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# Surface and Volume Energy Loss , Optical Conductivity of Rhodamine 6G dye (R6G)

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## Abstract

One of organic dye materials which have been long lasting investigated is rhodamine 6G(R6G) dye .This dye has been attracted with considerable interests due to the reason of its promising photochemical properties. In the present study we determine the optical parameters of thin films of R6G dye using transmittance spectra in the wave length region 200-900nm. Some optical constants are calculated and tabulated, such as index refraction ( n) , absorption coefficient ( $\alpha$ ), optical energy gap ($E_g$) , optical conductivity( $\sigma_{opt}$ ) ,electrical conductivity($\sigma_e$ ) as well as real and imaginary part of dielectric constant .The Wemple-DiDimenico that used to study the optical dispersion parameters . The volume energy loss (VELF) and the surface energy loss(SELF) functions are also investigated .

**Keywords** : Rhodamine 6G dye , dispersion parameters , optical conductivity, energy loss .

## 1.Introduction

Rhodamine 6G (R6G) is a chromophore from a family of xanthene dyes that commonly used as an active medium in tunable lasers . Use of this dye as amplifying medium in lasers goes back to the 1970'ties , and the dye has remained a preferred laser dye due to its large quantum efficiency and relatively long lifetime before bleaching, compared to other dyes Pure Rhodamine 6G comes in powders with a dark red color and liquid solutions of the dye are colored strongly in red, wherefore caution should be exerted during handling. It comes in various grades of which the laser grade is the most expensive . [ Schäfer 1973 ; Ibrahim 2012]

This dye is also used as sensor[Kim et.al. 2012],non-linear optical material[Rao *et.al.*2002],photosensitizer [Haghighat *et.al.*1992] and material protease lable[Blackman *et.al.*2002]The optical properties of dyes have been extensively studied in recent decades because of their wide range of applications and strong dependence on composition .

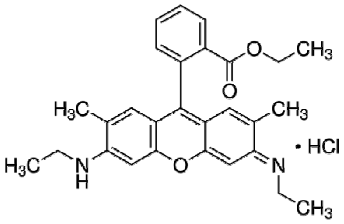
Optical experiments provide a good way of examining the properties of semiconductors. Particularly measuring the absorption coefficient for various energies gives information about the band gaps of the material. Knowledge of these band gaps is extremely important for understanding the electrical properties of a semiconductor, and is therefore of great practical interest.

In the present work we determined the optical energy gap ,optical conductivity and dispersion parameters for Rhodamine 6G dye ,loss energy were also determined .Wemple and DiDomenico relation used to calculate the dispersion parameters .The optical data analyzed by using transmittance spectrum in the wavelength range 200-900nm.

## 2. Experimental work

### 2.1 Preparation of thin films

The investigated samples were made in the form of thin films.is achieved by dissolving a certain weight of Rhodamine 6G dye(R6G) as shown in Figure(1) (provided by Fluka without any other purification) 0.1g in a fixed volume of methanol (5ml ).The solution was then stirred until a clear solution was obtained .The solution was dropped on glass substrate (1.5cmx1.5cm) washed thoroughly with acetone solvent then distilled water in ultrasonic .Thin films were prepared by using the spin-coating technique , UV/Vis absorption spectra were taken using a double beam spectrophotometer (Thermospectronic model HEλIOSα v 4.60 serial No.102024)at room temperature by normal incidence of light in the wavelength(λ) range of 200-900nm.



Figure(1):The scheme of Rhodamine 6G dye

## 3.Results and discussion

### *3.1 Optical measurements*

The spectral distribution of the transmission and reflectance of R6G dye films at the thickness 1μm as a function of wavelength region 200-900nm at normal incidence can be shown in Figure(2) . The reflection ( R ) can be determined using the following relation [Stenzel 2005]

$$A+T+R=1 \quad (1)$$

The films showed high transparency in high wave range at $\lambda > 600$ nm ( i.e. R+T=1) . The inequality (R+T < 1) at shorter wavelengths ($\lambda < 600$nm ) , Known as absorbing region ,is due to the existence of absorption.The reflectance of R6G dye films as a function of wavelength show tow peaks at 476nm and 548nm are clear. The maximum value of reflectance of film is 20% .

