Gamma ray effect on the properties of R590 and C480 laser dyes

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Abstract
In the current research, we investigated the absorption spectrum for R590 and C480 dyes in ethanol solvent for different dye solution concentrations of $10^{-4}$, $10^{-5}$ and $10^{-6}$M. These dyes have been prepared and studied before and after gamma irradiation (first, second ionization) using cesium-137 source with absorbed doses of 18.36 Gy (time exposure of 10 days) and 73.44 Gy (with time exposure of 40 days). We noticed that the absorption intensity was decreased with decreasing concentration, before gamma irradiation while the absorption spectrum peak shifted towards the short wavelength (blue shift). It was also found that the intensity of absorption spectrum increased and shifted the absorption spectrum peak towards the long wavelength (red shift) when irradiation exposure times and doses by gamma rays from (Cs137) source increased.

Key words
Laser dye, Absorption, Ionizing radiation.

Introduction
Dye lasers were first discovered by Sorokin and Lankard in 1966 [1] and the applications for these lasers have appeared in industrial, military, and medical instruments. In industry, these lasers have been used in semiconductor fabrication, chemical purification, catalyst production, curing of pigment coatings, and combustion diagnostics. In medicine, dye lasers have been used for removing birthmarks, breaking stones in the gallbladder, angioplasty, and for cancer studies [1]. Dye lasers have made a large impact on society due to their lasing potential, high quantum yield, wavelength tenability and self-mode locking capabilities. The dyes used in lasers contain rather large organic molecules which fluoresce [2].
Organic dye molecules have been widely used in solutions as amplifying media in tunable lasers [3]. Organic compounds have been the subject of intense theoretical and experimental studies due to their promising applications in different life science fields. The laser dyes are unsaturated hydrocarbon organic compounds containing a mutual series of carbon atoms with successive single and double bonds [4]. Coumarin dyes are well-known laser dyes for the blue-green region [5]. The Coumarin dyes usually show very strong solvent polarity dependent Stokes’ shifts substantial changes in the dipole moments while undergoing electronic transitions, and very high fluorescence quantum yields [6]. There are several classes of laser dyes including polymethine (700-1500 nm), xanthenes also known as Rhodamine (500 - 700 nm), Coumarin (400-500nm) and Scintillator (320 - 400 nm). Most dyes are strong absorbers in the ultraviolet region [7]. Gamma photons have about 10,000 times as much energy as photons in the visible range of the electromagnetic spectrum. Gamma photons are electrically neutral and do not steadily lose energy as they penetrate matter. Instead, they can travel some distance before interacting with an atom. How far a given photon will penetrate is governed statistically by a probability of interaction per unit distance traveled, which depends on the specific medium traversed and on the gamma photon energy [8].

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical formula</th>
<th>Color</th>
<th>structural formula</th>
</tr>
</thead>
</table>
| Rhodamine 590 laser dye   | C_{28}H_{31}N_{2}O_{3}Cl  
479.09 (g/mol) | orange | ![Rhodamine](image)  |
| Coumarin 480 laser dye    | C_{16}H_{17}NO_{2}  
255.32 (g/mol) | pale yellow | ![Coumarin](image)  |
| Ethyl alcohol             | C_{2}H_{5}OH  
46.07 (g/mol) | colorless | ![Ethyl alcohol](image)  |

When radiation passes through materials, it breaks chemical bonds [9]. Table 1 lists the specifications of the starting chemical materials.
Materials and Methods

The preparation of R590 and C480 dyes laser dyes solutions were done by dissolving the required amount of the R590, C480 dyes in ethyl alcohol. The weight of the dye (W) can be calculated using the following equation:

\[ W = M_w \times V \times C / 1000 \]  (1)

where \( M_w \) is the molecular weight of the dye (g/mole), \( V \) is the volume of the solvent in ml and \( C \) is the molar concentration (mole/liter). A high concentration of \( 10^{-3} \) M of R590 dye solution was prepared and then diluted to \( 10^{-4}, 10^{-5} \) and \( 10^{-6} \) M.

Firstly, two types of dye solutions; R590 and C480, were prepared in ethanol solvent at different concentrations \( 10^{-4}, 10^{-5}, 10^{-6} \) M. Absorption spectra were measured by UV-Visible spectrophotometer and FTIR- Spectrometer measurement before irradiation by gamma ray source (Cs-137).

Secondly, the two samples were exposed to different doses of gamma ray (Cs-137) two does of 18.36, 73.44 Gy and after each dose measurements of both FTIR and absorption have to follow up the changes in the characteristics and structural that may be occurred into samples.

Results and discussion

Effect of gamma radiation on the FTIR of dye solutions

In the Figs. (1 a, b) and (2 a, b) one can notice that the effect of 18.36 Gy and 73.44 Gy doses, there is no shifting or change in the position of bonds and no change in the molecular structures as well. This paved the way into performing spectroscopic measurements; otherwise, one has to interpret these modifications in bonds and/or molecular structures prior to start any of these measurements. However, the intensity of peaks rain FTIR spectra depends on factors such as molecular size, the nature of molecular-solvent molecular dopant, and the effect of the irradiation. Therefore, the change in intensity of IR vibration band confirms the irradiation effect on dyes solutions.

