Spectral Behaviour of the low concentrations of Coumarin 334 with Broadband Cavity Enhanced Absorption Spectroscopy

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Abstract:

The current research is a spectroscopic study of Coumarin 334 dissolved in methanol. The range of concentrations of the prepared stock solution was (3.39x10^-9 to 2.03x10^-5) M. Some optical characteristics of this dye were investigated such as absorbance and transmission spectra, absorption coefficient, refractive and extinction coefficients, oscillation and dispersion energies, and energy band gap. The absorbance spectra were recorded at 452 nm using Broad Band Cavity Enhanced Absorption Spectroscopy (BBCEAS) which depends on increasing the path length of the traveling light from the source to the detector. The minimum absorbance amount was 0.07 with a low concentration of 3.39x10^-9 M. As a result, the other optical properties were calculated on the basis of the lowest values of absorbance. The energy band gap, which is important to detect the electronic band structure of the material, was determined; it was found to be equal to ~2.55 eV. The low values of the concentration made less collision between the molecules in the materials and the incident light. This led to a reduction in the background noise and in the percentages of losses. Furthermore, the dispersion and single oscillator energies, which help to calculate the average strength of the inter-band optical transitions and to prepare the quantifiable information about the band structure of the material, were calculated to reduce with the increasing concentrations. The refractive and extinction coefficients were determined because they are considered important factors for the optical materials and found to increase with the increasing concentrations. As a result, the study of the optical behavior of Coumarin 334 highlighted the promising materials for photonics applications at very low concentrations. All these properties are considered the main factors to determine the usefulness of the materials in advanced applications and to develop the performance of the devices which depend on the optical characteristics.

Keywords: BBCEAS, Coumarin, Low concentrations, Nanotechnology, Optical properties

Introduction:

The continuous discovery of new types of materials depends not only on the engineering of the materials in a practical field, but also on understanding its properties. These properties are involved in determining the usefulness in the applications. For example, the optical properties of the materials have a big effect on the measurements because they are able to change or modify the light direction or its intensity and this results in the development of advanced applications in different fields, such as the communication systems, energy, lasers, photonic devices and industrial processing. More importantly, the optical properties of the material depend on the spectroscopic characteristics such as: the absorption and emission measurements of the samples. The organic dyes are considered a good choice with respect to studying these properties due to their strong absorption in the visible region of the spectrum. One of these organic dyes is Coumarin. It generates higher fluorescence quantum yield, good solubility, inexpensive, available, relative ease of synthesis, and responsible stability. The optical properties of Coumarin are studied using different types of spectrometers, such as: Camspec M 501 (UV-VIS) spectrophotometer and (PF-6300) spectrofluorometer, JASCO V-630
UV-VIS spectrophotometer, Perkin Elmer Lambda-35 UV-VIS spectrometer and Shimadzu UV-1601 double beam spectrophotometer. Considering all these types of the spectrometers, the low concentration one can be studied and its properties reach microscale. Thus, it would be better if the optical properties record uses a range of concentrations down to nanoscale levels. Nanotechnology aims to make reduction in the use of the material, energy, cost and waste. This leads to building an economic and universal range of products and to creating new materials with low temperature and pressures, disregarding both cost and sustainability. To determine the optical properties using nanomolar concentrations, the optical cavity techniques should be used as a spectroscopy system.

The recent studies identified the sensitivity measurements with different optical cavity techniques, starting with cavity ring-down spectroscopy (CRDS), cavity-enhanced absorption spectroscopy (CEAS) and (BBCEAS), which is considered the recent development by using the broadband light source. Generally, BBCEAS set up consists of light source, optical cavity contains two high reflectivity dielectric mirrors and a detector with high resolution, which is used to record the absorption spectra. These techniques depend on the use of the optical cavity to improve the interaction of the light with matter by increasing the path length between two high reflectivity dielectric mirrors to increase the sensitivity measurements of the absorption spectra. Optical cavity technique applies to HPLC detection, it allows to record the absorption spectrum of the analyte over a wide range of wavelengths. In addition, it is cheaper and simpler. In the biological field, BBCEAS is used as a detection system for immunoassay measurement, an essential bioanalytical technique. Moreover, it has been widely used in detecting trace species, studying the kinetics in the gas phase, determining weak molecular transitions, probing interfacial interactions and molecular dynamics. The applications of cavity enhanced techniques in the liquid phase have aroused considerable interest because of factors such as the broad line width of absorptions (>10nm); a wide range of species to study in the liquid phase.

The study is primarily concerned with measurements of the optical properties at very low concentrations of Coumarin 334. This was achieved by using the optical cavity techniques to determine the usefulness of the materials in advanced applications and to develop the performance of the devices which depend on the optical characteristics.

