.

Carotenoids such as β-carotene and lycophene are natural polymers which are present in vegetables, such as carrots and tomatoes and certain fruits. β-carotene is a long chain molecule having 22 conjugated carbon – carbon bonds. Lycophene has eleven double bonds. These molecules too have delocalized π – electrons, which are responsible for conductance [5].
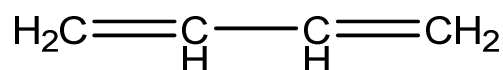
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All the poleyene molecules which we have discussed contain a long chain on which the electrons are delocalized. This chain length may be considered as a one dimensional box. This is a simple quantum mechanical model which can be used to predict the electronic energy levels arising from the delocalized π -electrons. The equation which can be used to get the electronic energy levels is represented as [6, 7], $E = n^2h^2/8ma^2$ where n=1, 2, 3.... α, 'a' is the length of the molecule i.e. chain, h = 6.623×10^{-27} erg.sec and m = 9.11×10^{-28} gms are Planck's constant and mass of electron. Maximum of two electrons can be placed in an energy level. In this assumption electron – electron repulsions are ignored. This models gives a rough idea of the λmax of the polymer molecule with length of the polymer chain as 'a'. In this study, we have tried to correlate the results of λmax i.e. predicted by one dimensional box model with those of actual experimental results. Jo Chen Autsch batch has used particle in a box model to predict the λmax and other properties for cyanin dyes [8]. Gion calzaferri has used particle in one dimensional box model for the description of few of the conjugated systems [9]. Many chemists around the world has devised laboratory experiments for the graduate and post graduate and also for undergraduate students based on one dimensional box model [10, 11]. Recently, this model has also been discussed with reference to the study of polymers by many authors [12, 13]. The structure of β-carotene and lutein has been studied with reference to one dimensional box model and experiment has been devised by Henery, Anderson & Todd wimpfheimer [14, 15].

So in the present work we have used one dimension box model to find the λmax of polymers. These results are compared with experimental results. Errors are calculated and interpreted. We too have predicted the λmax of hypothetical higher polyenes. Secondly we have studied the polyenes as electrical conductors and exploited their uses from the literature; thirdly we have designed an experiment for the undergraduate and graduate students of universities.

MATHEMATICAL METHODS

The π- electrons of polyenes are considered to form a one dimensional box, where length of the box is contributed by the carbon skeleton. The following steps or assumptions are important.

1. Add the C – C bond length to get the length of the box. Generally we use average C – C bond length as 1.4×10^{-8} cm. We assume that the π electrons are free to move approximately ½ bond length on the right and left of the straight chain. That is the length of the box is increased by one additional bond length. This is considered for all the polyenes being studied. The length of the box is calculated as (N+1) x 1.4×10^{-8} cm where N is the no. of bonds in the skeleton.
2. Each π - bond will contribute 2 electrons.
3. Each of the energy level of the box can occupy maximum of two electrons.
4. Let us take a simple example of 1, 3- butadiene. The length of this molecule as per our assumption (N+1) x 1.4×10^{-8} will be 3 + 1 x1.4×10^{-8} =
5.6x10^{-8}cm =0.56 nm.

$$H_2C = C_H - C_H = CH_2$$

1, 3 butadiene

The first and the second energy level occupy the two electrons. The highest occupied level (i.e. $E_2 = 4h^2/8ma^2$) can absorb radiation and can be excited to the third level.

-------------- $E_3 = 9h^2/8ma^2$
-------↑↓--- $E_2 = 4h^2/8ma^2$
-------↑↓--- $E_1 = h^2/8ma^2$
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Energy levels of 1, 3 butadiene

Therefore $\Delta E = E_3 - E_2 = 9h^2/8ma^2 - 4h^2/8ma^2 = 5h^2/8ma^2$

We know that $\Delta E = \dfrac{hc}{\lambda}$

Therefore $\lambda = hc/\Delta E = 8mca^2/5h$

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Inserting the value of Planck's constant h = 6.632 x 10⁻²⁷ erg s., mass of electron = 9.11 x 10⁻²⁸ gms, C – velocity of light = 3.00 x 10¹⁰ cm/s, 'a' – the length of the box = 5.6 x 10⁻⁸cm, the value of λmax can be calculated. For this system the λmax calculated comes to be λcal. = 207 nm

λ-experimental is the actual λmax obtained from the experimental results. The experimental value for this compound λexpt is 217 nm.