### *3.2Determination of the extinction coefficient and optical band gap*

The optical absorption coefficient (α) can be calculated from transmission data using this relation[Thangaraju *et.al.*2000]:

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad (2)$$

Where T and d are the transmittance and thickness of R6G dye samples respectively. The spectral distribution of the absorption coefficient(α) for R6G is shown in Figure(3) . A close examination of the absorption band in the visible region , known as Q-band appears in the region between 2 eV and 3eV .The Q-band consists of the one shoulder at 2.5eV which has been assigned to $\pi$-$\pi^*$ transitions. In UV spectral region at 3.1-4eV ,there is a weak band called B-band .This is due to the electronic transition from $\pi$-$\pi^*$ at 3.7eV .The many absorption peaks at region 4.1- 4.5eV is called N-band ,which has been attributed to the charge transfer from spz mixing orbital to the electron system of the spirolactm ring of the R6G.[El-Nahhas *et.al.*2012]

The calculated optical constants ,the extinction coefficient k is calculated using the values of α and λ by the relation [Faidah 2009]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

Where λ is the wavelength .

The refractive index n was approximately calculating by using the following equation [Abdullah *et.al.*2013]

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (4)$$

The spectral distribution of thee extinction coefficient k and mean values of ( n ) versus wavelength (λ) for R6G can be shown in Figure (4).The behavior of the extinction coefficient is very is very similar to the corresponding absorption spectra .

The refractive index n in the wavelength range 200-900nm .Normal dispersion is observed at $\lambda>600$nm and anomalous dispersion at $\lambda<600$nm besides two peaks at 2.29 eV , 2.64 eV in visible region and five peaks in UV region (3.73,4.18,4.24,4.36 and 4.55)eV .This is due to high energy transition [Pankove 1971.] .

### *3.3 Calculation of optical energy gap*

The study of the spectrum of the absorption coefficient of the a material in the fundamental edge provides us with valuable infprmation about the energy band structure of the material.

According to Tauc's relation [Tauc 1974],the photon energy dependence of the absorption coefficient can be described by :

$$\alpha h\upsilon = B(h\upsilon-E_g^{\ opt})^{\ r} \quad (5)$$

Where B is a parameters that depend on the transition probability ,$E_g$ is the optical energy gap and r an index which can be assumed to have values of 1/2,3/2,2 and 3 depending on the nature of the electronic transition responsible for the absorption ,r =1/2 for allowed direct transition , 3/2 for forbidden direct transition and r =3 for forbidden indirect transition ,and r =2 refers to indirect allowed transition .

The absorption coefficient for direct transition takes the value $\alpha \geq 10^4 \mathrm{cm}^{-1}$,while the absorption coefficient for indirect transition takes the values $\alpha \leq 10^4 \mathrm{cm}^{-1}$ .[ Thangaraju *et.al.* 2000]. Figure (5) shows the absorption coefficient in the form $(\alpha h\nu)^2$ versus hν for R6G film. The intercepts of the straight lines with the photon energy axis yield the values of the direct optical band gap .The value of direct allowed optical energy gap is about 2.2eV, at $\alpha \leq 10^4 \mathrm{cm}^{-1}$ the indirect optical energy gap can be estimated by plotting $(\alpha h\nu)^{1/2}$ versus photon energy .The value of of indirect energy gap is about 1.3 eV can be shown insert in Figure(5) .