Materials and Methods:
To determine the optical properties of the measurements, a range of concentrations from 3.39 to 30.5 nM was prepared from 0.1 g of Coumarin 334 (Sigma, Aldrich, UK), and dissolved in 25 mL methanol, which was diluted in water with percentage 2%, to get a stock solution 4.23 µM. After that, the concentrations were prepared by taking 0.02, 0.04, 0.06, 0.08, 0.1, 0.12, 0.14, 0.16, 0.18 mL from the stock solution respectively and then dissolved in 25 mL of methanol. In this study, a novel technique called Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS) which depends on the optical cavity principle, was used to study the analyte. BBCEAS consists of three main parts: a light source represented by 3 Watt white LED (Lumileds-SR-12) with an output power equal to ~500 mW, an optical cavity containing two dielectric mirrors (Layertec, Germany) with high reflectivity (R ≥ 0.99). This cavity was connected using a 2 m length fiber optic cable (Ocean optics) with the Avantes spectrometer (2048 pixel Avaspec-ULS2048L) as the detector and the construction consist of a series of lenses, irises, collimating lenses and filter, which are used to modify the path of the light.
Results and Discussion:

The absorbance spectra using the BBCEAS with the dual channel construction were recorded with a range of concentrations from $3.39 \times 10^{-9}$ to $2.03 \times 10^{-8}$ M Fig. 2. It is clear that the Coumarin 334 has an absorbance peak at 452 nm. It can also be noted that the results of the present study are the most sensitive when compared with those of the previous studies according to a very small amount of the recorded light absorbance (Tab. 1). For example, in AL-Aqmar et al., the amount of the absorbance was equal to 1.42, 1.57 for the concentration of $1 \times 10^{-4}$ M of Coumarin 334, and it was also equal to 2.5 of concentration $0.3 \times 10^{-3}$ M of Coumarin in Abhishek et al., study, while it was equal to 0.07 of the concentration $3.39 \times 10^{-9}$ M of the same dye in the present study. Such difference is related to the technique that is applied to determine the absorbance spectra which is presented as a long path length leading to a reduction in the background scattering and absorption losses. As a result, a very small amount of the light is absorbed by the sample and most of it will be detected by the detector. The study highlighted the very low concentrations that appeared with the availability of the materials; some materials are very expensive or they are very rare in nature, in addition, some of are related to the human samples. On the other hand, if the concentration of the solution is decreased, less collision will occur between the molecules with the light passing through them, so the light will not be blocked.

![Figure 1. A schematic diagram of the set up for BBCEAS](image-url)

![Figure 2. The absorbance spectra of the Coumarin 334 to the range of concentrations from $3.39 \times 10^{-9}$ to $2.03 \times 10^{-8}$ M using BBCEAS](image-url)
Regarding transmittance, which represents the ratio between the percentage of the emitted light and the percentage of the incident light, Fig. 3 demonstrates decreased transmittance due to a decrease in coumarin 334 concentration, in the range of the wavelengths between (400-500) nm; besides, its behaviour is reversed to that of the absorbance spectrum. This is due to the effect of the impurity atoms which are working on combining the levels localization in the energy gap.

As previously stated, the absorbance spectra were recorded using BBCEAS, and the principle work of this technique is to make an effective path length (l) represented by the multiplication of the path length (d) and by the cavity enhanced factor (CEF). The CEF values are defined as the number of passes through the cavity. At first, the absorbance values were converted to cavity absorption values using Eq. 1 below:\n\[
\frac{I_o(\lambda)}{I(\lambda)} - 1 = \frac{2.303\varepsilon C_l}{(1-R(\lambda))}
\]

Where \(\frac{I_o(\lambda)}{I(\lambda)} - 1\) can be obtained from the linear relationship between the values of the cavity absorption and the values of the concentrations (Fig. 4) as it is represented by the slope of this relation, and is proportional to the analyte concentration. The cavity absorption is different from the absorbance, as the absorbance can be determined using the single pass experiment which is equal to \((\log_{10}(I_0/I))\). Regarding the \(\varepsilon C_l\), (\(\varepsilon\)) represents the Molar absorptivity of Coumarin 334, (C) the concentration, and (l) the effect path length. So, the effective path length can be found by multiplying the path length (d) with the CEF values; it is equal to 90. This value was applied to calculate the absorption coefficient values in this study.

