Journal of Luminescence 31 & 32 (1984) 648-650
North-Holland, Amsterdam

LUMINESCENT FRACTAL REACTIONS: EXCITON FUSION ON PERCOLATION CLUSTERS*

Lola W. ANACKER, Paul W.KLYMKO[+] and Raoul KOPELMAN

Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109

Experimental measurements of exciton annihilation in isotopic mixed crystals of naphthalene-h_8 in naphthalene-d_8 exhibit fractal reaction kinetics on samples well below and slightly above the percolation threshold. The effective spectral dimensions are in very good agreement with the superuniversality conjecture and 2-dim. random walk simulations. Crystals well above the percolation threshold exhibit the expected classical behavior.

1. INTRODUCTION

We report here the first comprehensive experimental study of fractal binary reaction kinetics.[1-3] This fractal reaction is a prototype of homogeneous chemical kinetics and is of potential application to chemical catalysis and biological molecular transport.

Guest-guest triplet-triplet annihilation in highly purified mixed crystals of naphthalene (guest)-naphthalene-d_8 (host) was studied at 1.8 K via simultaneous spectral and time resolution of the phosphorescence and delayed fluorescence over a large range of guest concentrations. Note that the binary reactions of two triplets forming a singlet can be represented as

$$2T \rightarrow S \tag{1}$$

with the classical (Euclidean space) kinetic equation:

$$dS/dt \propto T^2. \tag{2}$$

However, on fractal spaces the equation is

$$dS/dt \propto T^2\, t^{-h} \qquad 0 < h < 1 \tag{3}$$

where $h = 1 - d_s'/2$ and d_s' is the effective spectral dimension of the fractal space. For the delayed fluorescence

$$F \propto dS/dt \tag{4}$$

and for the phosphorescence

$$P \propto T. \tag{5}$$

Equations 3-5 are combined to yield

$$F/P^2 \propto t^{-h}. \tag{6}$$

2. EXPERIMENTAL METHODS

The naphthalene and perdeuteronaphthalene were highly purified by zone-re-

---

[+]Present Address: IBM, East Fishkill, Hopewell Junction, NY 12533.

*Supported by NIH Grant No. 2R01 NS80116-16.

0022-2313/84/$03.00 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

fining and potassium fusion.[4,5] Impurity levels were below 10^{-7} mole fraction; none of the samples discussed below showed any β-methylnaphthalene phosphorescence. Thus we report here genuine exciton homofusion results to be distinguished from previously reported fusion occurring at impurity sites, i.e., heterofusion.[6] Moreover, the observed naphthalene delayed fluorescence intensity quantitatively accounted for the quenching of the 2.7 sec. natural phosphorescence decay,[7] thus eliminating the need for considering any third decay channel. Decay spectra were generated using shuttered xenon lamp excitation. Crystals were irradiated until steady emission levels were obtained, and the excitation subsequently shuttered off. The emission decays were spectrally resolved using a 1m Jarrell-Ash spectrometer and time resolved using a PAR Model 4202 signal averager.

3. ANALYSIS AND RESULTS

The phosphorescence decay was collected at longer time intervals than the delayed fluorescence. All the phosphorescence data were used in the analysis described below; however, weighted averages of the delayed fluorescence data were used when sampling times for the two decay curves did not match exactly. This average was obtained using the two fluorescence data points bracketing each phosphorescence sampling time. A nonlinear regression analysis was used to obtain the h values in Equation 6. Values of -h are given by the slopes of the straight lines in Figure 1; values of h are shown as a function of concentration in Figure 2. The regression analysis used the decay data from 20 ms to 200 ms after the light source was shuttered off. This early time span was chosen to avoid effects due to natural decay.