### *3.4 Determination Urbach tail*

The density of localized states in the band can be evaluated from the Urbach energy (ΔE).There are absorption tails at energies smaller than Eg ,and the absorption coefficient can exhibit exponential behavior [Urbach 1953]the Urbach energy can be calculated from the Equation :

$$\alpha = \alpha_o e^{\frac{h\nu}{\Delta E}} \qquad (6)$$

Where $\alpha_o$ is a constant and ΔE is the Urbach energy,by plotting lnα versus photon energy as shown in Figure(6)and taking the reciprocals of the slope of the linear portion in the lower photon energy of the curve. The value of Urbach energy is 184meV .

### *3.5 Determination of refractive index and dispersion parameters*

In the normal dispersion region (the transparent region the refractive index dispersions has been analyzed using the single oscillator model developed by Wimple and DiDomenico[Wemple & DiDomenico 1971].Wimple and DiDomenico have developed a model where the refractive index dispersion is studed in the region of transparency below the gap ,using the single oscillator approximation .defining two parameters,the oscillation energy $E_o$,and the dispersion energy $E_d$ ,the model concludes :

$$n^2 = 1 + \frac{E_o E_d}{E_o^2 + (h\nu)^2} \qquad (7)$$

One can develop some relationships between the dispersion parameters and $\varepsilon_2(\omega)$ spectrum via :

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \qquad (8)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad (9)$$

Where $M_{-1}$,$M_{-3}$ are moment of optical spectrum and the -1 , -3 moment are involved in computation of $E_o$ and $E_d$ .It is known that static dielectric constant of any substance is defined as:

$$\varepsilon_r(o) = \lim_{E \to o} n^2(E) = n_o^2 \qquad (10)$$

The static dielectric constant can be written in term of dispersion parameters simply as :

$$n_o^2 = \varepsilon_r(o) = 1 + \frac{E_d}{E_o} \qquad (11)$$

Plotting ($n^2$-1) versus ( hν)$^2$ as illustrated in Figure(7) for R6G thin films, which yield a straight line for normal behavior having the slope$(E_oE_d)^{-1}$ and intercept with the vertical axis equal to($E_o/E_d$) . The value of $E_o$ , $E_d$ , $M_{-1}$ ,$M_{-3}$ , n(o) and are listed in Table 1 .

### *3.6 Complex dielectric constant and optical conductivity*

The complex dielectric constant is a fundamental intrinsic property of the material .The real part of the dielectric constant shows how much it will slow down the speed of light in the material . , whereas the imaginary part shows how dielectric material absorbs energy from an electric field due to dipole motion .The knowledge of the real and imaginary parts of the dielectric constant provides information about the loss factor which is the ratio of the imaginary part to the real part of the dielectric constant . The real and imaginary parts of the dielectric constant can be estimated using the relation [ Bakry 2008].

$$\varepsilon_1 = n^2 - k^2 \qquad (12)$$

$$\varepsilon_2 = 2nk \qquad (13)$$

Figure(8) shows the relationship between real and imaginary part ($\varepsilon_1$ and $\varepsilon_2$) and photon energy. It is clear that the variation of $\varepsilon_1$ mainly depended on $n^2$ because of small values of $k^2$ , while $\varepsilon_2$ mainly depends on k values which are related to the variation of absorption coefficients . The dissipation factor (tanδ) is a measure of loss rate of power of a mechanical mode , such as an oscillation in a dissipation system . The dissipation factor (tanδ) can be calculated by following:

$$\tan\delta = \frac{\varepsilon_2}{\varepsilon_1} \qquad (14)$$

The variation of dissipation factor (tanδ) of the investigated film with photon energy is shown in Figure(9) .

From the figure, we can see that the dissipation factor (tanδ) increases with increasing the photon energy like $\varepsilon_2$ spectrum .

The optical response of a material is mainly studied in terms of the optical conductivity ($\sigma_{opt}$) which is given by the relation [abari Girisun & Dhanuskod. 2009] .

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \qquad (15)$$

where c is speed of light .

