PERCOLATION OF TRIPLET EXCITATION IN SOL-GEL MATRIX

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Triplet spectroscopy and energy migration among benzophenone chromophores have been studied in sol-gel matrix under steady state excitation. The energy migration process was observed by the rise of sensitised emission from triplet energy acceptors like, 1,4-dibromonaphthalene and 1-chloronaphthalene after excitation of benzophenone chromophore. The probability of donor excitation energy capture by the trap shows a critical concentration dependence on the benzophenonene molecules. The percolation model has been applied to evaluate the critical exponents. The evaluated critical exponents are in very good agreement with three dimensional excitation transport.

Keywords: A. disordered system, D. optical properties, E. luminescence.

1. INTRODUCTION

The physics of disordered systems and other restricted geometries has drawn considerable attention in the recent past. The spectroscopy of molecules embedded in such systems with strong microscopic inhomogeneity was investigated by Kopelman and his group [1, 2] and later expanded by Morgan and El-Sayed [3, 4], Blumen and Silbey [5], Trankle et al. [6], Bagnich and Dorokhin [7-9] and others. Investigations with strongly doped mixed crystals first revealed that cluster statistics and percolation model can be applied to the complex physical phenomenon of triplet excitation transport in such restricted geometries.

Since the mid-eighties, this fruitful approach has been applied to the study of energy migration in many other heterogeneous systems such as molecularly doped polymer matrix [10, 11], polymer blends [12], porous membranes [13, 14] and other inhomogeneous matrices. In some earlier communications we have reported that the percolation model is applicable for triplet excitation migration between an energy donor and an acceptor in frozen solution, polymers and copolymers [15-17], where the dimension of transport is determined by the microscopic inhomogeneity of the matrix.

The sol-gel process is a technique that can be used to prepare transparent oxide glasses by hydrolysis and polycondensation of alkoxides. Little or no heating is required, and consequently the gels can be doped with molecules whose poor thermal stability precludes their incorporation in traditional inorganic hosts. Such molecules become entrapped in the growing covalent gel network rather than being chemically bound to the inorganic matrix [18]. The transparency of sol-gel in the 300–700 nm range allows excitation and detection of the entrapped chromophores [19].

In this communication we extend our studies on migration of triplet excitation of benzophenone molecules in such doped tetraethylorthosilicate sol-gel glasses and show that the dynamical percolation model is indeed applicable in this case.

2. EXPERIMENTAL

1-Chloronaphthalene (CN) and 1,4-dibromonaphthalene (DBN) molecules were used as triplet energy acceptors, obtained from Fluka A.G. and Kodak Chemical Company, USA. Benzophenone (BZ) molecules, selected as donors were from Aldrich Chemical Company, USA. Alkoxide used for the preparation of silica glass by sol-gel method was tetraethylorthosilicate (TEOS) of Merck-Schuchardt. Samples were purified by repeated crystallisation, vacuum sublimation, vacuum distillation and zone refining processes. In the typical preparation of a silica glass by the sol-gel method, one starts with an
appropriate alkoxide, in our case TEOS, which was mixed with water, an acid catalyst such as HCl and a mutual solvent like MeOH. Hydrolysis leads to the formation of silanol groups (Si–OH), which further reacts with alcohol to give siloxane (Si–O–Si). After this process of condensation, drying stage involves careful removal of solvent phases, and formation of dried gels. The gels are rigid transparent materials with good thermal and dimensional stability.

In our case samples were prepared by mixing TEOS and water in a mole ratio of 1:8, whereas TEOS and HCl are in a mole ratio of 1:0.01. MeOH was used as a mutual solvent and mixed in a volume ratio of 1:1 with TEOS. Along with this required quantities of dopant molecules were added. Then the solutions were mixed well and dried at room temperature for ~30 h.

Doped samples were then mounted on a suitable support and inserted in a dewar containing liquid nitrogen. The emission spectra were recorded by using Hitachi 4500 spectrophotometer.

3. RESULTS AND DISCUSSION

In our system BZ acts as an energy donor whereas DBN and CN are energy acceptors. It is evident from the relative positions of their energy levels [15–17] that we can easily excite the lowest singlet state of BZ molecules without directly exciting the acceptors. So the observed phosphorescence emission from the acceptors are solely due to the triplet energy transfer from the donor.

Phosphorescence spectrum of pure BZ ($\lambda_{ex} = 380$ nm) and pure DBN ($\lambda_{ex} = 330$ nm) in sol-gel TEOS glass are shown in Fig. 1(a). In Fig. 1(b) we show the total phosphorescence emission from BZ-DBN ($\lambda_{ex} = 380$ nm) doped sol-gel TEOS glass, which shows overlapping phosphorescence emission from both. We have used 380 nm as the excitation radiation to avoid any singlet DBN excitation. With the fluorimeter’s spectral width this wavelength is sufficient to excite BZ singlet state. In this system fast intersystem crossing ensures BZ triplet–DBN/CN triplet energy transfer.

In both BZ-DBN and BZ-CN doped sol-gel matrix we have seen similar dependence of sensitised phosphorescence intensity on the concentration of donor molecules embedded in the matrix. At low concentration of BZ, the sensitised phosphorescence intensities are very weak. As the concentration of BZ increases, triplet excitation migration efficiency increases and acceptor phosphorescence intensity enhances. It has been found that there is a dramatic increase in acceptor phosphorescence intensity at some critical concentration of the donor where the donor and acceptor emissions become equal inspite of the fact that the acceptor concentration is orders of magnitude lower.

