A study of the solvent effect on the low temperature spectra of benzoanthracene molecules

Abbas J. Al-Watttar, Baha T. Chiad, Firas J. Kadhim, Asmaa N. Ahmed

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

E-mail: anr.asoo@yahoo.com

Abstract

Low temperature spectroscopy of benzoanthracene solutions at fixed molar concentration has been studied. The temperature range has been taken at room temperature down to liquid nitrogen temperature (77K). Polar and nonpolar solvents have been used to study the solvent effect on the absorption and fluorescence spectra of solute molecules. Some of the spectroscopic parameters have been determined as functions of solvent polarity and temperature. The results indicate that the band width FWHM increases with increasing the solvent polarity and temperature, while the peak emission cross section decreases with increasing of solvent polarity and decreases with increasing the temperatures. Clear vibrational structure spectra of benzoanthracene molecules have been observed in Nonane and Hexane solvents at 77K.

Key words

Benzoanthracene molecule, low-temperature spectroscopy, solvent effect.

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دراسة تاثير المذيب على اطياف درجات الحرارة الواطئة لجزيئات البنزوانثراسين

عباس جاسم الوتار, بهاء طعمة جياد, فراس جواد كاظم, اسماء ناجي احمد

قسم الفيزياء, كلية العلوم, جامعة بغداد, بغداد, العراق

الخلاصة

في العمل الحالي تم دراسة مطيافية درجات الحرارة الواطئة لجزيئة البنزوانثراسين المحضرة بالطور السائل عند تركيز مولاري ثابت. مديات درجات الحرارة بدات من درجة حرارة الغرفة وصولا الى درجة سائل النتروجين (77كلفن). تم استخدام عدة مذيبات قطبية وغير قطبية لتحضيرمحاليل جزيئة البنزوانثراسين لغرض دراسة تاثير المذيب على اطياف الامتصاص والفلورة لهذه الجزيئة. تم تحديد بعض المعلمات الطيفية من الاطياف المستحصلة كدالة لكل من قطبية المذيب ودرجة الحرارة. اظهرت النتائج ان عرض الحزمة عند منتصف القمة يزداد بزيادة قطبية المذيب ودرجة الحرارة بينما يقل المقطع العرضي لقمة الانبعاث مع زيادة قطبية المذيب ودرجة الحرارة. التركيب الدقيق لاطياف لجزيئات البنزوانثراسين ظهر بوضوح مع مذيب النونان والهيكسان عند 77كلفن.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are usually defined as a group of chemicals consisting of two or more benzene rings (C_6H_6) [1]. Benzoanthracene ($C_{12}H_{18}$) is a solid, planer, consisting of four fused benzene rings and form yellow substance [2,3]. The molecular spectra of aromatic compounds can be studied in solid, liquid or vapour states. They may be also studied under other suitable conditions in solid solutions or in a matrix of noble gas [4]. 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 [5]. The solvent shift arises because the excited state of the guest (solute) interacts with the solvent to a different extend than does the ground state of the guest [6]. 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 vapour 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 [7].

Low temperature spectroscopy is a technique used to obtain ideal spectra for the matter of molecular structure in the condensed phase as in gas phase. Thus the resulted spectroscopic parameters will be determined more accurately. In addition to, the vibrational structure, the electronic transitions can be studied [8].

Shpol'skii Method: low-temperature phenomena were first described by Eduard Shpol'skii. Academy of Sciences and Soviet Physics Uspekhi [9,10]. The Shpol’skii method refers to a dilute solution of a guest molecule, polycyclic aromatic hydrocarbon (PAH), in a solvent host (usually an n-alkane) where the solvent freezes to 77K or below into an ordered polycrystalline matrix. If the dimensions of the analyte and solvent match up well enough, PAH occupy a small number of crystallographic sites (ideally just one) in the host matrix. An alternative approach to the observation of vibrational fine structure of fluorescence spectra in solution was initiated by Shpol'skii. The fluorescence spectra of many aromatic molecules in solution in a frozen crystalline normal solvent (nonane, hexane,.....etc.) are observed to exhibit, highly resolved fine structure in which the relatively broad vibrational bands of fluid solution spectra and are split into a series of lines wide in favorable cases. The optimum conditions for appearance of the quasi-linear spectra of the linear or non-linear molecules are obtained when the length of the long axes of the solvent molecule and the solute molecule are matched [7]. Shpol’skii believed that, to obtain information on the individual properties of polyatomic organic compounds, one has to only “simplify” the luminescence spectra of these molecules and to create conditions under which commonly diffuse spectra of complex molecules would become discrete and comparable with the discrete atomic spectra in the gaseous phase, or, at least, with Raman spectra [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. 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 [12,13]. In the present study, the spectra of benzoanthracene molecules will study as a function of solvent polarity and temperature. Shpol'skii method will used to study the low temperature spectra.