The high magnitude of the optical conductivity ($10^{13}$ $sec^{-1}$) confirms the very high photo response of the film. The increasing optical conductivity at high photon energies is due to the high absorbance of R6G dye thin film and may be due to electron excitation by photon energy and at high photon energy > 2eV decreasing This is analogue to the α spectrum. The electrical conductivity can be calculated using the relation [Sabari Girisun & Dhanuskodi 2009].The optical and electrical conductivities have different profiles with increasing photon energy with optical conductivity higher than electrical as shown in Figure(10)

$$\sigma_e = \frac{2\lambda\sigma_{opt}}{\alpha} \qquad (16)$$

Furthermore, the values of n and k have been used to define the complex dielectric constant ,real and imaginary part labeled by[Madhup *et.al.* 2010]:

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\infty - \frac{e^2 N}{4\pi^2 c^2 \varepsilon_o m^*}\lambda^2 \qquad (17)$$

where $\varepsilon_1$ , e , c , $N/m^*$ , $\varepsilon_\infty$ ,and $\varepsilon_o$ are the real part of dielectric constant, the electron charge, the speed of light, the ratio of the free charge carrier concentration to the effective mass, the high frequency dielectric constant(the lattice dielectric constant), the permittivity of free space ($8.854\times10^{-12}$ F/m). The parameters $\varepsilon_\infty$ and $N/m^*$ could be determined from equation (17) by plotting $n^2$ ($\varepsilon_1 = n^2$ ) versus $\lambda^2$ as shown in Figure(11) . It is observed is linear at large wavelengths. Extrapolating the linear part of this dependence to zero wavelength give the value of $\varepsilon_\infty$ and from the slope the values of $N/m^*$ . The evaluated values of the $\varepsilon_\infty$ and $N/m^*$ were listed in Table 1 .

The average interband oscillator wavelength $\lambda_0$ can be calculated by applying the following relation :

$$\frac{n_o^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \qquad (18)$$

$n_0$ is the reflective index at infinite wavelength $\lambda_0$, plotting $(n^2-1)^{-1}$ versus $\lambda^{-2}$ shows linear part, was below the absorption edge as shown in Figure(12) . The average oscillator strength is given by :

$$S_o = \frac{n_o^2 - 1}{\lambda_o^2} \qquad (19)$$

The value of at $\lambda_o$ and $S_o$ are listed in table 1 .

Third order nonlinear optical properties provide the means to control light with light to change the frequency of colour of light ,to amplify one source of light ,switch it , or alter its transmission characteristics through a medium . According to wagner et.al.[Wagner *et.al.* 2005],the Miller rule it is very convenient for visible ,nonlinear and near infrared frequencies, which relates the third order of nonlinear polarizability parameter $\chi^{(3)}$, the so-called nonlinear optical susceptibility, and the linear optical susceptibility, $\chi^{(1)}$, through the equation:

$$\chi^{(3)} = A(\chi^{(1)})^4 = A[E_o E_d / 4\pi(E_o^2 - (h\nu)^2]^4 = \frac{A}{(4\pi)^4}(n^2 - 1)^4 \qquad (20)$$

where $A$ is a constant , $A=1.7\times10^{-10}$ .

The volume and surface loss functions are proportional to the characteristics energy loss of fast electrons traveling the bulk and surface of the material ,respectively .The volume energy loss function (VELF) and surface energy loss function (SELF)are related to the real and imaginary parts of the complex dielectric function[ Park 2012] The energy-loss functions are related to real and imaginary parts $\varepsilon_1$ and $\varepsilon_2$ of the complex dielectric constant by the following relations:

$$VELF \ = -Im[\frac{1}{\varepsilon}] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} \qquad (21)$$

$$SELF \ = -Im[\frac{1}{\varepsilon + 1}] = \frac{\varepsilon_2}{[(\varepsilon_1 + 1)^2 + \varepsilon_2^2]} \qquad (22)$$

Where($-I_m$ [1/ε]) is the volume term of energy loss and ($-I_m$[1/ε+1]) is surface term of energy loss. The surface energy and volume energy loss functions generated from the dielectric functions ( $\varepsilon_1$ and $\varepsilon_2$ ) are calculated and shown in Figure(13) . The two energies were computed in the energy rang from 2eV to 3eV , respectively a typical experimental energy range from visible to VUV . Also the surface and volume energy loss functions generated from the Lorentz oscillator dielectric functions ( $\varepsilon_1$ and $\varepsilon_2$ ) have the same oscillator shape as seen from figure(8) . Many optical parameters were recorded in Table 1 .

