

Influence of Solvent Environment on the Shpol'skii Spectra of Anthracene and Benzoanthracene Molecules

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Abstract--- *In the present work, the low temperature spectroscopy of anthracene and benzoanthracene molecules in different solvents has been studied at a fixed molar concentration. The temperature range has been taken from room temperature down to liquid nitrogen temperature (77K). Polar and nonpolar solvents; Ethanol, Isopropanol, Hexane, Heptane and Nonane, have been used in order to study the environment effect on the absorption and fluorescence spectra of these molecules. Some of the spectroscopic parameters have been determined as functions of solvent polarity and temperature. Thus, the fluorescence lifetime has been measured using the PTI instrument. The results indicate that the band width at FWHM increases with increasing the solvent polarity and temperature, while the peak emission cross section decreases with increasing of solvent polarity and temperatures. The Shpol'skii spectra of these molecules show clearly enhancement, in which sharp and highly-resolved fine structure spectra have been observed at 77K and thus, give the best results at 77K.*

Index Terms— Anthracene and Benzoanthracene molecules, low-temperature spectroscopy, Fluorescence lifetime

I. INTRODUCTION

The temperature effect is one of the important parameters that one may vary during spectroscopic measurements. The low temperature spectroscopy technique by Shpol'skii method is discovered in 1950, and used to study the spectroscopic properties and structure of polyatomic molecules [1]. In 2005 M.A. Haidekker studied effect of solvent polarity and solvent viscosity on the fluorescent properties of molecular rotors. The photo-physical characteristics depend on their environment [2]. In 2008 G.I.Romanovskaya wrote an article that covers the history of the discovery of the Shpol'skii effect on which a sensitive luminescence method for determining some organic compounds and analyzing their mixtures is based [3]. In 2013 Petlechner and A.Slenczka studied electronic spectroscopy of 9, 10 dichloroanthracene in side helium droplets. Electronic spectra of 9, 10-dichloroanthracene in helium droplets were presented and compared with corresponding gas phase spectra to unravel the influence of the helium environment [4]. Polycyclic aromatic hydrocarbons (PAHs) are usually defined as a group of chemicals consisting of two or more benzene rings (C_6H_6) [5]. Anthracene ($C_{14}H_{10}$) is a solid, planar, consisting of three fused benzene rings, derived from residues of thermal pyrolysis, benzoanthracene ($C_{12}H_{18}$) consisting of four

fused benzene rings and form yellow substance [6, 7]. They may be also studied under other suitable conditions in solid solutions or in a matrix of noble gas [8]. For many aromatic molecules, in liquid phase, the position and the structure of the fluorescence spectrum are strongly dependent on the solvent. The wavelength shift can often be correlated with changes in solvent dielectric constant and the solvent index of refraction [9].

The solvent shift arises because the excited state of the guest (solute) interacts with the solvent to a different extent than does the ground state of the guest [10]. In addition to the spectral shifts, the vibrational structure of the fluorescence and absorption spectra are influenced by interactions with the solvent environment. If the molecular spectra exhibit vibrational structure in the vapor phase, this structure is normally broader and more diffuse in solution, and the change of environment may modify the vibration spacing and the shape of the Franck-Condon envelope [11].

The Shpol'skii effect is of important scientific and applied value. First of all, it opens new ways to study the properties and structures of organic molecules, inaccessible for other spectroscopic methods. In particular, the Shpol'skii spectra allow the determination of the structure of electronic and vibrational levels in complex organic molecules with high accuracy and the investigation of various manifestations of fine intra- and intermolecular interactions [12]. The fine linear structure of the Shpol'skii spectra is responsible not only for their extreme specificity and differences even for molecules with similar structures, but also for their high line intensity. The conventional broad bands turn to narrow lines; this determines their exclusive practical value as a method for the detection and quantitative determination of individual organic compounds in complex mixtures [13,14]. This method will be used in the current research.

In the present work, the spectroscopy of some condensed aromatic compounds with different structure series are studied at low temperature down to 77K. Also the spectroscopic parameters of these aromatic in different types of solvent are investigated to describe the solvent effect on these parameters at low temperatures.

