



## PHOTOPHYSICAL PARAMETERS OF BENZENE IN THE SOLID, LIQUID AND VAPOUR PHASES

*Experimental photophysical parameters of benzene molecule, contained in solid, liquid and gaseous samples, are reviewed. An analysis, of the values obtained for radiative and non-radiative rate constants of the de-excitation of the first singlet excited state, is established in terms of temperature and environment alterations.*

### 1 — INTRODUCTION

A considerable amount of literature has been published on the behaviour of excited states of benzene molecule in its solid, liquid and vapour phases [1-5].

The major interest in the investigation of the properties of the excited state of benzene arises from its importance as a general model for studies of  $\pi$ ,  $\pi^*$  excited states of more complex systems.

The lowest singlet excited state,  $^1B_{2u}$ , corresponds to the symmetrically forbidden band situated in the 260 nm region as a result of the transition  $^1A_{1g} \rightarrow ^1B_{2u}$ . The lowest triplet state is assigned to  $^3B_{1u}$ , appearing at about 3.95 eV above the ground-state and is responsible for the observed phosphorescence in highly viscous matrices [6,7].

The  $^3B_{1u}$  state can transfer its energy to *cis*-butene-2 molecule from which it is possible to measure the triplet yields of benzene in fluid media, using Cundall's technique [8-11]. The results obtained with both this technique and the method of CUNDALL-PEREIRA [12] have allowed a detailed knowledge of various photophysical parameters involved in the de-excitation of benzene and derivatives, under various experimental conditions [2,4].

The photophysics of benzene has stimulated a great deal of research in the last two decades and the subject has been reviewed quite extensively [2-4,6,13]. Nevertheless a clear knowledge of the various radiative and radiationless transitions involved has not yet been achieved [14-16].

In a recent note AL-CHALABI [17] has reported some fluorescence decaytimes in solid benzene, between 278K and 173K, using a single photon counting apparatus. According to this author there is a good correlation between the fluorescence decaytimes and spectral measurements in both vapour and solid phases, which would indicate that the dipole-dipole coupling between benzene and its host is very weak or negligible. This conclusion was based on a comparison established between the fluorescence rate constant,  $k_{FM}$ , and the temperature independent internal quenching rate,  $k_{IM}^0$ , of solid benzene at 77K, and also of benzene in EPA at 77K and of the zeroth-point vibrational level of gaseous benzene at room temperature.

In order to give an overall picture of the problem it is convenient to establish a proper comparison of the photophysical parameters measured for benzene

molecule, in the solid, liquid and vapour phases, at various concentrations and temperatures.

The experimental results of AL-CHALABI [17] were compared to results previously obtained in similar conditions by LUMB and PEREIRA [18], from which new data of  $k_{FM}$  in polycrystalline medium were estimated.

On the other hand it will be shown that further results obtained by the author [19] for dilute benzene in *n*-dodecane between 293K and 473K, are consistent with results reported elsewhere [11].

Furthermore the implications of the so-called  $n^2$  correction, generally accepted in photolumines-

tive processes internal conversion and intersystem crossing, respectively  $E_{IC}$  and  $E_{TM}$ , discussed elsewhere [10].

From results reported in references [17] and [18] it is possible to estimate  $k_{FM}$  as a function of temperature for solid neat benzene which shows a variation from a limiting value of  $3.4 \times 10^6 \text{ s}^{-1}$  below 213K up to  $3.8 \times 10^6 \text{ s}^{-1}$  at 278K. This behaviour is in good agreement with results measured in dilute solutions [1,33].

Studies carried out with benzene solutions as a function of temperature [1,27] have shown that the rate constants  $k_{FM}$ ,  $k_{TM}$  and, in particular,  $k_{IC}$ , increase

Table 1

Fluorescence quantum yields, ( $\phi_{FM}$ ), triplet yields ( $\phi_{TM}$ ), and fluorescence lifetimes, ( $\tau_{FM}$ ), of benzene molecule in different phases

Benzene phase	$\phi_{FM}$	$\phi_{TM}$	$\tau_{FM} \times 10^8 \text{ (s)}$
Low pressure vapour <sup>a)</sup> (Zeroth level)	0.18 <sup>e)</sup>	—	100 <sup>f)</sup>
Moderate/high pressure vapour <sup>a)</sup>	0.18 <sup>g)</sup> 0.19 <sup>h)</sup>	0.71 <sup>g)</sup> 0.85 <sup>i)</sup>	72 <sup>j)</sup> 80 <sup>e)</sup>
Dilute solutions <sup>a)</sup>	0.04–0.065 <sup>m)</sup>	0.07–0.24 <sup>n)</sup>	15–39 <sup>p)</sup>
Dilute solutions <sup>b)</sup>	0.20–0.26 <sup>q)</sup>	0.74–0.80 <sup>q)</sup>	115–120 <sup>q)</sup>
Dilute solutions <sup>c)</sup>	0.37 <sup>r),s)</sup>	—	100 <sup>r),s)</sup>
Neat benzene <sup>d)</sup>	0.29 ± 0.03 <sup>t)</sup>	0.71 ± 0.03 <sup>t)</sup>	—
Neat benzene <sup>d)</sup>	0.22 ± 0.01 <sup>u)</sup>	0.78 ± 0.01 <sup>u)</sup>	83.7 <sup>u)</sup>

a) Data at room temperature; b) At 77K in rigid glasses; c) In gaseous matrices at 12K; d) At 170K; e) Ref. [25]; f) Ref. [26]; g) Ref. [27]; h) Ref. [28]; i) Ref. [29]; j) Ref. [30]; l) Ref. [31]; m) See ref. [11]; n) Ref. [32]; p) Ref. [33]; q) Ref. [2]; r) Ref. [15]; s) Ref. [34]; t) See ref. [18]; u) See ref. [17].

