Fluorescence Lifetimes and Quantum Yields of 9,10-Diphenylanthracene, Benzene, and [$^2H_6$]Benzene in Frozen Gas Matrices at 12 K

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Summary The single photon counting technique has been used to determine the fluorescence lifetimes of 9,10-diphenylanthracene, C_6H_6, and C_6D_6 in a variety of frozen gas matrices at 12 K; the fluorescence quantum yields of C_6H_6 and C_6D_6 in CH_4 at 12 K have been determined as 0·35 and 0·45 respectively.

IN order to investigate radiative and non-radiative processes of excited states of molecules it is essential that fluorescence and phosphorescence lifetimes can be measured. Generally fluorescence measurements are made in the gas phase, exciting into the 0–0 band, and extrapolating to zero pressure. However such an approach is often impractical because of the low vapour pressure of the molecule under consideration. Many studies have been made of the phosphorescence of benzene in rare gas matrices,[1] but none of the fluorescence lifetime. The lifetime of chromyl chloride emission in an argon matrix at 4 K has been measured as 39 μs.[2] Recently the single photon counting technique has been used to measure the fluorescence lifetime of formaldehyde in Xe[3] and of C_6H_6 in Ar.[1c] We report here the first use of frozen gas matrices at 12 K to mimic the zero-pressure, isolated-molecule case of the fluorescence lifetime of a typical non-volatile molecule, 9,10-diphenylanthracene (DPA), and a study of the fluorescence lifetimes of C_6H_6 and C_6D_6 in a range of frozen gas matrices.

TABLE 1. Fluorescence (τ_f,ns) and phosphorescence (τ_p,s) lifetimes of C_6H_6 and C_6D_6 in gas matrices[a] at 12 K.

	C_6H_6		C_6D_6	
Matrix	τ_f	τ_p	τ_f	τ_p
CH_4	98 ± 2	15·5 ± 0.3	157 ± 1	20·3 ± 0·3
CF_4	96 ± 2	14·6 ± 0·3	129 ± 3	20·4 ± 0·3
N_2	100 ± 2	14·0 ± 0·3	146 ± 3	19·0 ± 0·3
CO	77 ± 1	8·7 ± 0·3	113 ● 2	9·2 ± 0·3
SF_6	100 ± 1	13·4 ± 0·1	123 ± 5	23·0 ± 0·3
Ar	46 ± 1	12·1 ± 0·3	66 ± 2	18·1 ± 0·3
Kr	—[b]	0·87 ± 0·04	—[b]	0·85 ± 0·01
Xe	—[b]	0·020 ± 0·001	—[b]	0·020 ± 0·001

[a] Substrate : host matrix = 1 : 200. [b] No fluorescence observed.

The fluorescence lifetimes of C_6H_6 and C_6D_6 were measured in a variety of gas matrices at 12 K in order to ascertain the feasibility of using the single photon counting technique to determine fluorescence lifetimes in frozen gas matrices (Table 1). In agreement with earlier work,[1a] no fluorescence was observed from either C_6H_6 or C_6D_6 in Kr or Xe at 12 K. The phosphorescence lifetimes in CH_4, Ar, Kr, and Xe are in good agreement with the work of Robinson and Frosch.[1a] CO was chosen as a matrix gas as it is isoelectronic with N_2; the quenching of both the fluorescence and the phosphorescence lifetimes in CO is being investigated at present. It was decided to include CF_4 and SF_6 as matrix gases because they could signifi-

cantly extend the temperature range available without increasing the spin–orbit coupling as in the case of Xe. It is interesting that the fluorescence lifetime of C_6H_6 is of the order of 100 ns in CH_4, CF_4, N_2, and SF_6, and is halved in Ar, whereas the phosphorescence lifetime in these five matrices is approximately constant. The measured fluorescence lifetimes of C_6D_6 are more dependent upon the choice of matrix than those of C_6H_6, but the same trend is evident.

TABLE 2. Fluorescence lifetimes (τ_f,ns) of C_6H_6 in gas, solution, and solid phases.

Phase (Temp.)	τ_f
Gas (298 K)	100[a]
Cyclohexane solution (298 K)	28[b]
MCHIP[c] solution (298 K)	30
MCHIP[c] glass (77 K)	74
CH_4 matrix (12 K)	98

[a] Zeroth level, low pressure, ref. 5. [b] Ref. 4. [c] Methy'-cyclohexane–isopentane (1 : 1 v/v), this work.

The data presented in Table 2 for the fluorescence lifetime of C_6H_6 show good agreement between our value of 30 ns obtained in solution at 298 K and the previously reported value.[4] More interesting is the excellent agreement between our value of 98 ns obtained in CH_4 at 12 K and the value of 100 ns obtained in the zeroth level, low-pressure limit.[5] We have recently measured the fluorescence lifetime of DPA in CH_4 at 12 K as 9·4 ns.† This value compares well with those obtained by Olmsted[6] who showed that the decrease in fluorescence lifetime of DPA from 8·8 to 7·5 ns in isopentane on cooling from 293 K to 113 K was due to the change in the refractive index of the solvent. Furthermore, Olmsted demonstrated that the radiative lifetime, τ_R, was not constant, but that the product of the square of the refractive index, n, and τ_R, was constant to within 10%. Thus, assuming that the fluorescence quantum yield of DPA at 12 K in CH_4 is unity, we can evaluate the refractive index of CH_4 at 12 K as 1·2820. Therefore assuming zeroth level, low-pressure lifetimes of 100[5] and 200 ns,[7] and quantum yields of 0·22[8] and 0·35[7] for C_6H_6 and C_6D_6 respectively, we can calculate the fluorescence quantum yields of C_6H_6 and C_6D_6 in CH_4 at 12 K as 0·35 and 0·45 respectively. Thus the apparent agreement between the fluorescence lifetimes of C_6H_6 in CH_4 at 12 K and in the zeroth level, low-pressure limit is coincidental and is due to the increased fluorescence quantum yield in CH_4 at 12 K.

The determination of the fluorescence quantum yields of C_6H_6 and C_6D_6 is especially important as it will allow evaluations of quantum yields to be made routinely in frozen gas matrices using the comparative method of Parker and Rees.[9] Work is currently in hand to extend the range of temperatures available and to enable measurements of lifetimes in the range 10^{-3} to 10^{-6} s to be made in order to study the photophysical processes of some unstable intermediates of photochemical reactions.

We thank the S.R.C. and the University of Southampton Research Fund for support (to A.J.R. and K.S.).

(*Received, 20th July* 1979; *Com.* 788.)

† DPA was vaporized at 389 K and co-deposited with CH_4 on to the cold window over a period of 2 h. The optical density of the S_0–S_1 bands was *ca.* 0·2. It is not possible to estimate the matrix ratio obtained under these conditions but the fluorescence emission spectrum showed no signs of self-absorption, whereas at a vaporization temperature of 400 K self-absorption was evident and the measured fluorescence lifetime was 12 ns.

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