II. EXPERIMENTAL

The solution of anthracene and benzoanthracene molecules was prepared by dissolved into a specific solvent at constant concentration (1×10^{-4} M). Heptane, Nonane, Hexane, Ethanol and Isopropanol were used as

solvents and were selected according to molecular size and polarity.

The solution was introduced to vessel V which is connected to the cell C, by means of a funnel. The sample was frozen by immersion the vessel V in liquid nitrogen. The whole apparatus was evacuated and closed through the tap T. The system was pumped down to a pressure of 10^{-2} mbar and the tab T then closed again. The whole system could then be disconnecting from the vacuum line. The vessel was then re-immersed in liquid nitrogen and the system is then re-evacuated by connecting it again to the vacuum line. The solution then was transformed internally to the cell c. The cell was then sealed off while still being connected to the pump and immersed in liquid nitrogen. The residual pressure was less than 10^{-2} mbar prior to sealing off the cell. There are two advantages in using the vessel V; to prevent cracking of the cell after freezing the solution and to degas the sample. The low temperature spectroscopy down to 77K was achieved using suitable cryostat, were made of aluminum and consist of thermocouple of Ni Al, Ni Cr and connected to temperature controller (Thermometer Type -K). This thermocouple was used for precise temperature measurements. The thermocouple was directly attached to the sample cell. For low temperatures (from 300-77K) liquid nitrogen was used as refrigerant. Lowering the temperature was achieved by controlling the liquid nitrogen flow rate.

UV-Visible absorption spectra of the prepared solutions were recorded at room temperature and at 77K, using UV-Visible double-beam (Halogen and deuterium lamps) spectrophotometer (Metertech SP-8001 UV/Visible) which operates in wavelength range of 190 nm to 1100 nm. On the other side, the fluorescence spectra of prepared solutions were obtained using spectrofluorimeter setup contains GaN UV-LED light source ($\lambda_{ex}=382\text{nm}$), connected to a DC power supply (PS-1502DD). The resulting fluorescence spectrum was analyzed using a Jarrell Ash monochromator (model 82-000, which operates in wavelength range from 190 nm to 600 nm with resolution 0.2 Å in the first order). The instrument has 0.5 meter focal length, with eight speed electric drive, and a plane reflection grating of 1180 groove/mm. The detection unit was a photomultiplier PMT (type R 666 Hamamatsa) which was connected to an X-Y recorder (Siemens) to detect the output signal.

The PTI (Photon Technology International) lifetime instrument was used to measure the fluorescence lifetime for some of the prepared samples. This instrument includes: nanosecond pulsed LED excitation sources in different ranges from 300 nm to 700 nm, and fast PMT in the range (185-900 nm) as a detector.

III. RESULTS AND DISCUSSION

The study of absorption spectra is the first step for describing the excited electronic states of molecules as well as much information about to $S_0 \rightarrow S_{vn}$ excitation transitions of the molecules under study. Anthracene molecule has absorption spectrum rang between $\sim 200\text{-}390$ nm, of $S_0 \rightarrow S_{vn}$. Figure (1,a) shows the absorption spectra of anthracene solute in heptane solvent at room temperature and 77K. Figure (1,b) also, shows the absorption spectra of benzoanthracene solute in nonane solvent at 300K and 77K.

