FLUORESCENCE LIFETIME MEASUREMENT OF C_6H_6 AND C_6D_6

A.M. Taleb, N.A.L. Talfah*, K.H. AL-Mossawi**

Dept. of Physics , College of Science , University of Baghdad, Iraq
* Institute of laser and plasma for postgraduate studies, University of Baghdad, Iraq.
** Dept. of Physics , College of Science , AL- Mostansyria University, Baghdad, Iraq

الخلاصـــة: أجريت قياسات لطيف امتصاص وزمن العمر لجزيئاتي C_6H_6 و C_6D_6 في الحالة الصلبة النقية وفي متجمد شبيكات Ar, N_2 CO, CO_2 و CH4 وقـد أجـريت هذه القياسات في درجات حرارة واطئة تراوحت بين 12-50 كلفن . استخدمت طريقة متطورة لملائمـة المربع الأصغر لإزالة الالتفاف لغرض حساب زمن عمر الفائق وبنسبة خطأ تقل عن 1%. بينت النتائج أن استخدام تقانة عزل الشبيكة تقدم ظرفا فريدا من نوعه لتقليل اضطراب النظم الذرية أو الجزيئيه مما يسهل تحليل أطيافها.

Abstract:

Absorption and lifetime measurements were made for C_6H_6, and C_6D_6 molecules in pure solid phase and in solid matrices of Ar, N_2, CO , and CO_2. All measurement are made at low temperatures ranging between 12-50 K. A modified least square fitting deconvolution was utilized to measure the fluorescence lifetime with an error less than 1%. The results show that the use of matrix isolation technique offer a unique environment that minimize the perturbation of the molecular or atomic system and hence facilitate spectral analysis .

Keywords: Fluorescence lifetime, Matrix isolation technique, Absorption spectra, Single photon Counting.

Introduction

Measurements of fluorescence and phosphorescence lifetimes of molecular systems may considered as an essential steps for investigating the radiative and irradiative channels of releasing the energy of excited states . However only limited data on fluorescence lifetime of organic molecules at cryogenic temperature are yet available since experimental work is complicated by scattering and other experimental difficulties. Further more, a fruitful results obtained only when such a study is made for isolated molecules when the interaction between molecules and hence the perturbation is minimized . In a short communication Gibson et al.[l] were able to measure the fluorescence lifetime of benzenes CsH, A-CeDs in variety of gas matrices at 12K. Their work shows that the fluorescence lifetime of C_6H_6 ranging between 100~45 ns depending on the kind of matrix used. Although the aim of this work is to measure the fluorescence lifetime of matrix isolated C_6H_6 and C_6D_6 molecules, a preliminary work was undertaken to measure the absorption spectrum of those molecules under the same condition. The purpose is to check on the purity of material under study and to choose a proper sample to matrix (S/ M) molar ratio where optimum molecular isolation is achieved. The study of pure samples, for comparison, shows the maximum effect influenced by the molecular interaction and approve the role played by the matrix isolation technique. A deconvolution program (LTD) was developed to analyze the data in the range of Pico seconds.

Experimental Work

Both matrix isolated (M.I) technique and single photon counting (SPC) technique were used to achieve the present work.

The M.I. technique:

In the matrix isolated studies, the molecules of interest are mixed with the host gas in order to keep them fully surrounded. However, the concentration of the guest molecules must be kept small to reduce scattering and other imperfection effects of relatively thick samples. The flow rate of gaseous mixture into the cold substrate is an another important parameter affecting the recorded results. A slow deposition rates causes amorphous solids and crystal imperfections, thus yield multiple sites [2], while fast flow rates lead to considerable warming of the matrix gas, particularly near the surface. This results in localized annealing and diffusion [3]. In the present work deposition of 100 mole/min is used as was demonstrated by the sharpness of the absorption bands. Fig (1) shows a schematic diagram of the absorption measurement layout. The sample chamber is evacuated to about 10^{-7} m bar using turbo-molecular pump. The cold head of a closed helium cycle (model R210) supplied from Leybold – Heraeus is placed inside the vacuum chamber. The sample mixing system is also connected to the vacuum chamber via a capillary tube to inject the gas mixture on a Lif window fixed at the bottom of the head. The exciting monochromator is a 0.5 m Jobin Yavon ASM 50 vacuum monochromator with concave grating of 1200 L/mm and is blazed for maximum efficiency at 200 nm. The discharge lamp is a GCA-Mc Pherson model 630-Hintergger used to produce a continuous background of hydrogen gas from 200-280 nm.