Table 1 . Optical Constant of R6G Dye Thin Film

| **Quantity** | **Value** | **Quantity** | **Value** |
|---|---|---|---|
| $E_g^d (eV)$ | 2.2 | $n_\circ$ | 1.96 |
| $E_g^{ind} (eV)$ | 1.3 | $\varepsilon_\circ$ | 3.87 |
| $\Delta E_{Urbach} (meV)$ | 184 | $N / m^* (m^3.kg)^{-1}$ | $3.66 \times 10^{39}$ |
| $E_\circ = 1.6 E_g (eV)$ | 3.53 | $\varepsilon_\infty$ | 3.27 |
| $E_d (eV)$ | 10.15 | $\chi^3 (0)(esu)$ | $4.45 \times 10^{-13}$ |
| $M_{-1} (eV)^2$ | 2.87 | $\lambda_\circ (nm)$ | 206.58 |
| $M_{-3} (eV)^2$ | 0.23 | $S_\circ (m^{-2})$ | $6.65 \times 10^{12}$ |

## 4.Conclusion

Optical transmission spectrum are used to calculate the optical, and dielectric properties (i.e. absorption coefficient , α , refractive index , n , extinction coefficient , k , optical and electrical conductivity($\sigma_{opt}$ & $\sigma_e$ ) , real and imaginary part of dielectric constant($\varepsilon_1$&$\varepsilon_2$) , optical band gap(Eg), the third order of nonlinear polarizability parameter $\chi^{(3)}$ , The average interband oscillator wavelength $\lambda_0$,and surface and volume energy loss function) for R6G thin film. The high extinction coefficient value ($10^{-2}$ ) and the high magnitude of optical conductivity ($10^{13}$ $s^{-1}$) confirms the presence of very high photo response of the material. Calculate the direct optical band gap $E_g^{Opt}$ values about 2.2eV by two methods ,first ,by Tauc relation and from Wemple DiDomenico relation were $E_o \approx 1.6\ E_g$ .Surface energy(SELF) and volume energy loss(VELF) were also investigate by depending on real and imaginary parts of dielectric constant ,It has maximum peak at energy region 2eV . The R6G thin film is exhibited more transmittance at high wavelength. The calculated optical parameters of R6G thin film is useful to make the materials a prominent one for solar cell applications.