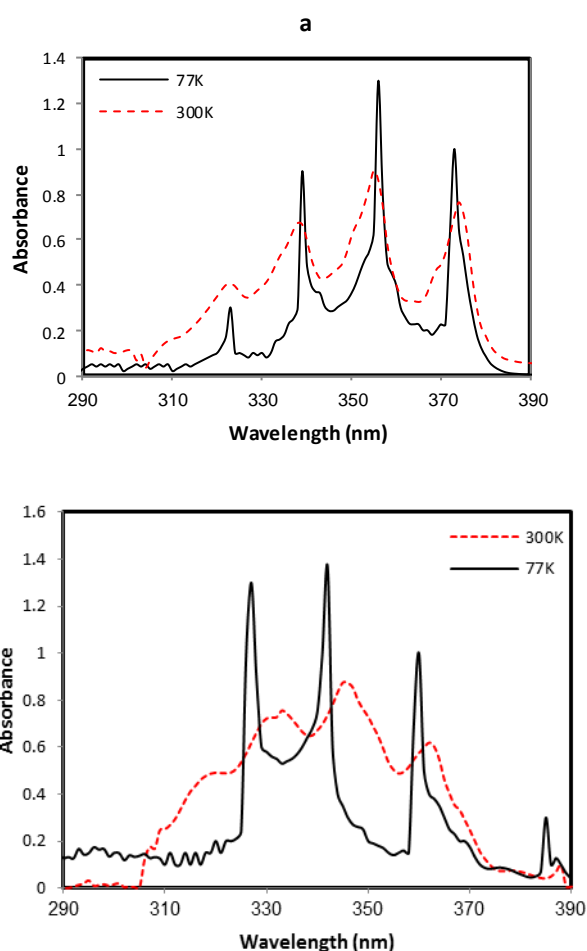


Fig. (1): The Absorption Spectra of ($10^{-4}M$) of (a) Anthracene in heptane (b) Benzoanthracene in nonane at 300K and 77K

According to figure (1,a), four absorption bands are observed at around 321nm, 337nm, 355nm and 374nm and due to the electronic transition ($S_0 \rightarrow S_{vn}$) of the condensed aromatic hydrocarbons. Clar's, [15] distinguished three types of absorption band systems (α , β , γ) for these compounds, and classified them by their intensity, vibrational structure and frequency shifts. In Anthracene molecule the α -band becomes obscured by

the more intense p-band. The spectral line width is sharp at 77K compared with 300K. This give an indication that the absorption transition start from S_{00} state to S_{vn} and thus reducing the other effects such as hot band transitions.

Figure (1,b) the recorded absorptions spectra of Benzoanthracene solutions as a function of solvent type show four bands at around 327nm, 342nm, 360nm and 385nm. The absorption band at about 361nm (0-1 transition) represents p-band according to Clar's classification [15], while α -band appears in the minimum of the absorption spectrum 387nm. It can be seen the clearly enhancement in the spectral line width at 77K. The same behavior is observed as in Anthracene molecules.

The fluorescence measurements of Anthracene and Benzoanthracene solutions, which were recorded using spectrometer fluorescence setup as described in section experimental, were achieved at different temperatures starting from room temperature, passing through freezing point of each solvent and down to liquid nitrogen temperature.

The fluorescence spectra of Anthracene solution in different solvents are illustrated in figure (2, a, b, c and d).

In figure (2), it can be seen three fluorescence bands. The band width at full width half maximum is at about 378nm, 400nm and 427nm. The fluorescence band at 400nm is due to 0-1 transition [11] and show higher intensity compared with the other two bands. Also, the fluorescence spectrum becomes sharp and more narrowing as the temperature down to freezing point of each solvent and 77K. Thus, the enhancement in spectral line width can be clearly observed in the low temperature range. In the same way, the fluorescence spectrum exhibit vibrational structure at frozen solution. Some quasi-line fluorescence spectra display a doublet or multiple structure, thus the spectra consist of two or more series of lines. Shpol'skii proposed that this multiple structure arises from local differences in this field in which the fluorescent solute molecules are situated [16]. This structure is normally broader and more diffuse at 223K and 300K. The optimum conditions for the appearance of quasi-linear spectra of linear molecule are obtained when the molecular length of the solvent and the solute molecule are matched. The best result of the vibrational structure of fluorescence spectra observed in Heptane solvent whose linear molecular sizes 10\AA are close to or coincide with the sizes of the Anthracene molecule 10\AA .

The fluorescence spectra of benzoanthracene solute in different solvents are show in figure (3, a, b, c and d).