Percolation theory [20–22] accounts for this behaviour. In this model the excitation transfer between the donors and the acceptors (donor’s excitation capture by the trap) is thought to depend on the establishment of connectivity between them by infinite cluster formation. It is recognised that as long as the molecules are within their interaction distance, they belong to the cluster. The probability of excitation capture by a trap can then be written as

$$P = \frac{I_A}{I_A + q_A \alpha D}$$,

where $I_A$, $I_D$ are the phosphorescence intensities and $q_A$, $q_D$ are the phosphorescence quantum yields of acceptors and donor respectively.

The variation of excitation trapping probability $P$ on BZ concentration in two different cases are shown in Fig. 2. The value of phosphorescence quantum yields are taken to be 0.74, 0.18 and 0.04 for BZ, CN and DBN respectively [7, 14]. The low value for $q_{DBN}$ is due to its anti-batic behaviour [23]. The phosphorescence of DBN varies according to the wavelength of excitation, when the excitation energy is put selectively into the singlet state the phosphorescence is very much quenched [24–26]. The values for quantum yields used were actually measured in vitreous solutions like ethanol, diethylether, etc. We have used the same values for the sol-gel matrix because the phosphorescence decays of CN, DBN at 77 K in sol-gel matrix are found to be similar with those in vitreous solution.

For each dependence study a constant relative concentration of the dopants i.e. $C_A/C_D = S$ was maintained to avoid any effect of static energy transport, where $C_A$
and $C_D$ are the acceptor and the donor concentrations respectively. Figure 2 shows that the probability of excitation capture by the traps increases abruptly as the donor concentration reaches a critical value $C_c$ and this happens in a very narrow range of BZ concentration variation. From Fig. 2 it is also evident that $C_c$ is very much dependent on the trap concentration.

Theory of dynamic percolation [20] accounts for such dependence. In cluster dynamics, the two mathematical functions $P_\alpha$ (cluster percolation probability) and $I_{av}$ (average infinite cluster size) in disordered systems [20] bear the following relations with critical concentration.

$$P_\alpha \sim |C/C_c - 1|^{\beta}, \quad C \gg C_c \quad \text{and} \quad S \ll 1,$$

$$I_{av} \sim |C/C_c - 1|^{-\gamma}, \quad C \ll C_c \quad \text{and} \quad S \ll 1,$$

where $C$ is the donor concentration, $C_c$ is the critical concentration, and $\beta$ and $\gamma$ are the critical exponents. These critical exponents are universal within small error bars, in two and three dimensions when various lattices are compared. With large error bars exponents seem unchanged if clusters are defined not just as nearest neighbour connected groups but longer distance were allowed to connect the sites as has already been pointed out in our situation.

In the supertransfer model [1] it is shown that the probability of excitation capture by the trap above the percolation threshold is determined by the cluster percolation probability i.e.

$$P = P_\alpha, \quad C \gg C_c, \quad S \ll 1.$$

Below the percolation threshold the probability of trapping is associated with the average number of molecules in the cluster.

$$P - I_{av}, \quad C \ll C_c, \quad S \ll 1.$$

In dynamic percolation theory [20] it has been shown that $C_c$, $I_{av}$ and $P_\alpha$ also depend on the temperature and concentration of traps along with the connectivity of the molecules. However such dependences can be eliminated in the cluster with leakage model by using reduced concentration $C/C_c$ [20].

In Fig. 3 plot of $P$ against $C/C_c$ clearly demonstrates the universal dependences of $P$ on reduced concentration.

$$P = P_\alpha, \quad C \gg C_c, \quad S \ll 1.$$

$$P - I_{av}, \quad C \ll C_c, \quad S \ll 1.$$
Table 1. Theoretical and experimental values for critical exponents

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<tr>
<th>Theory</th>
<th>Experiment</th>
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<tr>
<td></td>
<td>2D</td>
</tr>
<tr>
<td>β</td>
<td>0.14</td>
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<tr>
<td>γ</td>
<td>2.2 ± 0.1</td>
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$C/C_c$ for both the acceptor systems. The plots are in good agreement with cluster-leakage model. The behaviour of large infinite cluster at the concentration very close to the critical concentration represent the critical behaviour region of percolation theory and is known as the scaling region. The traditional way of checking for scaling and critical exponents consists of appropriate log–log plots. From the plots as shown in Fig. 4 we have obtained two asymptotic straight lines giving critical percolation exponents ($\beta$ and $\gamma$). The striking phenomena is the wide range over which the lines are straight as well as the fact the lines are still straight for values of donor concentration far above and far below critical concentration.

It is well established that the critical exponents are function of dimensionality. In Table 1 we compile averaged numerical estimates of the exponents along with the experimental values as a function of dimensionality [22]. It is observed that the experimental values for $\beta$ and $\gamma$ are in very good agreement with 3-dimensional percolation model. Thus we conclude that the sol-gel TEOS glass has isotropic structure and three dimensional percolation of donor triplet excitation generates acceptor phosphorescence in the system.

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REFERENCES