The results for samples of 2%, 3%, 4% and 6% naphthalene-h_8 (well below dynamic percolation, 8%) give an h value of 0.45 with a corresponding $d_s' \sim 1.1$. This is in good agreement with simulations of long-range random walks on 2-dim. percolation clusters[8] ($d_s' = 1.1$), but contradicts the Euclidean (classical) result ($d_s = 2.0$, $h = 0.0$). The 8%, 10% and 12% samples are at or a little above percolation and have $h \sim 0.35$, i.e., $d_s' \sim 1.3$. This is remarkably close to the conjectured superuniversality[9] ($d_s = 1.3$). Values of $h = 0.27$, $d_s' = 1.5$ are obtained for the 14% sample. At long times this sample appears to show a crossover[8] to classical behavior, as expected. For the 16% sample, values of $h = -0.05$ are obtained in excellent agreement with classical behavior in Euclidean space ($h = 0$).

In conclusion, we observed fractal kinetics for the binary reaction of exciton homofusion. It is fully consistent with 2-dim., long range, exciton percolation. Similar results have been obtained from disordered naphthalene and naphthalene doped polymeric glasses[10] and from recent simulations.[8,10]

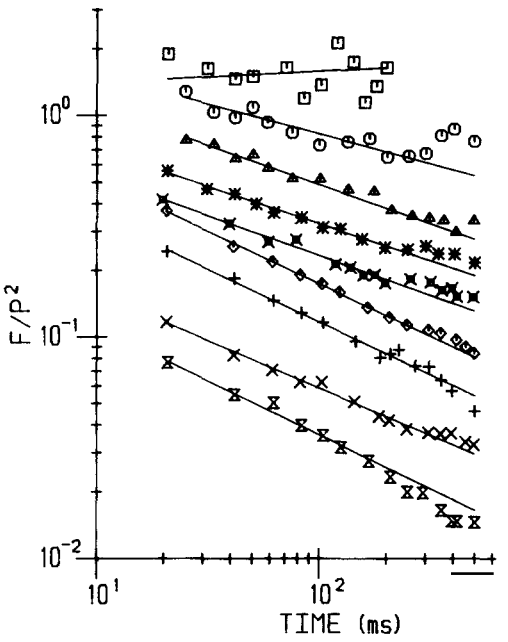

FIGURE 1
log (F/P^2) vs. log time (ms) for (bottom to top) 2%, 3%, 4%, 6%, 8%, 10%, 12%, 14%, and 16% naphthalene-h8 in naphthalene-d8. The straight lines are the fits to Equation 6 with slope (-h). Curves have been shifted.

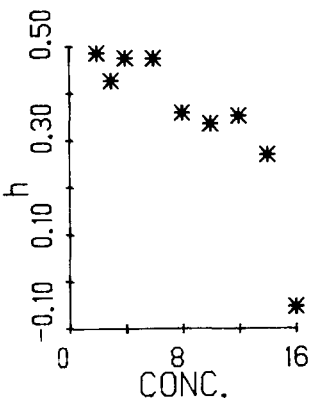

FIGURE 2
Heterogeneity exponent h vs. concentration of naphthalene in perdeutero-naphthalene.

REFERENCES

1) P.W. Klymko and R. Kopelman, J. Phys. Chem. 87 (1983) 4565.

2) P. Meakin and H.E. Stanley, J. Phys. A: Math. Gen. 17 (1984) L173.

3) R. Kopelman, P.W. Klymko, J.S. Newhouse and L.W. Anacker, Phys. Rev. B 29 (1984) 3747.

4) D.M. Hanson and G.W. Robinson, J .Chem. Phys. 43 (1965) 4174.

5) F.W. Ochs, Ph.D. Dissertation, The University of Michigan (1974).

6) P. Evesque, J. Phys. (Paris) 44 (1983) 1217.

7) P.W. Klymko, Ph.D. Dissertation, The University of Michigan (1984).

8) P. Argyrakis and R. Kopelman, Phys. Rev. B (in press); this volume.

9) S. Alexander and R. Orbach, J. Phys. (Paris) Lett. 43 (1982) L625; A. Aharony and D. Stauffer, Phys. Rev. Lett. 52 (1984) 2368.

10) E. I. Newhouse and R. Kopelman, this volume; L. Harmon and R. Kopelman, this volume; J.S. Newhouse and R. Kopelman, this volume.