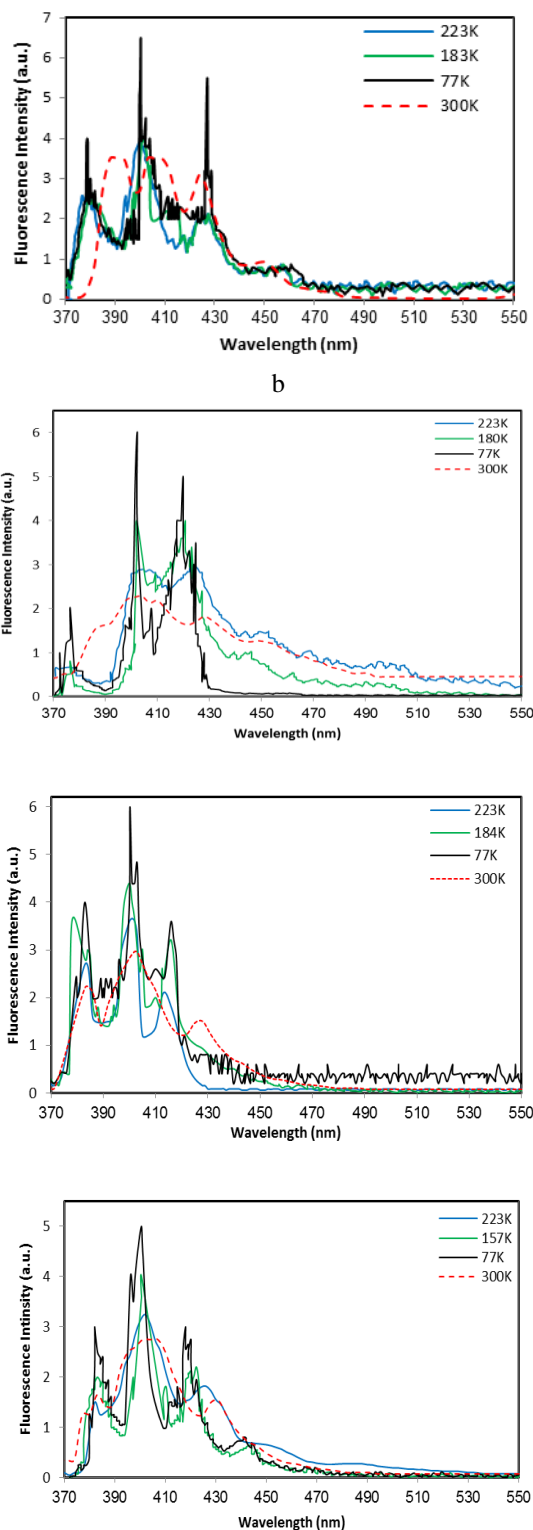
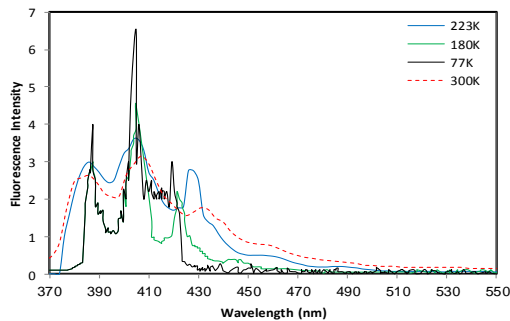
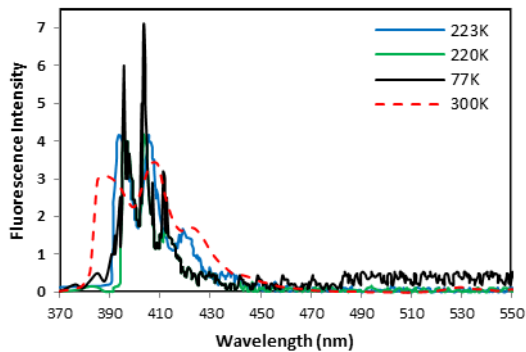
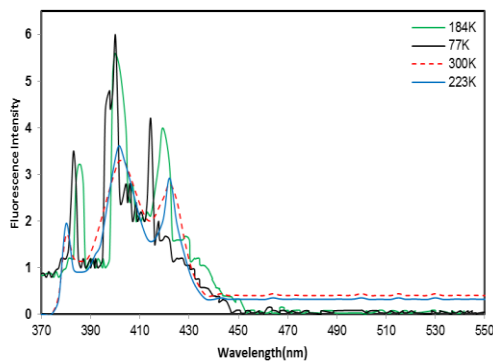