Experimental

1. Samples preparation

The solution of benzoanthracene molecules was prepared by certain weight into a specific solvent at constant concentration (1×10^{-4} M). Nonane, Hexane, Ethanol and Isopropanol were used as solvents and were selected according to molecular size and polarity.

2. Sample cell

The sample cell layout is shown in Fig.1, in this method 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.

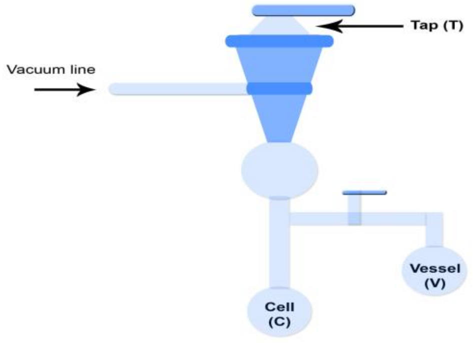

Fig.1: Sample cell layout.

3. Sample holder (cryostat)

In the present investigation, the low temperature spectroscopy down to 77K was achieved using suitable cryostat as shown in Fig.2. The cryostat was made of aluminum and consists of thermocouple of NiAl, NiCr 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.

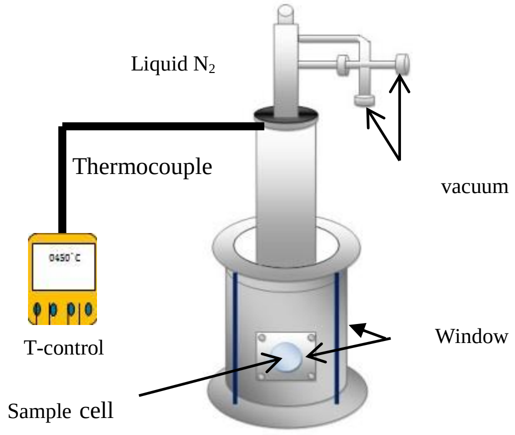

Fig.2: The cryostat used in the present work.

4. Spectroscopic measurements

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 spectrofluormeter setup as show in Fig.3.

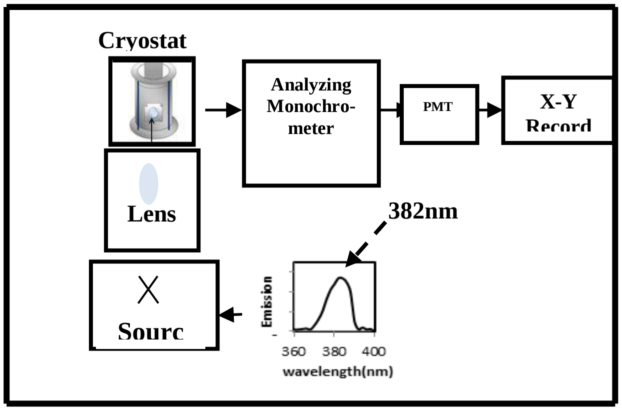

Fig. 3: Schematic diagram of the components of fluorescence setup.

The used spectrofluormeter contains GaN UV-LED light source (λ_{ex}=382nm), connected to a DC power supply (PS-1502DD). The resulting fluorescence spectrum was analyzed using a Jarrell Ash monochrometer (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.

Results and discussion

Absorption spectra

The study of absorption spectra is the first step for describing the excited electronic states of molecules as well as much information about to $S_o \rightarrow S_{vn}$ excitation transitions of the molecules under study. Benzoanthracene molecule has absorption spectrum range between ~ 26600 - 40,000 cm^{-1} (200-390 nm), of $S_o \rightarrow S_{vn}$ transition.

Fig.4 shows the absorption spectra of benzoanthracene solute in different solvents (ethanol, isopropanol, hexane and nonane) at room temperature.