cence studies, [20,21] are critically discussed in terms of recent work reported in the literature [22–24].

## 2 — RESULTS AND DISCUSSION

The fluorescence quantum yields,  $\phi_{FM}$ , the triplet yields,  $\phi_{TM}$  and the fluorescence lifetimes,  $\tau_{FM}$ , obtained for benzene photophysics, by various authors, under different conditions, are shown in Table 1.

In Table 2 we illustrate the calculated values of  $k_{FM}$  and of the intersystem crossing rate constant,  $k_{TM}$ , and also the activation energies for the non-radia-

upon temperature, which implies that  $\phi_{FM}$ , and  $\phi_{IC}$  and  $\phi_{TM}$  are temperature dependent.

In condensed medium, at temperatures below 173K, the fluorescence quantum yield approaches a value which is similar to that obtained in gaseous samples at room temperatures (0.18–0.26), except for the value of  $\phi_{FM}$  reported by GIBSON and co-workers [34] that was estimated by an indirect method.

The decrease of  $k_{IC}$  at lower temperatures is the responsible for the observed limiting value of 100 ns (within ±20%) similar to the lifetime of vapour samples at room temperature, in which the internal conversion  $S_1 \rightarrow S_0$  is unimportant.

In the present discussion we shall not consider the photophysical parameters of concentrated samples

Table 2

Values of  $k_{FM}$ ,  $k_{TM}$  of benzene molecule under various conditions, and activation energies for internal conversion ( $S_1 \rightarrow S_0$ ) and intersystem crossing ( $S_1 \rightarrow T_1$ )

Benzene phase	$k_{FM} \times 10^{-6} \text{ s}^{-1}$	$k_{TM} \times 10^{-6} \text{ s}^{-1}$	$E_{IC}(\text{eV})$	$E_{TM}(\text{eV})$
Low pressure vapour <sup>a)</sup> (Zeroth level)	2.2 <sup>e)</sup>	7.8 <sup>f)</sup>	0.31 <sup>g)</sup>	—
Moderate/high pressure vapour <sup>a)</sup>	2.8 <sup>h),i)</sup>	9.8 <sup>h),i)</sup>	0.40 <sup>h)</sup>	0.04 <sup>h),i)</sup>
Dilute solutions <sup>a)</sup>	1.5–1.8 <sup>j)</sup>	$7 \pm 1$ <sup>j)</sup>	0.25–0.37 <sup>j)</sup> 0.24 <sup>l)</sup>	—
Dilute solutions in rigid glasses <sup>b)</sup>	1.6–1.8 <sup>g)</sup>	6.7 <sup>q)</sup>	—	—
Dilute solutions <sup>c)</sup>	3.70 <sup>m)</sup>	6.3 <sup>m)</sup>	—	—
Neat benzene <sup>d)</sup>	3.4–3.8 <sup>n),p)</sup>	8.4 <sup>n),p)</sup>	$0.26 \pm 0.02$ <sup>n),p)</sup>	—
Neat benzene <sup>d)</sup>	2.6 <sup>n)</sup>	9.3 <sup>n)</sup>	—	—

a) Data at room temperature; b) At 77K; c) In gaseous matrices at 12K; d) At 170K; e) See ref. [26]; f) See ref. [25]; g) See ref. [2]; h) See ref. [27]; i) See ref. [30]; j) See ref. [11]; l) See ref. [19]; m) See ref. [15]; n) See ref. [17]; p) See ref. [18].

in regions of low viscosity where fluorescent excimers are produced [35,36]. Upon an increase in viscosity the formation of intermolecular excimers is prevented, this explaining the absence of the excimer band in the neat solid benzene [18,37]. This was also confirmed with experiments carried out in our laboratory [19], from 293K down to 273K, showing a drastic decrease in the excimer band of neat benzene in a very narrow range of temperature, near 279K.

The variation of  $k_{FM}$ ,  $k_{TM}$  and  $k_{IC}$  vs temperature was measured for solid, liquid and gaseous samples, in which a slight variation of  $k_{FM}$  and  $k_{TM}$  and a large variation of  $k_{IC}$  were found [2,27]. A similar behaviour was shown for dilute solutions of toluene [10], although, in this case,  $k_{FM}$  is invariant.