Fig.(2): The Fluorescence Spectra of (10^{-4} M) of Anthracene at Different Temperatures in (a) Heptane (b) Hexane (c) Isopropanol and (d) Ethanol



c



d

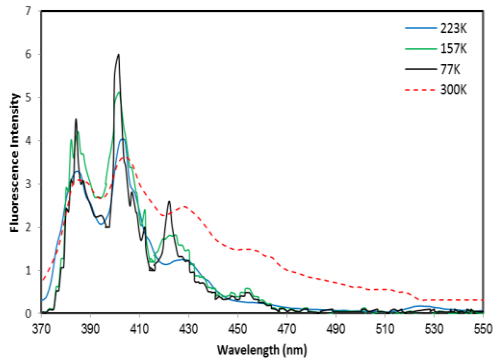


Fig.(3): The Fluorescence Spectra of 10^{-4} M of Benzoanthracene at Different Temperatures in (a) Nonane (b) Hexane (c) Isopropanol and (d) Ethanol

In figure (3), it can be seen three fluorescence bands is at about 395nm, 403nm and 409nm. The fluorescence band at 403nm is due to 0-1 transition and show higher intensity compared with the other two bands [11]. The molecular spectra exhibit vibrational structure at freezing point of each solvent and 77K, so that the spectra consist of two or more series of lines. Shpol'skii proposed that this multiple structure arises from local differences in this field in which the fluorescent solute molecules are situated [16]. One can observe the highly-resolved fine structure with Nonane solvent at freezing point (220K) and 77K may be attributed to this solvent whose linear molecular size (13.7\AA) approaches the sizes of the benzoanthracene molecule (12.8\AA). The spectral line widths are narrowing at frozen solutions, due to the minimal solvent-solute interaction. The best result of Benzoanthracene solutions observed at 77K, because of reducing the solvent-solute interaction.

Figure (4a, b) describe the variation of both full width at half maximum (FWHM) and peak emission cross-section (σ_p) with solvent polarity for Anthracene solutions and figure (4,c and d) show the temperature as a function of FWHM and σ_p at different solvents.

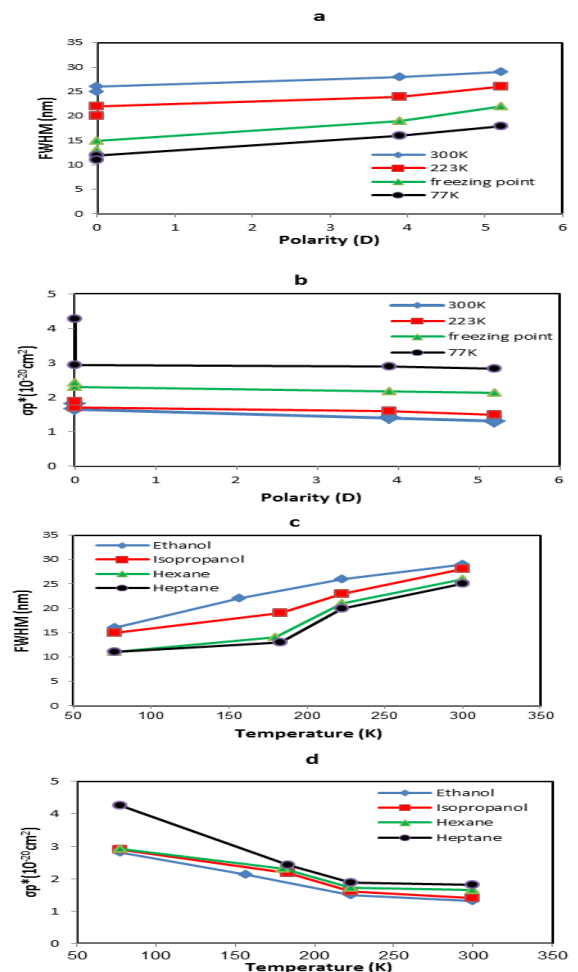


Fig.(4) Dependence of (a) FWHM and (b) σ_p for 0-1 transition of anthracene on the polarity of solvents at