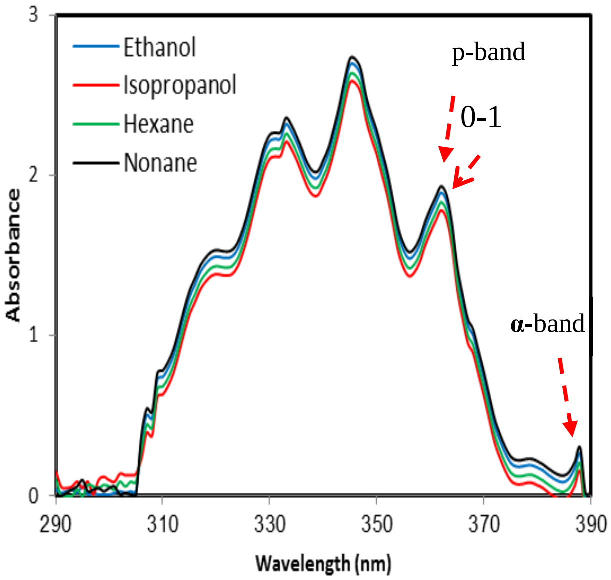

Fig.4: The absorption spectra of the benzoanthracene solute in different solvents at room temperature.

The recorded absorptions spectra of Benzoanthracene solutions as a function of solvent type show four bands at around 333, 345, 361 and 387nm respectively. The absorption band at about 361nm (0-1transition) represents p-band according to Clar's classification [14], while α-band appears in the minimum of the absorption spectrum 387nm. No considerable change can be seen in the absorption spectral shape occurring by substitution. This indicates that there is no specific chemical effect of the solvent on one or both electronic states of the solute.

The absorption spectra of benzoanthracene solute in different solvents at 77K, are shown in Fig.5.

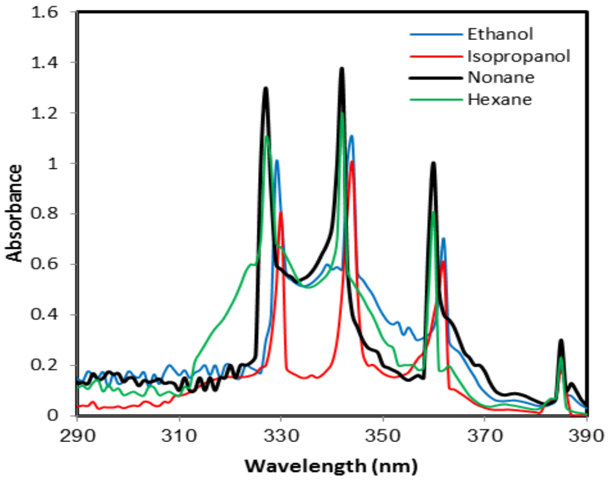

Fig.5: The absorption spectra of (10^{-4}M) of benzoanthracene in different solvents at 77K.

It can be observed four absorption bands at around 327, 342, 360 and 385nm respectively. The spectral line widths are narrower than that of 300K (see Fig. 4). 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. Also, it can be seen blue shift with nonpolar solvent due to the minimum solvent-solute interactions.

The spectroscopic parameters which can be determined from the absorption spectra (molar extinction coefficient $\varepsilon_{(v)}$ and oscillator strength $f_{(v)}$ are listed in table one and which determine by the Eq. (1) [7]:

$$f = \frac{4.39\times10^{-9}}{n} \int \varepsilon_{(\bar{v})}\, d\bar{v} \qquad (1)$$

Here, the integral is over the appropriate electronic or vibronic absorption band; n is refractive index of the solvent.

Table 1: Some of spectroscopic parameters as a function of solvent polarity of benzoanthracene at room temperature and 77K.

Solvent	***Temperature (K)***	***λ_{abs} (nm)***	***ε_v ($mol^{-1} l\ cm^{-1}$)***	***f(v)***
Ethanol	300	361	1865.3	0.712
Isopropanol		362	1766.9	0.701
Hexane		361	1868.5	0.818
Nonane		362	1934.8	0.913
Ethanol	77	357	7000	0.303
Isopropanol		357	6000	0.285
Hexane		360	8000	0.477
Nonane		362	10000	0.509

In Table 1, it can be seen that nonpolar solvent such as nonane and hexane, result in high values of extinction coefficient (ε_v) and thus high values of oscillator strength (f_v). Maximum values of ε_v and $f_{(v)}$ can be observed for nonane solvent with benzoanthracene solute.