After that, the cavity enhanced factor values were calculated using the relationship in Eq. 2 below:\n\[
CEF = \frac{\frac{I_o(\lambda)}{I(\lambda)} - 1}{2.303\varepsilon C_l}
\]

So, the enhancement can be calculated by dividing the cavity absorption over the single pass absorbance.
The Urbach’s energy of the Coumarin 334 was determined by studying the relation between \( \ln(\alpha) \) with the values of photon energy to a range of concentrations of the Coumarin 334. The Urbach formula can be specified using Eq. 4 below:

\[
\alpha = \alpha_0 \exp\left(\frac{\hbar \nu}{E_g}\right)
\]

Fig. 6 illustrates that the value of \( \ln(\alpha) \) increased with the increase in the concentration. Additionally, the Urbach energy of the Coumarin 334 of the linear portion in the curve can be recorded; they were listed in Tab. 2.

On the other hand, the bandgap energy measurements of the Coumarin334, which is necessary to reveal the electronic band structure of the material, were determined using the Taue’s relation (Tab. 2). This relation can be drawn from this Eq. 5:

\[
\alpha \hbar \nu = A(\hbar \nu - E_g)^r
\]

Where (A) is constant and (P) which is related to the type of the optical transition whether or not it is direct because it is equal to \( \frac{3}{2} \) and \( 2 \). It is clear from Fig. 7 that the values of the energy gap of the Coumarin 334, which are obtained as a result of the intercept values of the straight line with the x-axis at zero absorption, were around \(-2.55\) eV. The linearity of the plot is related to the type of the optical transition which is the direct band gap nature of the dye. After determining the absorption coefficient, the refractive index and the extinction coefficient of the Coumarin 334 can be calculated. They are considered important parameters for the optical materials and for their applications because they are related to the interaction of the incident light with the material. The values of the refractive index can be calculated using Eq. 6 which depends on the transmittance values as shown below:

\[
n = \sqrt{(T^{-2} - 1) + (T)^{-1}}
\]
Figure 7. The relationship between $(a\nu)^{1/2}$ with the photon energy for a range of concentrations of Coumarin 334 using BBCEAS

Fig. 8 shows the variation of the refractive indices with the range of the wavelengths of the Coumarin 334. It is noted that the refractive index values increased with the increasing concentration and that they slowly changed, about ~2 at 452 nm. This change is attributed to the existence of the defects\(^{28}\).

Regarding the extinction coefficient (K), it can be determined using the relation in Eq. 7 as below\(^{24,29}\):

$$K = \frac{\lambda \alpha}{4\pi}$$

It is apparent that (K) increased with the rise in the concentration Fig. 9. The increase indicated that the coumarin dye allows the electromagnetic waves to pass through without any damping in the visible spectral region of the wavelength\(^{29}\). The similarities between the changes of the refractive indices and the extinction coefficients with the range of the wavelength are related to the increase in the free carrier of the concentration.

Figure 8. The variation of the refractive index values as a function of the wavelengths for Coumarin 334 using BBCEAS

Figure 9. The variation of the extinction coefficient values as a function of the wavelengths for Coumarin 334 using BBCEAS.
Additionally, it is possible to determine the single effective oscillator energy \( E_o \) and dispersion energy \( E_d \) from examining the relation between the \( (n^2-1)^{-1} \) values and the values of \( (h\nu)^2 \) for the different concentrations of the Coumarin 334. The multiplication of these energies can be determined from the inverse of the slope of the linear plot. These values are presented in Table 1. The energies were obtained using the Single effective oscillator model, which is also known as the “Wemple and Di-Domenico”. They can be derived from Eqs. 9 and 10 as shown below:

\[
\begin{align*}
(n^2 - 1) &= \frac{E_o E_d}{\left( E_o^2 - (h\nu)^2 \right)} & \text{(9)} \\
(n^2 - 1)^{-1} &= \frac{E_o E_d}{(E_o^2 - (h\nu)^2)} & \text{(10)}
\end{align*}
\]

The dispersion energy is used to measure the average strength of the inter-band optical transitions. Regarding the effective oscillator energy, which is equal to \( 2E_o \), it measures the average energy gap \( E_o \) and provides quantifiable information about the bond structure of the material because the two energies are formed the chemical bonds of the composition which refer to the energy stabilization in the clusters for the atoms of the material. In other words, increasing concentration of Coumarin 334 leads to decreased number of bonds in its structure thereby decreasing the energy of the bonds and change its ionicity values leading to the reduction in the \( E_o \) and \( E_d \) values. These results are in agreement with the study reported by Hassanien, et al.

This Table shows the relation between change of concentration with energy gap, and it can be noticed that the increasing in concentration will give a small change in \( E_o \), so, if concentration increased to be higher than the same result will happen. In addition, \( E_o \) and \( E_d \) will decrease with increasing the concentration as well. Finally, the optical conductivity of the different concentrations of the Coumarin 334 can be computed based on the values of the refractive index and the absorption coefficient according to the Eq. 11 below:

\[
\sigma = \frac{\alpha n c}{4\pi}
\]

The variations of the optical conductivity with the \( h\nu \) values are presented in Fig. 11 which shows that the optical conductivity increased with increasing concentrations. This increase is related to the increase in the excited electrons by raising the energy of the incident light.