We have also worked out how much length of the box corresponds to the experimental λmax. We have also tried our level best to predict the lowering or increase in the bond length due to either increase or decrease in delocalization of the electrons. We have followed the same method in the study of polyenes by use of one dimensional box model.
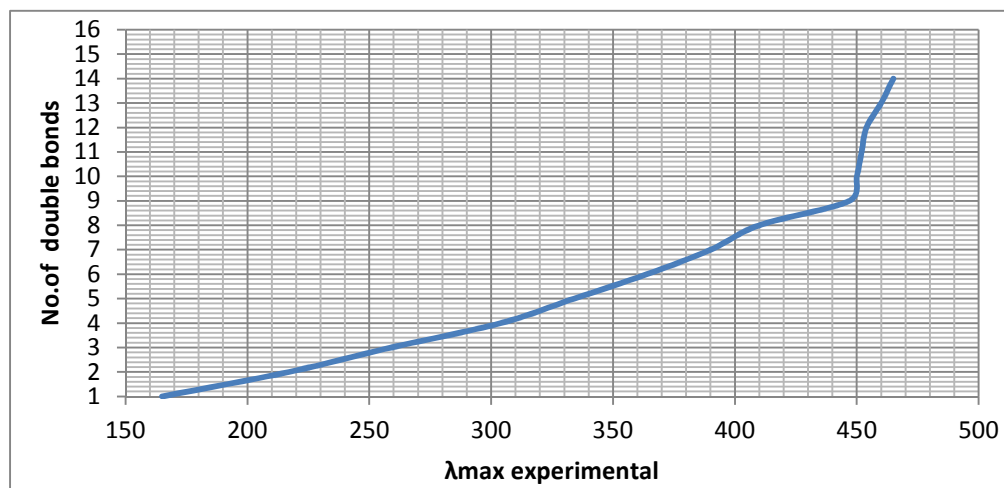
The following Table-1 illustrates the experimental λmax, calculated λmax using one dimensional box model, the error in the value of λmax and the % relative error.

Table: 1

polyene	double bonds n	λmax expt	λmax cal nm	Error in nm	% error
C_2H_2	1	165	103	62	37.6
C_4H_6	2	217	205	12	5.5
C_6H_8	3	259	329	70	27.0
C_8H_{10}	4	304	455	151	49.7
$C_{10}H_{12}$	5	334	581	247	74.0
$C_{12}H_{14}$	6	364	708	344	94.5
$C_{14}H_{16}$	7	390	835	455	116.6
$C_{16}H_{18}$	8	410	963	553	134.9
$C_{18}H_{20}$	9	447	1092	645	144.3
$C_{20}H_{22}$	10	450	1217	711	158.0
$C_{22}H_{24}$	11	452	1344	893	197.6
$C_{24}H_{26}$	12	454	1471	1016	1223.0
$C_{26}H_{28}$	13	460	1599	1139	246.0
$C_{28}H_{30}$	14	465	1727	1259	269.1

From the results shown in the above table it is clear that the error in the calculated result increases with increase in the double bonds or π -conjugation. Let us try to understand the trend, by the following graphs.

(1) No. of conjugation vs. λexpt

Fig-1.Conjugation verses the experimental value of λ max

The maximum absorption increases with chain length. As the chain length increases the λmax increase. We can observe from the graph that at higher conjugation the increase is very law. Polyenes having nine or more than nine conjugated double bonds, the increase in λmax is very low.

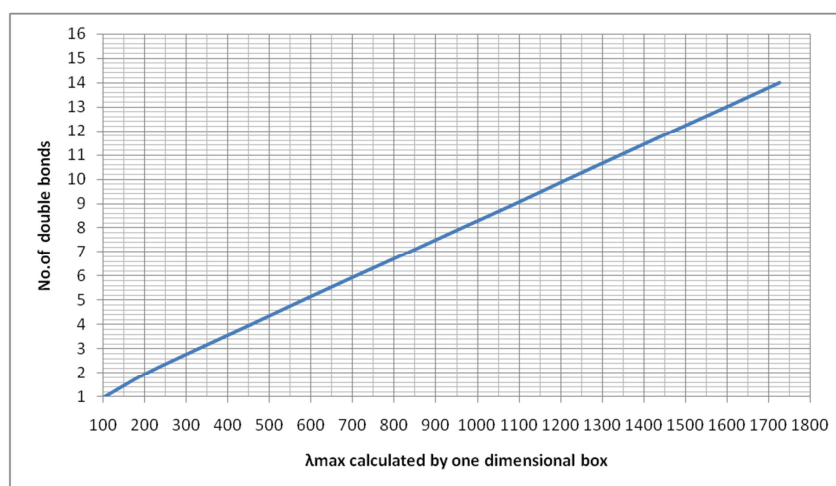(2) No. of conjugation vs. λmax calculated by PIB model