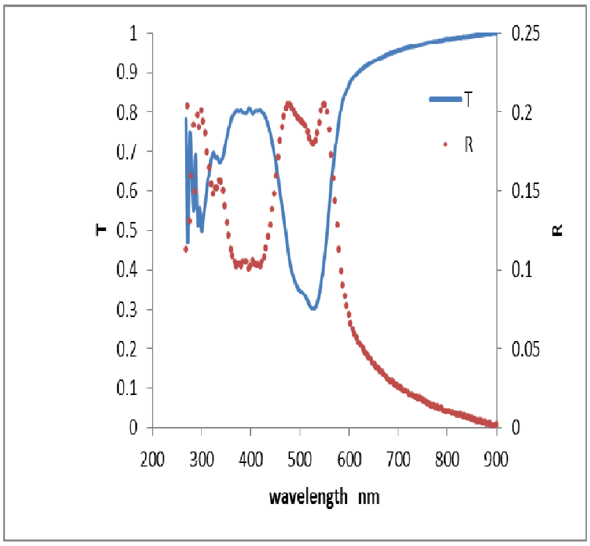


Figure 2. The transmittance and reflectance spectrum for R6G

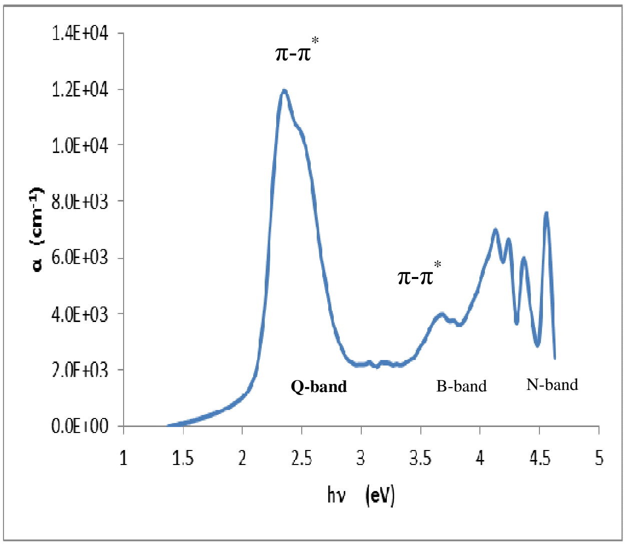


Figure 3. Dependence of α on the photon energy for R6G

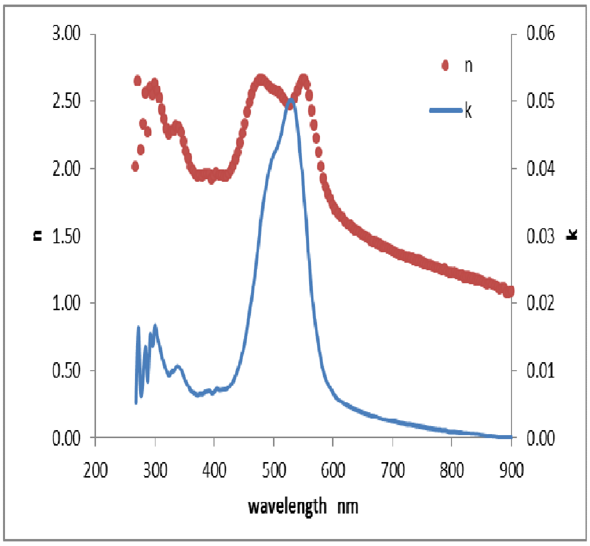


Figure 4.The extinction coefficient k and refractive index n dependent on the wavelength for R6G .

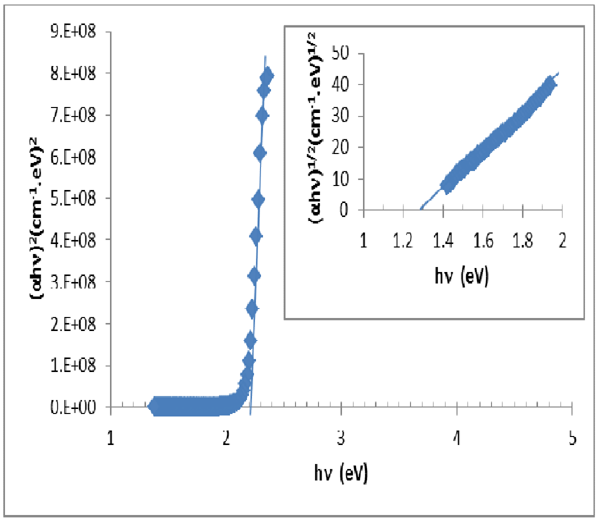


Figure 5. Plot of $(\alpha h\upsilon)^2$ vs. hν for R6G insert $(\alpha h\upsilon)^{1/2}$ vs.