Fig. 1 (a and b): FTIR spectrum of the dye solution (R590 x10^{-3}) M before and after gamma ionizing with (Cs-137) source.
Absorption spectra measurements before and after ionizing

Upon comparing absorbance spectra of the dye solutions prepared at the previously mentioned concentrations following the two irradiation exposures of gamma radiation (the first 10 days dose of 18.36 Gy and the other 40 days dose of 73.44 Gy) with those before irradiation, a shift in the peak wavelength towards long wavelength (red shift) was observed as shown in Fig.3 (a, b and c), Fig. 4 (a, b and c) and Fig. 5 (a, b and c). The blue or red shift in absorption spectra may be caused by solvation effect. It has been noticed that the red shift increased with increasing the concentration of dye solution. The absorption spectra of many organic dyes in liquid solution depend on the local electric field which is generated by the surrounding polar solvent molecules. This "solvation effect" is a result of intermolecular solute-solvent interaction forces (such as dipole-dipole or dipole-induced dipole) that tend to stretch the molecular bonds and shift charge distribution on molecules and thus altering the energy difference between the ground and excited states of the solute. This shift increased with irradiation exposure period; and is due to reducing of the energy gap of the dye solutions. This long wavelength shift was accompanied by a noticeable increase in intensity of spectra with increasing gamma irradiation exposure period. The reason for this is due to the transforming of dye solutions from a transparent to a cloudy medium, i.e., increasing the density causing increasing in concentration [10].

Fig. 2 (a and b): FTIR spectrum of the dye solution (C480 x10^-4) M before and after gamma ionizing with (Cs-137) source.

Fig.3 (a, b and c): Absorption spectra for (C480x10^-4, R590x10^-4) M before ionizing, first ionizing (18.36 Gy) and second ionizing (73.44 Gy) ionizing.
Fig. 3 (a, b, c): Absorption spectra for \((C480x10^{-4}, R590x10^{-4})\) M before ionizing, first (18.36 Gy) and second (73.44 Gy) ionizing.

Fig. 4 (a, b, c): Absorption spectra for \((C480x10^{-5}, R590x10^{-5})\) M before ionizing, first (18.36 Gy) and second (73.44 Gy) ionizing.
Fig. 5 (a, b, c): Absorption spectra for (C480x10^{-6}, R590x10^{-6}) M before ionizing, first (18.36 Gy) and (73.44 Gy) second ionizing.

Each of the two tables (Table 2 and Table 3) involves the exact values of the maximum intensity and its corresponding wavelength both prior to and after the different irradiation doses (18.36 Gy and 73.44 Gy).

Table 2: Absorbance data for C480 for different concentrations of 10^{-4}, 10^{-5} and 10^{-6} M, before and after first (18.36 Gy), second (73.44 Gy) ionizing.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Concentration (M)</th>
<th>Wavelength (nm)</th>
<th>Intensity</th>
<th>Wavelength (nm)</th>
<th>Intensity</th>
<th>Wavelength (nm)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C480</td>
<td>10^{-4}</td>
<td>390</td>
<td>0.812</td>
<td>393</td>
<td>1.204</td>
<td>396</td>
<td>1.356</td>
</tr>
<tr>
<td>C480</td>
<td>10^{-5}</td>
<td>388</td>
<td>0.086</td>
<td>391</td>
<td>0.119</td>
<td>393</td>
<td>0.129</td>
</tr>
<tr>
<td>C480</td>
<td>10^{-6}</td>
<td>386</td>
<td>0.010</td>
<td>389</td>
<td>0.015</td>
<td>391</td>
<td>0.023</td>
</tr>
</tbody>
</table>
Table 3: Absorbance data for R590 for different concentrations of $10^{-4}$, $10^{-5}$ and $10^{-6}$ M, before and after first (18.36 Gy), second (73.44 Gy) ionizing.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Concentration</th>
<th>Absorbance before ionizing</th>
<th>Absorbance after first (18.36 Gy) ionizing</th>
<th>Absorbance after second (73.44 Gy) ionizing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Wavelength (nm)</td>
<td>Intensity</td>
<td>Wavelength (nm)</td>
</tr>
<tr>
<td>R590</td>
<td>$10^{-4}$</td>
<td>530</td>
<td>2.718</td>
<td>534</td>
</tr>
<tr>
<td>R590</td>
<td>$10^{-5}$</td>
<td>527</td>
<td>1.060</td>
<td>530</td>
</tr>
<tr>
<td>R590</td>
<td>$10^{-6}$</td>
<td>525</td>
<td>0.176</td>
<td>528</td>
</tr>
</tbody>
</table>

Conclusions

1- The irradiation by low doses did not change the chemical structure of all the studied dyes. This behavior was confirmed by FTIR spectroscopy test, which showed no change in the bonds positions. Whereas the intensity of these peaks changed with the irradiation process, which can be attributed to the increments in the molecular size; in other words, cross linking may be happened in the structure of the dyes.

2- Red shift in the absorption spectra was noted and measured for gamma irradiation. The increase in gamma dose led to a corresponding increase in red shift. Furthermore, the decrease in the concentration of laser dye solutions shifts the absorption spectrum peak towards the short wavelength (blue shift). Therefore, these results strongly suggest that one can use the irradiation by gamma rays to get new dyes, which are useful in several applications.

References