Fig:2 No. of double bonds vs. maximum absorption as calculated by one dimensional box model

From this graph it is evident that there is a linear relationship between conjugation and λmax calculated by PIB model. As seen in the previous equations, λ is directly proportional to the length of the box assumed and this relationship is clearly observed from this graph.
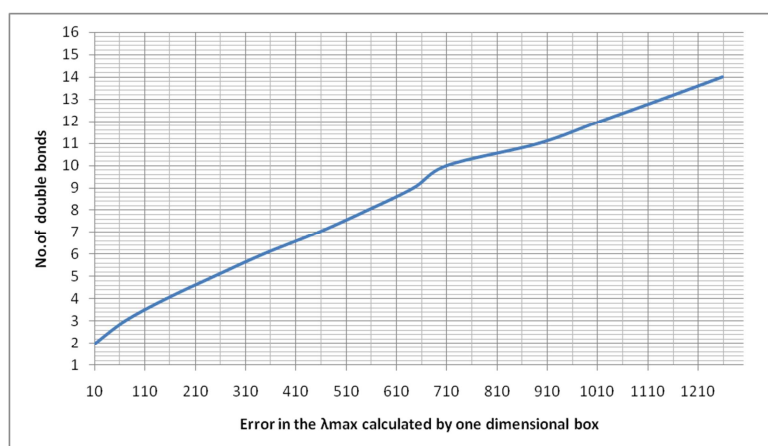
(3) Conjugation vs. error

Fig: 3 Variation in absorption values of poly acetylene with conjugation as calculated by one dimensional box model
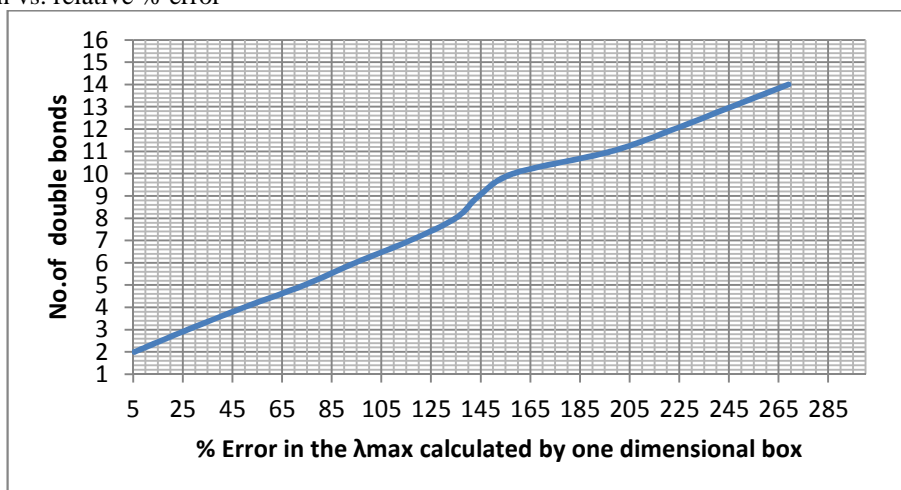
(4) Conjugation vs. relative % error

Fig: 4 Relative % errors in the lambda max values with increase in conjugation as calculated by one dimensional box model

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From the above curve it is clear that the error in the determination is less when the conjugation or double bonds are less. The error increases with conjugation.

The following Table-2 shows the actual length of the polymers and also the length of the chain 'a'as calculated by PIB model.