Fluorescence spectra

The fluorescence spectra of benzoanthracene solute in different solvents and at different temperatures are illustrated in Figs.6, 7, 8, and 9. These spectra are recorded using 382nm excitation source.

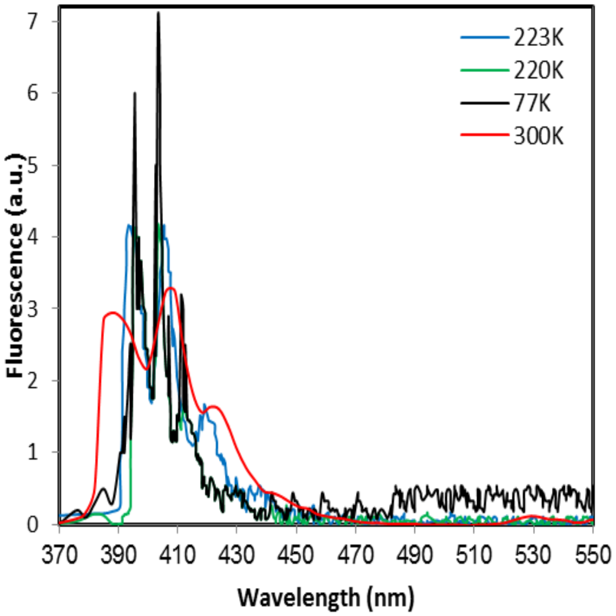

Fig.6: The fluorescence spectra of benzoanthracene in nonane at different temperatures.

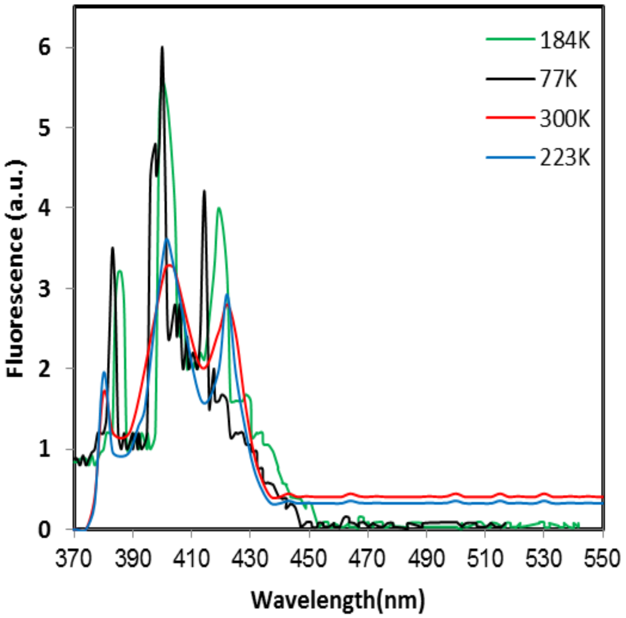

Fig.8: The fluorescence spectra of benzoanthracene in isopropanol at different temperatures.

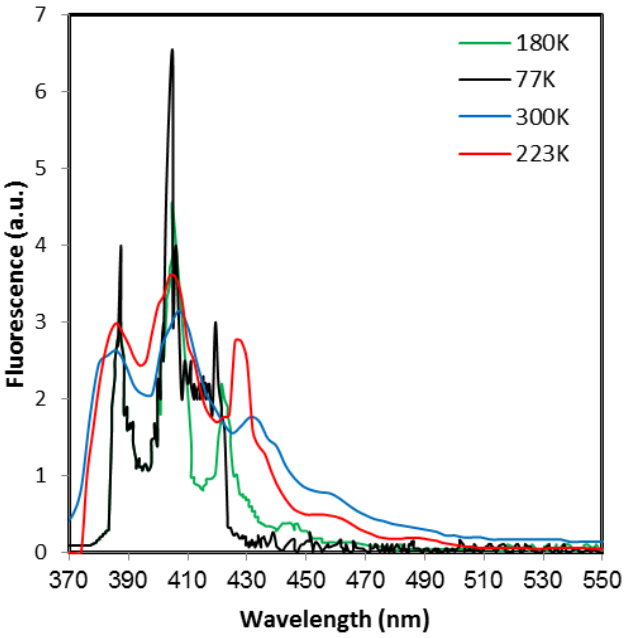

Fig.7: The fluorescence spectra of benzoanthracene in hexane at different temperatures.