Gas matrices are of high purity supplied from Air products company, C_6H_6 and C_6D_6 are of spectroscopy grade supplied from seelze-Hannover and Uvasol respectively.

The S.P.C. Technique : The main parts of the single photon counting system (fig. (2)) are :

i) The gated flash lamp, which is a fully demountable unit with a hydrogen thyratron (English Electronic no. FX2530 /6777). The instrumental profile of the flash lamp at A = 258nm gives 1.2 ns for the FWHM and Ins for the rise time and 2.5 ns for the lifetime of the flash lamp.
ii) The analyzing monochromator, which is an Edinburgh inst. model 121 S15 M with 1200 L/mm grating blazed for maximum efficiency at 300 nm.
iii) The electronic subsystems, which enable the measure of decay times using the signals from the synchronization (start) and main (stop) photomultipliers. The out put pulses from the detector are shaped and timed using a discriminator. The pulses are correlated using time to amplitude convector (TAC 467). The out put of the TAC is analyzed and stored using an Orland 5400 multi-channel analyzer.

Results and Discussion

I- The absorption spectra:

The first excited states of the electronic absorption spectra of pure solid C_6H_6 and C_6D_6 and in CO_2 matrix are shown in fig (3). The first week line on the low energy side of the pure solid

spectrum (fig 3- c,d) is assigned to the 0-0 transition induced by the crystal field [4]. The dissapearance of this line in the matrix spectrum (fig 3- a,b) indicates clearly the isolation of the guest molecules (C_6H_6 and C_6D_6) in the host environment. Such isolation is necessary for the following measurements. II- Life time measurements The fluorescence decay curves were recorded for C_6H_6 and C_6D_6 , in CO_2 , Ar, N_2 , CH_4 , and CO matrices and for pure solid excited at 258 nm. Figs(4-7) show samples of these curves where the x-axis represent the channel number and the y-axis represents the emission intensity.

Due to the long tail of the H_2 flash lamp profile , a deconvolution method should be used for analyzing the data [5]. Analysis of all fluorescence lifetime data in the present work, was achieved using LTD program [6]. The results were typed on the upper right side of each figure. Values of the fluorescence lifetime for isolated benzene and deuterated benzene in CO matrix at 12 K for example were 67.9, 81.9 ns respectively.

In order to show the importance of employing the deconvolution method even for long lifetimes a comparison of these results with that calculated without using deconvolution (i.e. without considering the lamp profile effect) at the same range of analysis were carried out. Values of 165.15 and 256.36 ns for benzene and deuterated benzene in CO matrix respectively were obtained. These values are inconsistent with the previous results [7,8].

Figures (4-7) show that some scattered light contamination [6] and instrumental response [9] are observable at the maximum of the decay curves and these effects can be ignored because they are out of the fitting region.

A best fitting was obtained after 10-12 channel in the right side of the peak of the decay curves. The value of χ^2_ν was considered as a good indicator for the data analysis. χ^2_ν for all fluorescence lifetime was measured and analyzed by LTD program in the range of 0.8 -1.2 which is the recommended range [10,11].

The LTD program were designed to calculate the fluorescence lifetime when the value of χ^2_ν becomes fixed after many iterations.

Table (1) summarizes a comparison of fluorescence lifetime for gas phase and pure solid of C_6H_6 and C_6D_6 molecules with that of the same molecules trapped in different gas matrices at the same temperature.