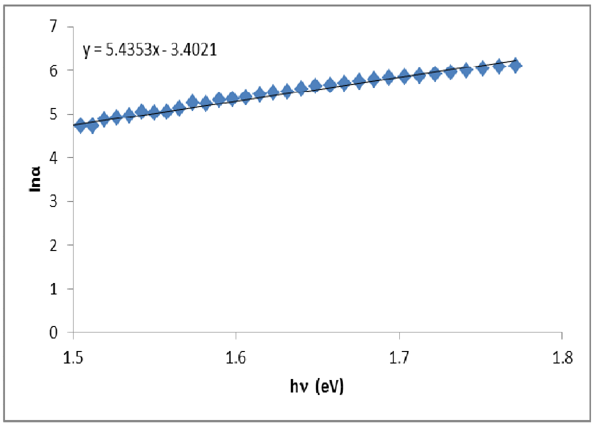


Figure 6.The relationship between ln α and hν for R6G

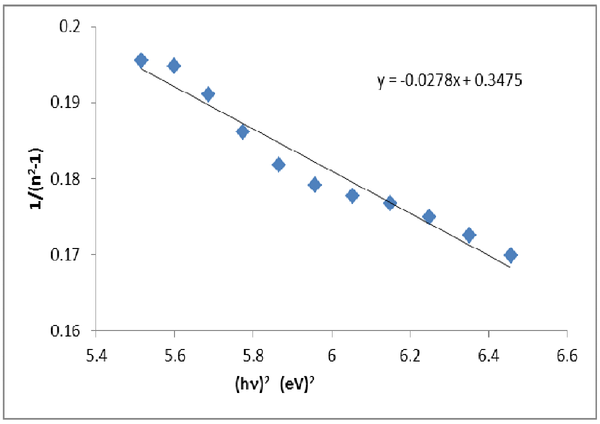


Figure 7. Plots of $(n^2-1)^{-1}$ against $(h\upsilon)^2$ for

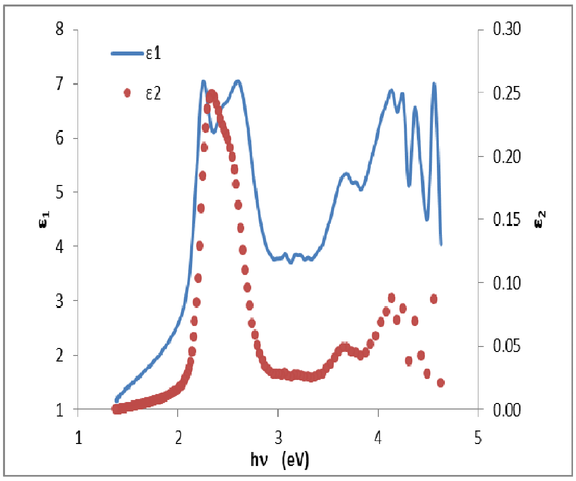


Figure 8.The relationship between $\varepsilon_1$ , $\varepsilon_2$ and hν for

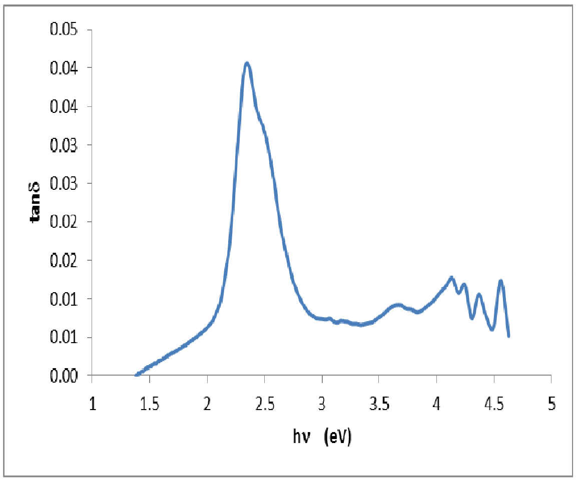


Figure 9.The relationship between dissipation factor and hν for R6G

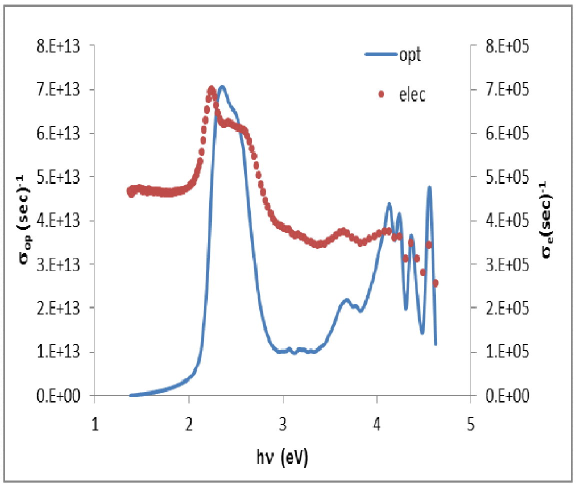