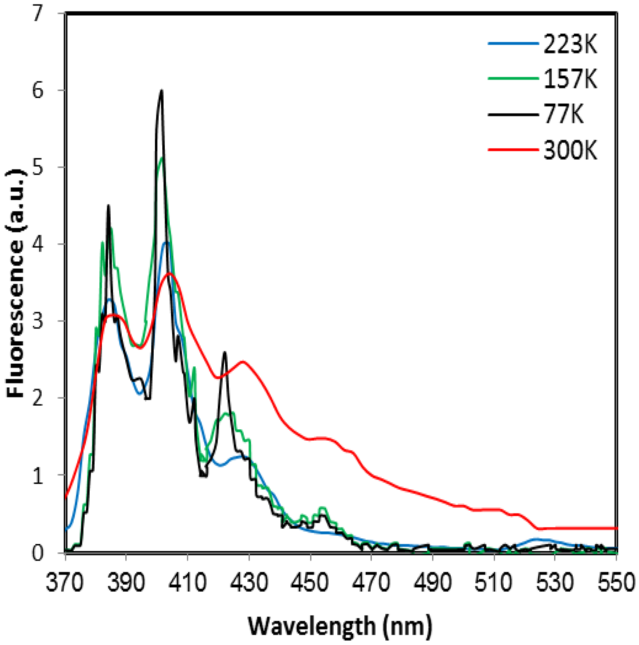

Fig.9: The fluorescence spectra of benzoanthracene in ethanol at different temperatures.

In these figures, it can be seen three fluorescence bands. The band maximum is at about 390, 406 and 421nm respectively. The molecular spectra exhibit vibrational structure at freezing point of 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[13]. 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 (12.8A˚) approaches the sizes of the benzoanthracene molecule (13.7A˚). The spectral bands widths are narrowing at frozen solutions, due to the minimal solvent-solute interaction between molecule solvent and molecule solute at low temperatures. The best result of these solutions observed at 77K, because of reducing the solvent-solute interaction.

Fig.10a and b, for benzoanthracene solutions show the variation of polarity of solvent with full width at half maximum (FWHM) and peak emission cross-section (σ_p) at different temperatures. It can be observed that the FWHM increases with increase of solvent polarity. While the peak emission cross section decreases with increase of solvent polarity at different temperatures.

Fig.11 a and b, show the FWHM and peak emission cross-section (σ_p) as a function of temperature, for benzoanthracene solution. The FWHM increases with increase of temperature, while the peak emission cross-section decreases with increase of temperature.