![Figure 11](image_url)

Figure 11. The variation of the optical conductivity with the photon energy values of a range of concentration of Coumarin 334 using BBCEAS

### Conclusion:

In the current study, the optical properties of Coumarin 334 have been specified at 452 nm. The important factor in these measurements is the increase in the path length of the optical cavity of the BBCEAS technique and this is considered the novelty and scientific reliability of the work as it is the first study that deals with the nanomolar concentrations to measure the optical properties of the materials. The experimental values of the energy band gap are recorded for all concentrations; they are equal to \(~2.55\) eV. Furthermore, the dispersion and single oscillator energies are found to decrease with the increasing concentrations. These values provide information about the band structure of Coumarin 334. The refractive and extinction coefficients are calculated; and found to increase with the increasing concentrations. As a result, the study of the optical behavior of Coumarin 334 highlights the promising materials for the photonics applications at very low concentrations.

### Table 2. Some of the measurement of the absorption spectra at 452 nm using BBCEAS

| C (M)      | Abs. | \( E_o \) (eV) | \( E_d \) | Urbach energy |
|------------|------|----------------|----------|---------------|
| 3.39 \times 10^{-9} | 0.073 | 2.55 | 5.11 | 1.17 | 0.102 |
| 6.78 \times 10^{-9} | 0.087 | 2.55 | 5.10 | 1.17 | 0.105 |
| 1.36 \times 10^{-8} | 0.102 | 2.54 | 5.07 | 1.16 | 0.110 |
| 1.69 \times 10^{-8} | 0.120 | 2.53 | 5.07 | 1.15 | 0.117 |
| 2.03 \times 10^{-8} | 0.132 | 2.53 | 5.08 | 0.73 | 0.119 |
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Authors’ declaration:
- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for republication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in Mustansiriyah University.

Authors’ contributions statement:
Hanan A. Naif carried out the design, acquisition of data, analysis, interpretation, and participated in the drafted the manuscript. Asrar A. Saeed helped in interpretation and analysis. Mahasin F. Al-Kadhemy contributed to manuscript conceptualization, and interpretation. All authors read, revision and proofreading the final manuscript.

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دراسة طيفية لتراكيز منخفضة من صبغة الكومارين مع تقنية تحصين فجوة الامتصاص ذات المدى الطيفي

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الخلاصة:

إن الدراسة الحالية هي دراسة طيفية لصبغة الكومارين 334 مذابة في محلول الميثانول. مدى التراكيز المحضرة من المحلول الرئيسي كان ممثل بالقيم المحصورة بين 3.39x10^{-9} to 2.03x10^{-8} مولي. تم دراسة بعض الخصائص البصرية مثل اطعاف الامتصاصية والنفاذية، معامل الامتصاص، معامل الانعكاس ، معامل الانكسار، طاقة التذبذب، طاقة الامتصاص، طاقة التشتت وايضا فجوة الطاقة. اطياف الامتصاص سجلت عند الطول الموجي 452nm باستخدام تقنية التجويف البصري Broadband Cavity Enhanced Absorption Spectroscopy. اصغر مقدار امتصاص تم قياسه هو 0.07 مع أقل تركيز والذي هو 3.39x10^{-9} مولي. وبالتالي، فإن الخصائص البصرية تم حسابها بالاعتماد على اصغر قيمة الامتصاصية. فجوة الطاقة تم تحديدها وكانت تساوي ~2.55eV. إن التراكيز المنخفضة تؤدي إلى تصلبات قليلة بين الجزيئات في المادة مع الضوء الساطع وهذا الإحذف يوحي إلى تقليل الضوضاء والخسائر. بالإضافة إلى ذلك، طاقة التذبذب والتشتت تم حسابها ووجد أنها تقل بزيادة التركيز مع العلم أن هذه الطاولات تساعد في إعطاء المعلومات حول تركيب الأصورة للكومارين 334. وكذلك قيمة معامل الانكسار والخمود وجدت أنها تزداد بزيادة التركيز. وتم الاستنتاج في هذه الدراسة أن السلوكي الطبيعي لكلومارين مع التركيز المنخفض جدا يعتبر مثالاً لباقى المواد لكي نستخدم في التطبيقات الفوتونية مع التركيز المنخفض جدا. ان الخصائص البصرية تعتبر العامل الرئيسي لتحديد مكافأتية استخدام المواد في التطبيقات المعقدة وتطوير أداة هذه الأجهزة التي تستند على الخصائص البصرية.

الكلمات المفتاحية: تراكيز منخفضة، تقنية BBCEAS، خصائص بصريّة، علم النانوتكنولوجي، كومارين