Comparing the fluorescence lifetime of C_6H_6 and C_6D_6 in pure solid phase with that in the gas matrices at the same temperature, it is clear that $(\tau_f)_{solid} < (\tau_f)_{matrix}$. This may be attributed to the high perturbation caused by the neighboring molecules in the pure solid with respect to the isolated molecules by the matrix surrounding. The matrix isolation technique, hence, provides a tool to reduce such perturbations leading to an ideal environment to study the molecular structure.

Table (1) FluoresceLifetime (τ_f, ns) of C_6H_6 and C_6D_6 in deferent gas matrices (S/M = 1: 200), and pure solid at 12K.Gas phase values are listed for comparison.

Host matrix	τ_f (ns)	
	C_6H_6	C_6D_6
CO_2	89.3 ±0.39	147.5 ±1.00
Ar	76.9±0.15	116.3 ±0.26
N_2	71.1±0.21	098.2 ±0.63
CH_4	68.5 ±0.27	089.7 ±0.59
CO	67.9 ±0.23	081.9±0.10
pure solid	55.8 ±0.25	066.3 ±0.37
gas phase	100 [12]	200 [is]

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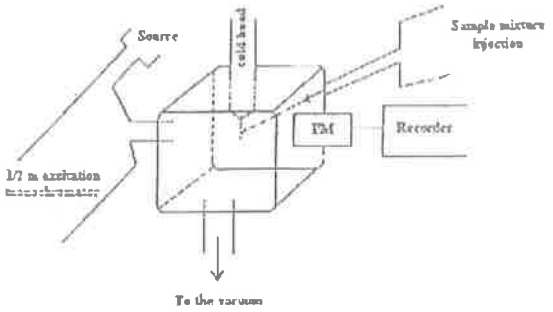