Table: 2

Polyene	conjugation	Length of the linear chain that is 'a' as calculated by λexpt value(actual length)	Length of the linear chain that is 'a' assumed by PIB model $(N+1) \times 1.4 \times 10^{-8}$ cm
C_4H_6	2	5.7×10^{-8} cm	5.6×10^{-8} cm
C_6H_8	3	7.31×10^{-8} cm	8.4×10^{-8} cm
C_8H_{10}	4	9.07×10^{-8} cm	11.2×10^{-8} cm
$C_{10}H_{12}$	5	10.51×10^{-8} cm	14.0×10^{-8} cm
$C_{12}H_{14}$	6	11.93×10^{-8} cm	16.8×10^{-8} cm
$C_{14}H_{16}$	7	12.24×10^{-8} cm	19.6×10^{-8} cm
$C_{16}H_{18}$	8	14.45×10^{-8} cm	22.4×10^{-8} cm
$C_{18}H_{20}$	9	15.98×10^{-8} cm	25.2×10^{-8} cm
$C_{20}H_{22}$	10	16.86×10^{-8} cm	28×10^{-8} cm
$C_{22}H_{24}$	11	17.69×10^{-8} cm	30.8×10^{-8} cm
$C_{24}H_{26}$	12	18.48×10^{-8} cm	33.6×10^{-8} cm
$C_{26}H_{28}$	13	19.33×10^{-8} cm	36.4×10^{-8} cm
$C_{28}H_{30}$	14	20.14×10^{-8} cm	39.2×10^{-8} cm

We calculate the λmax by the relation.

λ= 8mca^2/ (n$_i$ - n$_j$) h

Where m=mass of electron, c=velocity of light,
h=plank's constant, n$_i$=unoccupied energy level, n$_j$=occupied energy level and a=length of the box.

The wavelength- λ is sensitive to the length of the box. It seems that the error occurs due to the calculated value of length of the box 'a' calculated by our assumed method (PIB model). It is evident that as the delocalization of electrons over the entire chain increases, there must be a decrease in the length of the linear chain as it is observed from the above table. From this observation we conclude that the calculated length of the linear chain or length of the box- 'a' is greater than the actual value. There is a shrinkage in the length- 'a' as there develops a partial double bond between each carbon atom in the chain and we suppose that the electron cloud moves over the entire skeleton in such a way that it leads to the reduction in the length of the entire chain. During the above mentioned studies we have predicted the λmax of the hypothetical polyenes such as $C_{26}H_{28}$ and $C_{28}H_{30}$ which may range from 460nm to 465 nm respectively.

β-carotene is a natural polyene. The observed λmax is 452nm.There is 11 conjugated double bonds in the molecule. The λmax calculated by PIB assumptions comes to be 1344 nm which is highly erroneous. The cause of error being higher value of length of box that is 'a.' It is obvious that the length 'a' is decreased due to delocalization of the electrons.

Developing a novel experiment:-
Lycophene is present in tomatoes. Lycophene contains long conjugated system which is linear and therefore the one dimensional box model can be used to predict the λmax of this natural compound. This experiment may be of interest for the graduate and undergraduate students. The following procedure may be followed.

Crush the tomato pulp (about one spoon) and dissolve it in about 5 to 8 ml of alcohol. Light color develops after sometime (two hours).Filter the content and record the absorption spectrum from 400 nm to 800nm. Draw a graph of absorbance vs. wavelength. Find out the λmax from the curve of absorbance vs. wave length. Lycophene contains 11 conjugated double bonds. Its structure can be represented as follows.

The experimental value of λmax is 474 nm.

Now use one dimensional box model to calculate the length of the chain or box, by the following formula.

λmax = 8mca^2/23h

Where
m = mass of electron=9.11x10^{-28}gms
c = velocity of light= 3.0x10^{10}cm/sec
a = length of box or chain =???
h = plank's constant =6.623x10^{-27}erg.sec
λmax   = obtained from the experiment= 474 nm.

Thus the length of the linear chain which is considered as a box is obtained.

Alternatively, the students can be asked to write the structure of the molecule and to calculate the length of the chain or box considering average bond length between carbon atoms.

Construct various energy bands and find out the value of ΔE

Where

ΔE = E$_{12}$ - E$_{11}$ = 12^2 h^2 /8ma^2 - 11^2 h^2 /8ma^2 = 23h^2/8ma^2

$$\Delta E = \frac{hc}{\lambda}$$

We know that

Therefore   λ = hc/ΔE=   8mca^2/23h

Compare the value of λmax obtained by using one dimensional box model with the experimental value of λmax. Calculate the error, relative error and relative % error.