These figures, it can be observed clearly increasing FWHM with increase of solvent polarity and temperature, while the peak emission cross-section decreasing with increase of solvent polarity and temperature.

Figure (5a, b) for Benzoanthracene solutions show the solvent polarity as a function of FWHM and σ_p at different temperatures and figure (5,c and d) show the variation of temperature with FWHM and σ_p at different solvents.

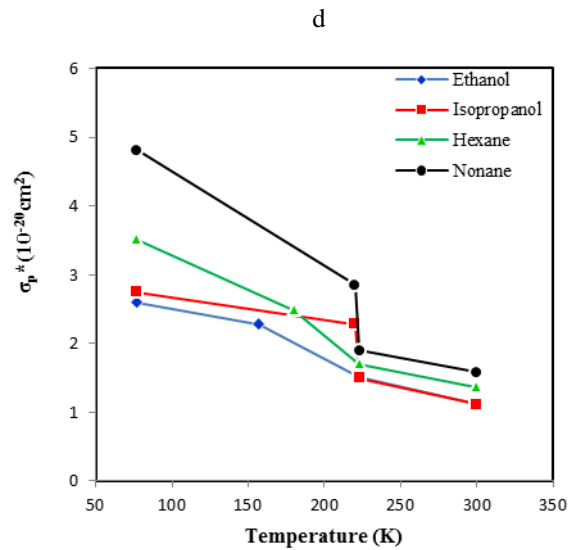
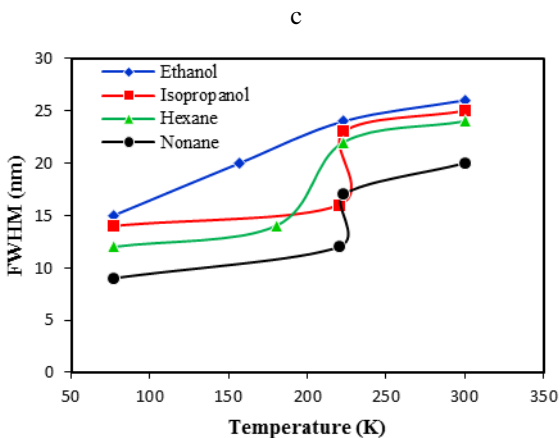
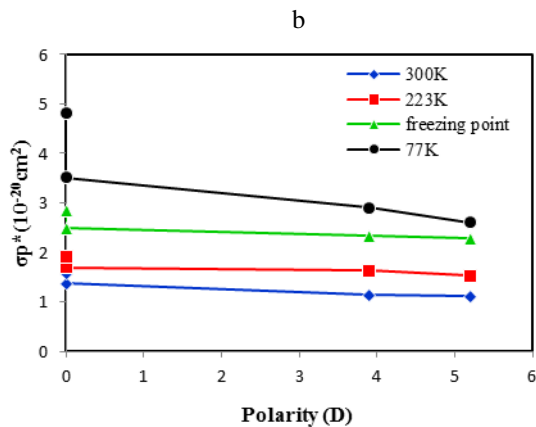
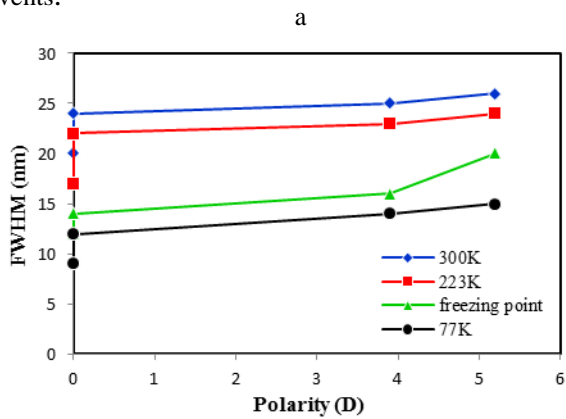
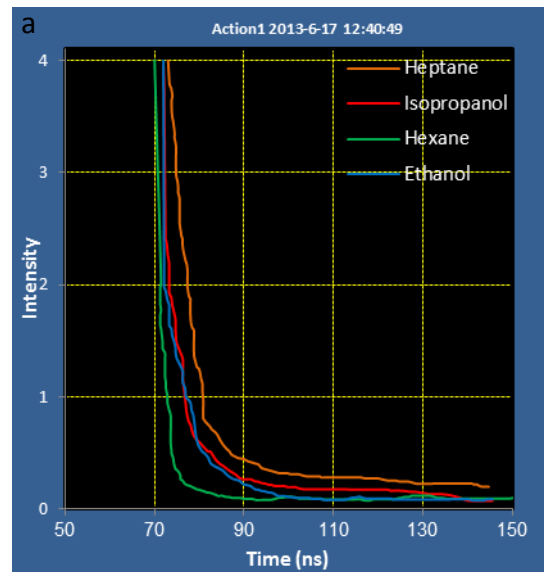