Fig (1) : Schematic diagram for absorption system

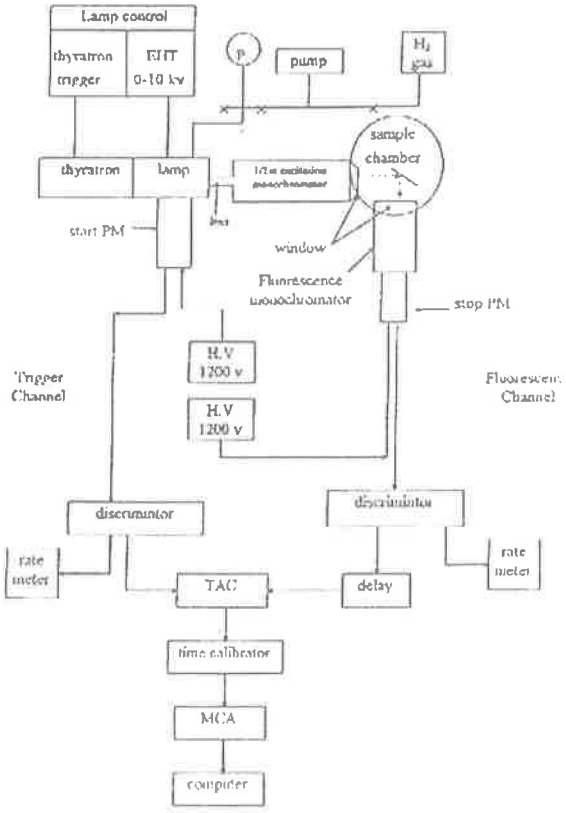

Fig (2) : Block diagram of the single photon counting apparatus

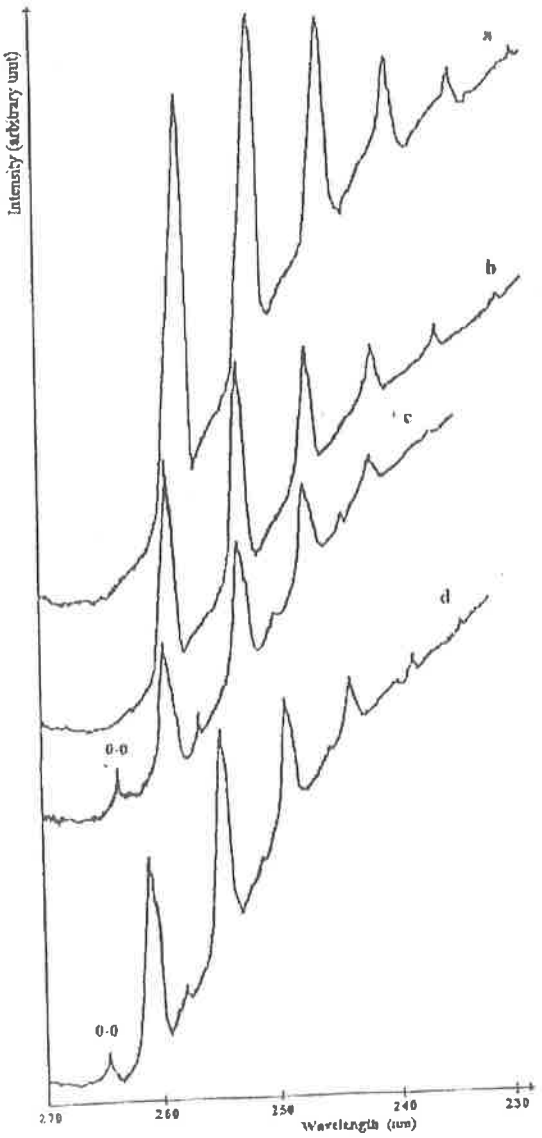

Fig (3): Absorption spectra of 20 μm film of (a) C_6D_6 , (b) C_6H_6 ; isolated in CO_2 matrix at 12 K, (c) and (d) for similar but pure solid

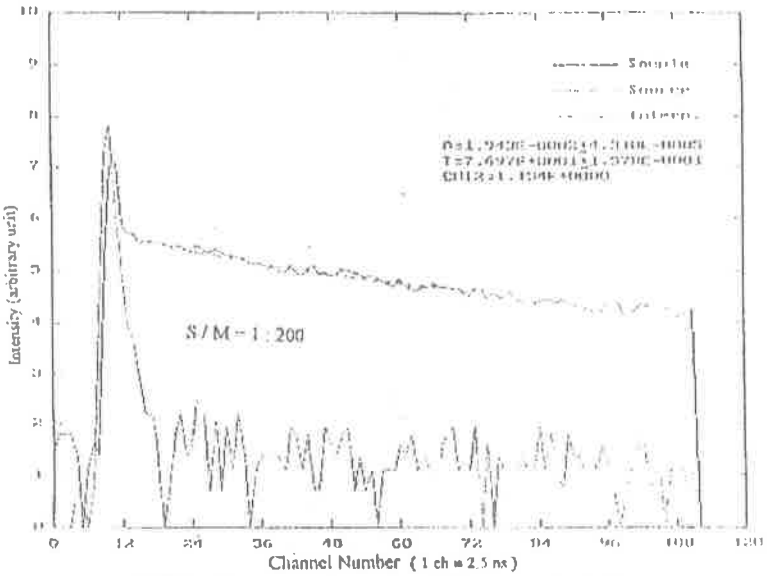

Fig (4) : Fluorescence decay curve of C_6H_6 in Ar matrix at 12 K .