Such an experiment may be useful for graduate or undergraduate students

Studies of the polyacetylenes (exploiting the properties) as electrical conductors.
Polyacetylenes are the conjugated molecules which has free electrons which are not completely bound to the atoms. These molecules have alternate double bonds. The polyacetylene as such is not a conductor. In order to make the electrons move, the polymer has to be disturbed either by removing electrons, i.e. oxidation or inserting more electrons into the material i.e. reduction. This process is technically known as doping. This is done by adding halogen or alkali metal into the polymer material.

(a) When halogen is added which is known as p-doping, it removes electrons and forms halide ion.
(b) When alkali metal is added, it is known as n-doping where it inserts electrons into the polymer and Na$^+$is formed. The doped material becomes good conductors.

Two strips of polyacetylene were taken. The strips were placed in a solution which contained the doping ions. Both the strips were connected and an electric current was passed. The positive ions were accumulated at one strip and the negative ions towards the other. After this, the current source was replaced by an electric light bulb. The current passed in other direction and the bulb was found to be illuminated. During this process, the dopants travelled back from the polymer strips into the solution. After some time, the polymer strips regained their original state that is

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undopped state and therefore the bulb stopped illuminating as there was no current. On passing the current, the strips can again be charged and again it can be used as a battery [16].

During the process of charging the strips are not taken out of the solution and other important thing is no chemical reaction occurs in the cell. Therefore it was observed that such batteries might not degrade over many charge cycles.

CONCLUSION

The PIB model has been used to determine λmax of polyenes. The results obtained by use of PIB model indicates that the error in the determination increases with the increase in conjugation. The cause of the error is due to the fact that we have fixed the value of length of box 'a' by PIB assumptions. In actual practice, the length is affected by delocalization of electrons. Higher the delocalization, shorter is the length of molecule. It is observed that the length of the linear chain remains nearly same in the range of conjugation n = 9 to n = 14. We have made an effort to develop an experiment based on PIB model. We have studied the properties of polyenes which contain free electrons that absorb radiation, emit radiation and can even conduct electric current.

Applications
The polyenes have applications as transistors, Light Emitting Diodes, Lasers used in flat Televisions, Solar Cells, Compact capacitors etc. and many more.

Acknowledgement

REFERENCES

[1] H. Shirakawa, E.J. Louis, A. G. MacDiarmid., C.K. Chiang and A. J. Heeger, *J. Chem. Soc chem. Comm.* **1977**, 579

[2] K. Ziegler and G. Natta, Nobel Prize in Chemistry, **1966**.

[3] C. K. Chiang, C. R. Fischer, Y.W. Park, A. J. Heeger, H. Shirakava, E.J. Louis, S. C. Gau and A. G. MacDiarmid, *phys. Rev. Letters.* 39 ,**1977**, 1098.

[4] C. K. Chiang, M. A. Druy, S.C. Gau., A. J. Heeger, E.J. Louis, A. G. MacDiarmid, y.w. park and H. Shirakawa, *J. Am. Chem. Soc.,* 100 ,**1978**, 1013

[5] Joachim, C. Roth, S., Eds. *Atomic and Molecular wires;* Kluwer : Dordrecht, **1997**, Vol. 341.

[6] M. Barrow, *"Physical Chemistry"*, Mcgraw Hill Book company, **1988**.

[7] I. N. Levine *"Quantum Chemistry"* Mcgraw Hill Book Company, 2nd Ed^{n} **1985**.

[8] Jo Chen Aut schbach *J. Chem. Educ.,* **2007**, 84 (11), p – 1840 DOI : 10.1021/ed084p,1840

[9] Separat druck qus *CHIMIA* 41, **1987**, Nr. 7-8 (Juy – August), p-248-250.

[10] D. P. shoemaker, C.W. Garland, and J. W. Nibbler, *experiments in physical chemistry,* 8th ed. Newyork, McGraw – Hill, **2009**, pp-393-397.

[11] R. J. Sime, *Physical chemistry methods, Techniques and experiments*, Philadelphia Saunders college, **1990**, pp-687-694

[12] Soltzberg, L. J., **2001**, *J. Chem., Educ.* (78), 1432.

[13] Anderson, B.D. **1997**, *J. Chem. Educ.* (74) 985.

[14] Particle in box lab experiment, *journal of laboratory chemical education,* Vol. 3, No. 2, **2015**, pp. 19-21.

[15] Henery, M, Roth H., and Anderson, **2012**, the particle in a box redux: improved experimental conditions for the laser synthesis of Polyenes, *J.Chem. Educ.,* (89), 960-961.

[16] Hatala-**1997**, Technology and Engineering- Google books.