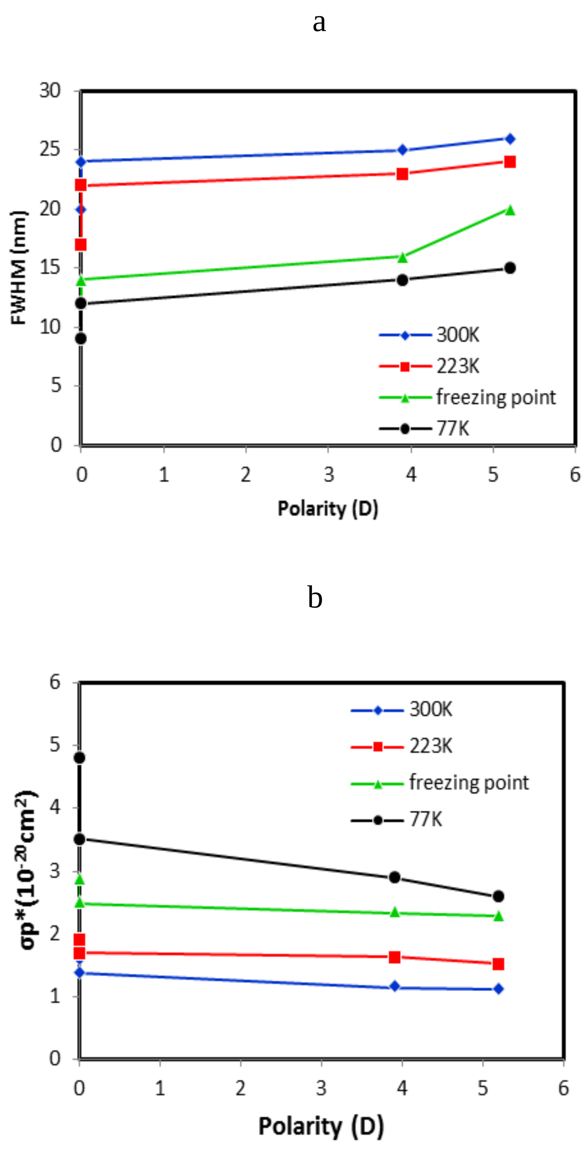

Fig.10: Dependence of (a)FWHM and (b)σ_p for (0-1) transition of benzoanthracene solution on the polarity of solvent at different temperatures.

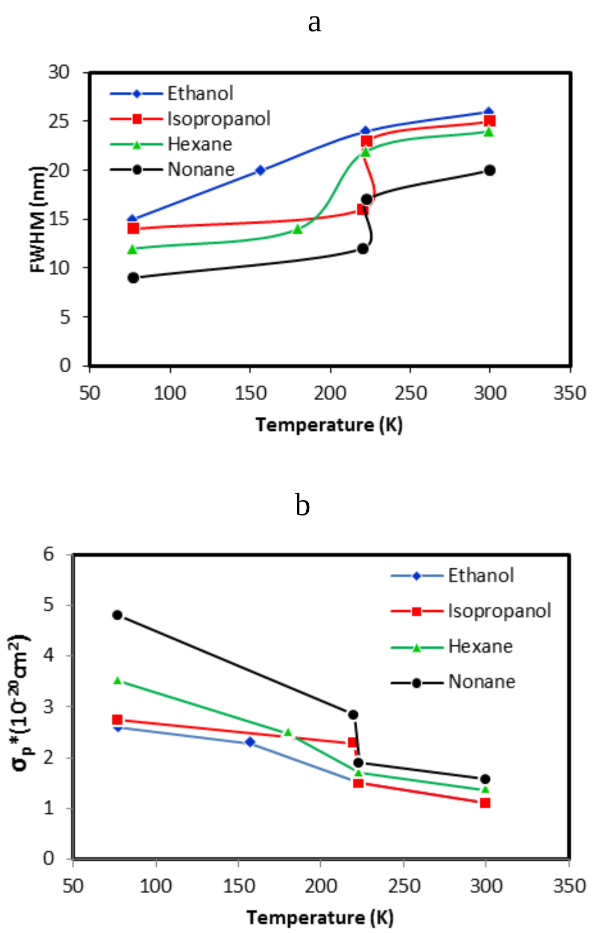

Fig.11: Temperature dependence of (a) FWHM and (b) σ_p of 0-1 transition for benzoanthracene solution at different solvents.

Conclusions

At low temperature spectroscopy, clearly enhancement can be observed for the spectra of benzoanthracene molecules. Also, the vibration fine structure can be observed at 77K. In different temperatures reducing the solvent-solute interaction between solvent molecule and solute molecules lead to obtain ideal spectra. Thus the low temperature spectroscopy of nonane as solvent for benzoanthracene molecules gives the best results, i.e. vibration structure spectra, minimum band width at FWHM and high peak emission cross-section.

Table 2: The spectroscopic parameters for 0-1 transition of benzoanthracene solutions.

Solvent	Ethanol	Isopropanol	Hexane	Nonane
Molecular size (A˚) [3,7]	4.5	5.5	8.8	12.8
Polarity (D) [15]	5.2	3.9	0	0
Temperature (K)	300	300	300	300
	223	223	223	223
	157	184	180	220
	77	77	77	77
λ_{abs} (nm)	361	362	361	362
	357	357	360	362
λ_p (nm)	404	401	406	406
	402	401	404	404
	401	401	404	403
	401	400	404	403
FWHM (nm)	26	25	24	20
	24	23	22	17
	20	16	14	12
	15	14	12	9
$\sigma_p * (10^{-20}$ cm^2)	1.11	1.14	1.37	1.58
	1.52	1.63	1.70	1.90
	2.28	2.33	2.49	2.85
	2.60	2.90	3.51	4.81
τ_{FM} (ns)	19	20	18	16

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