In the case of gaseous benzene, at moderate pressures ( $p \sim 10$  torr), using results of DUNNICLIFF [27] and of LOCKWOOD [30], between 293K and 393K, an activation energy for intersystem crossing of 0.04 eV was estimated. The variation of  $k_{FM}$  is less marked (from  $2.8 \times 10^6 \text{ s}^{-1}$  at 293K to  $3.3 \times 10^6 \text{ s}^{-1}$  at 393K), while the variation of  $k_{IC}$  shows an activation energy of 0.4 eV.

The results of Table 2 show that it is reasonable to establish an activation energy, within the range 0.26–0.40 eV, for the non-radiative channel  $S_1 \rightarrow S_0$ .

The results were obtained from the variation, of the quantum deficit  $\Phi_{IC} = 1 - (\phi_{FM} + \phi_{TM})$ , with temperature, in the various phases. The activation energy  $E_{IC}$  falls within the interval of  $3000 \text{ cm}^{-1}$  which is the accepted channel 3 threshold [2,16,18].

Several tentative explanations for channel 3 have been put forward but a proper and definitive experiment to its identification is still lacking. CALLOMON and co-workers, using absorption line broadening experiments [16] have suggested that the channel 3 is due to a vibrationally activated transition from  $^1B_{2u}$  to a  $(\pi, \pi^*)$  state. Solvent studies carried out for benzene solutions show that  $k_{IC}$  values support a possible  $^1(\pi, \pi^*) \rightarrow ^1(\sigma, \pi^*)$  mechanism [11]. The hypothesis of the existence of a physical isomer distorted into a metastable non-planar form by out-of-plane vibrations [13,14] and a tunneling effect model [38] have also been proposed to explain the channel 3 in benzene.

A channel 3 threshold of  $2800\text{--}3800 \text{ cm}^{-1}$  was established by SUMITANI and co-workers [25] for gaseous benzene at very low pressures, who have attributed to internal conversion the dominant decay route at high excess energies.

An important result observed from the analysis of the tables is the non validity of the introduction of  $n^2$  in the theoretical expression of STRICKLER and BERG [39]. CUNDALL and PEREIRA [33] have measu-

red  $k_{\text{FM}}$  of a large variety of benzenoid compounds and concluded that the expression  $\tau_{\text{FM}}^0 = \tau_{\text{FM}} \times n^2$  is reasonably valid, except for benzene solutions in which a slight increase with temperature is shown for  $k_{\text{FM}}$ . This was also demonstrated to be the case in the solid [17,18] and vapour phases [27,30].

It is obvious from the results of Tables 1 and 2 that  $k_{\text{FM}}$  in condensed medium is far from being  $n^2$  times larger than in vapour phase except for the results reported by GIBSON and co-workers [15,34], but this is not surprising because the authors have used the expression  $k_{\text{FM}} = k_{\text{FM}}^0 n^2$  to estimate  $\phi_{\text{FM}}$  in the glassy environment. The same expression was used by LUMB and AL-CHALABI [40] for calculating  $\phi_{\text{FM}}$  of solid benzene samples at low temperatures, and this could explain the discrepancies between  $\phi_{\text{FM}}$  reported in references [17] and [18].

Radiative lifetime anomalies in benzene were also reported by GREGORY and HELMAN [41] and discussed by BIRKS [14]. Higher order terms neglected in deducing the theoretical expression of Strickler and Berg may explain the anomaly in cases of forbidden or weak transitions, as it is the case of the transition  $^1A_{1g} - ^2B_{2u}$  in benzene. HIRAYAMA and LIPSKY [22] have reviewed the role of refractive index correction in vapour and in liquid solutions and have shown that  $k_{\text{FM}}$  of 9-methylanthracene depends on  $n^2$ , as follows

$$\tau_r(\text{vapour})/\tau_r(\text{solution}) = n^2$$

in which  $\tau_r = 1/k_{\text{FM}}$  is the radiative lifetime.

They have proposed that the above ratio holds in cases where the experimental integrated area under the absorption curve is independent of the medium. The same result was later established for DPA and other molecules in various solvents [24], making use of an integrated sphere to avoid the need for geometrical refractive index corrections [21,23].

It should be pointed out that results here reviewed for benzene are not consistent with an  $n^2$  dependence of the radiative rate constant, although the experimental integrated area under the absorption curve is not dependent on the solvent, as demonstrated by EASTMAN and REHFELD [42]. Some other factors, as internal reflection, diffuse reflectance in non-transparent samples and photoselection of the emission due to instrumental artifacts [43,44] can cause experimental errors on the measured values of  $\phi_{\text{FM}}$ . However the experimental results reported for benzene, by so many authors in a large variety of conditions, are always consistent, with  $\phi_{\text{FM}}$  approach-

ing 0.20-0.25 at low temperatures or at moderate pressures, which seems to discard any possible source of error due to experimental considerations.

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## RESUMO

### Parâmetros fotofísicos da molécula de benzeno nas fases sólida, líquida e gasosa

São revistos os parâmetros fotofísicos da molécula de benzeno, contida nas fase sólida, líquida e gasosa. É feita uma análise crítica sobre os valores obtidos para os parâmetros referentes à desexcitação do primeiro estado singuleto excitado, em termos da variação da temperatura e da natureza do meio que contém a amostra.