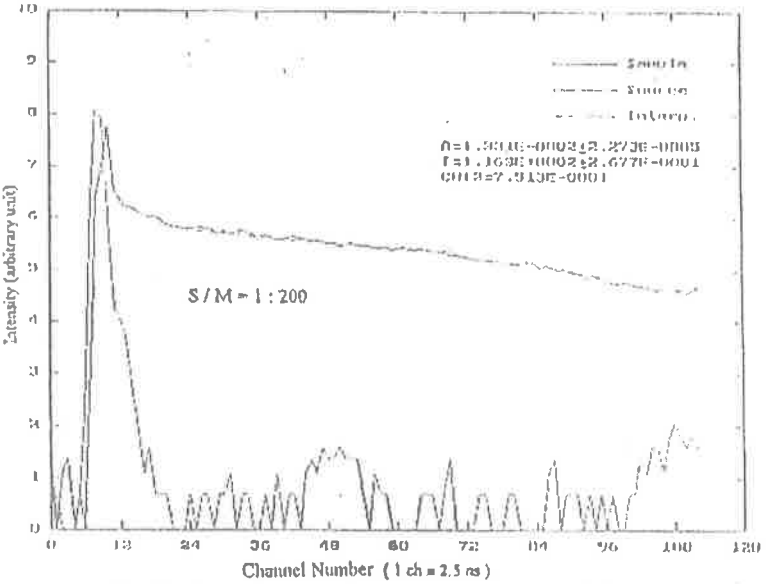

Fig (5) : Fluorescence decay curve of C_6D_6 in Ar matrix at 12 K .

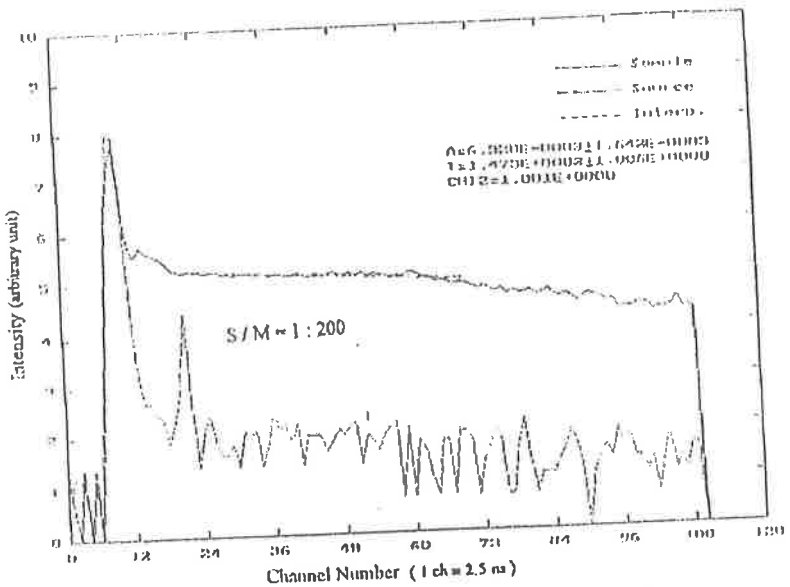

Fig (6) : Fluorescence decay curve of C_6D_6 in CO_2 matrix at 12 K .

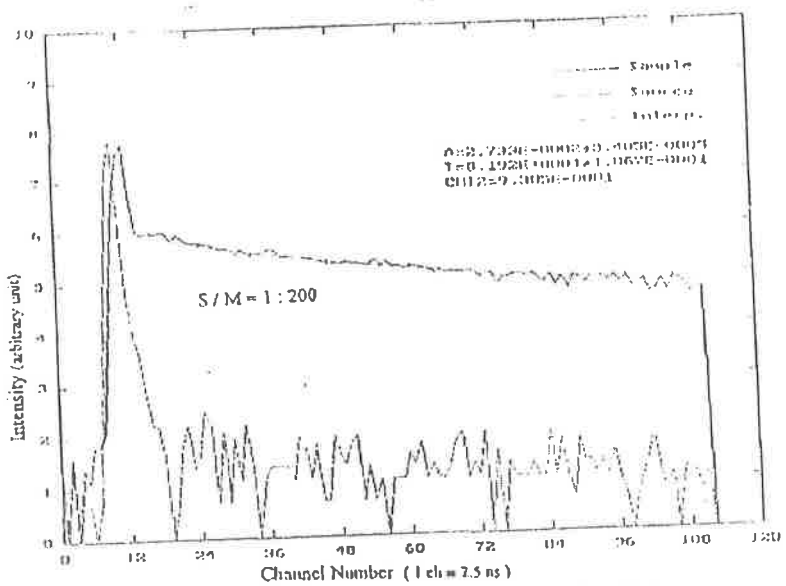

Fig (7) : Fluorescence decay curve of C_6D_6 in CO matrix at 12 K .