Figure 10. Plot optical conductivity $\sigma_{opt}$ and electrical conductivity as a function of photon energy for R6G

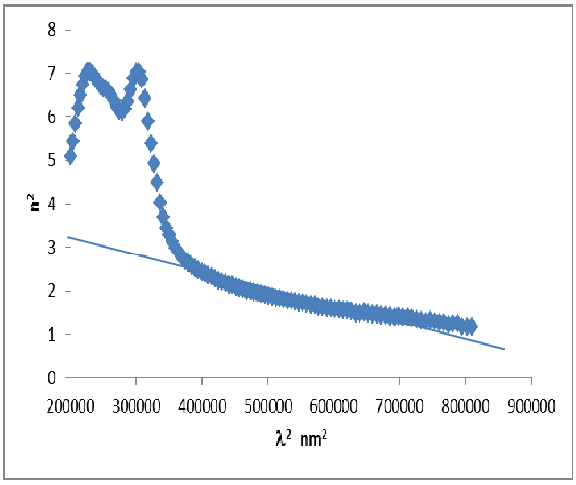


Figure 11. Plots of $n^2$ against $\lambda^2$ for

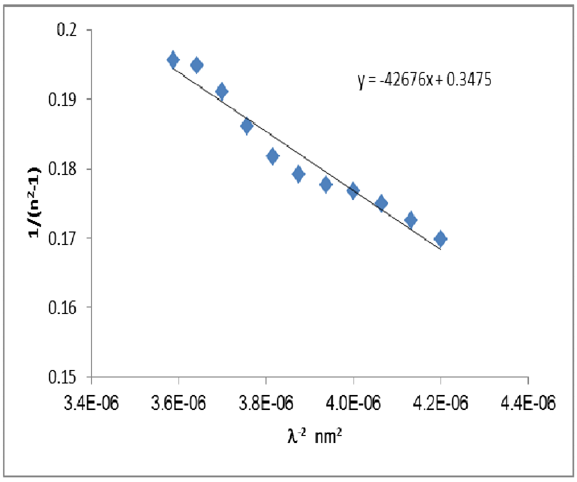


Figure 12. Plots of $(n^2-1)^{-1}$ against $\lambda^{-2}$

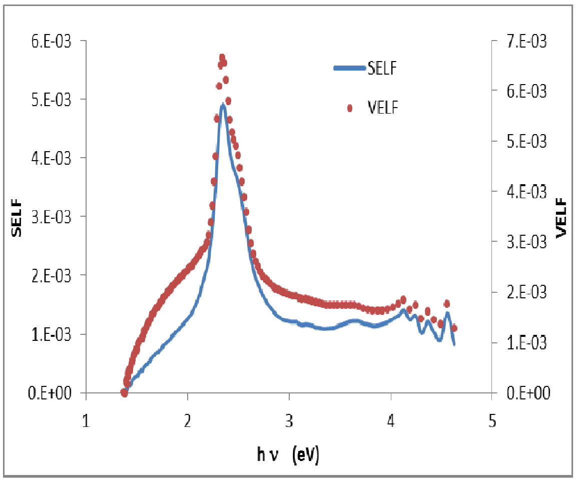


Figure 13. The relationship between volume , surface energy and hν for R6G

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