Fig.(5) Dependence of (a) FWHM and (b) σ_p for 0-1 transition of benzoanthracene on the polarity of solvents at different temperatures and (c) FWHM and (d) σ_p on the Temperature for different solvents

The results indicate that the FWHM increasing with increase of solvent polarity and temperature, while the peak emission cross-section decreasing with increase of solvent polarity and temperature. May be attributed to the effect of low temperatures, when the solute molecules are semi-isolated about molecules solvent. Therefore, the behavior makes of these molecules as in gas phase [3].

The fluorescence decay of Anthracene and Benzoanthracene solutions in different solvents is show in figure (6, a, b).



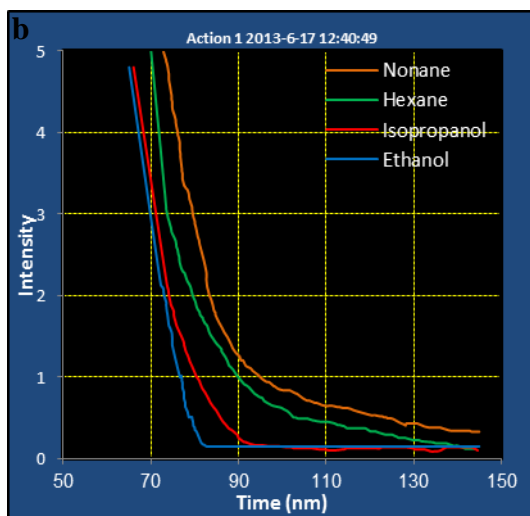


Fig.(6): Fluorescence decay of the (a) Anthracene (b) Benzoanthracene solution in different solvents at 300K

The results indicate that the fluorescence decay of these molecules indicates that no considerable change occurs in the fluorescence decay shape by substitution. This indicates that there is no specific chemical effect of the solvents at 300K.

IV. CONCLUSIONS

Spectroscopic study of Anthracene and Benzoanthracene molecules has been investigated as a function of both solvent polarity and temperature. The room temperature absorption spectra of these molecules are similar in different solvent, and indicate no specific solvent chemical effect on the solute electronic state. On the other side, the low temperature absorption spectra show small blue shift with nonpolar solvent due to the specific solvent- solute interactions is minimal.

The Shpol'skii spectra of these molecules show clearly enhancement, in which sharp and highly- resolved fine structure spectra have been observed at 77K. Also the matching in the molecular size between solvent and solute molecules have play a key rule for obtaining high resolution spectra with vibrational structure at low temperatures. Thus, heptane and nonane solvents for Anthracene and Benzoanthracene solutions, respectively, give the best results compared with other solvents.

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