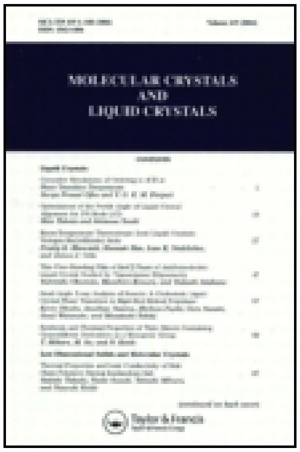

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Optical Probes in the Study of Restricted Geometries

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OPTICAL PROBES IN THE STUDY OF RESTRICTED GEOMETRIES

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Abstract Geometrical restrictions are known to modify the transport properties of embedded molecules. In this contribution we briefly summarize our recent results on dynamics within pores obtained by using optical probes, with an emphasis on crossover behaviors typical to such systems.

INTRODUCTION

The role of confining spaces in modifying the fundamental properties of molecules and of molecular liquids has recently gained some understanding and has been the subject of a number of review articles.[1-3] Examples of confined geometries are: porous silica gels, porous Vycor glass, micelles, microemulsions, zeolites and membranes. All these materials provide model systems for restricted geometries and act as convenient hosts for studies of molecular diffusion and reactions and of liquid properties under spatial restrictions.

Geometrical constraints restrict the spatial distribution of molecules and their motions. The molecular locations reflect both the nature of the geometrical constraints and the detailed molecule-system interactions (chemistry). The effects on molecular motion depend on whether the molecules diffuse within the confined space in gas phase[4] or if the confinement is filled with solvent.[5] Questions on the role of surfaces in modifying the behavior of bulk solvent has been recently addressed from various points of view both theoretically and experimentally. These include surface wetting,[6] phase transitions in pores[7] and dielectric properties of water in oil microemulsion[8].

One possible way to shed light on these interesting but yet complex systems is to use optical probes which are designed to sense different aspects of these materials. Luminescent labels have been used for a long time as probes of static and dynamical properties of a broad range of systems, i.e. in studying translational and rotational diffusion in bulk solution,[9] in experiments on diffusion of labeled polymers[10] and in electronic energy transfer in porous glasses and in polymers[11]. The large span in available lifetimes of excited dye molecules makes it possible to follow dynamical behavior on time scales from picoseconds to milliseconds. Optical probes serve then as sensors of microenvironments and provide information on local (short time) and global (long time) dynamical properties. In order to be able to draw conclusions, as general as possible, on molecular behavior under geometrical restrictions by using optical probes, one needs a well-characterized group of confining systems. Ideally, the aim is to change the restriction in a controlled and continuous way, and choose a nonperturbing probe to study both statics and dynamics at the molecular level. In our work we have concentrated on porous systems; we believe, however, that our method and conclusions are applicable to other restricted geometries as well.

We have chosen as model systems porous silica gels of varying pore size and porous Vycor glass on which we performed characterization measurements: surface areas, pore size distributions, molecular adsorption, small x-ray and neutron scatterings.[12] Our work to date has provided us with a detailed understanding of the structure of both silica gels and porous Vycor. A striking result of our materials characterization work is that, although morphologically disordered, they have a dominant length scale which characterizes the void space, the mean pore size R_p. R_p turned out to be the relevant length which entered directly, as a scaling parameter, into the dynamical observables.[13] We have studied experimentally and theoretically the following cases:

(a) Direct energy transfer between an initially excited static donor and static acceptors.[14] Here one studies scales ≈ 100 Å.

(b) Quenching of excited donors adsorbed on porous surfaces by gas phase quenchers which diffuse within the pore network.[4]

(c) Molecular self-diffusion in pores using transient grating technique.[5] This is a long time and large scale experiment (~ microns).

(d) Local rotations of excited molecules in confinements.

From the characterization work and the dynamical studies a consistent picture emerges that relates the transport properties to the morphological details in these materials. We will focus on cases (a) and (b) which present two different scenarios for relaxation in donor-acceptor systems embedded in porous silica gels. We believe that both cases are related to the morphology of porous silicas and that the dynamical process in each case directly senses the local structure. In the first case the donor and acceptors are adsorbed on the surfaces of the porous solids. Thus, the locations of the participating molecules are dictated by the underlying geometries. In the second case, the donor is still adsorbed on the interface, but the acceptors diffuse within the pore network with a diffusion constant which is controlled by scattering from the interface, introducing again a geometrical contribution. In both cases one expects a crossover behavior in the dynamical properties which is typical to confined systems. We will not provide a detailed discussion of the experimental studies which can be found in refs. [12-15].

DIRECT ENERGY TRANSFER

It has been suggested that energy transfer methods can be used to characterize local morphology of porous systems. The basic ideas behind direct energy transfer (DET) measurements is to tag an interface with a random distribution of donor (rhodamine 6G in this case) and acceptor (malachite green in our case) molecules at concentrations low enough to allow for only a one step transfer of the initially excited donors to the acceptors. Excitation transfer among the donors or among the acceptors themselves is excluded in the concentration range and time scale of the experiment. One then follows the time evolution of the fluorescence of the donors. Within a generalized Förster framework for DET the survival probability of the donor has been calculated and has the form[16]:

$$\Phi(t) = \exp[-(t/\tau_D)-p\int dr\,\rho(r)\,\{1-\exp\{-tw(r)\}\}] \qquad (1)$$

where p is the density of acceptors ($p \ll 1$), τ_D is the fluorescence lifetime of the isolated donor and $\rho(r)$ is a site density function. *Eq. (1) relates the time evolution of the excited donor to the spatial arrangement of the molecules involved in the energy transfer.* This spatial arrangement may be dictated by the local morphological details. Therefore, for random distributed molecules it is possible to obtain geometrical information about the underlying porous structure. In our studies we assumed dipolar donor-acceptor interaction.

$$w(r) = \frac{3}{2}\kappa^2\left(\frac{R_0}{r}\right)^6 \cdot \frac{1}{\tau_D} \qquad (2)$$

where κ is the anisotropy factor τ_D is the donor lifetime and R_0 is a critical radius which is determined from the spectral overlap of donor fluorescence and the absorption of the acceptor on the silica surface. R_0 provides an estimate for the length scale which can be sensed by DET. For a regular infinite system $\rho(r)$=constant and we recover the Förster decay law

$$\Phi(t) = \exp[-At^{d/6} - t/\tau_D]. \qquad (3)$$

where d is the spatial confinement. The situation is different when an additional length scale typical to a confinement is introduced. As an example we choose an infinite cylindrical pore of radius R_p. The acceptors are distributed within the volume, while the donor is located on the surface of the cylinder at the origin $O=(0,0,0)$. The axis of the cylinder lies at distance R_p from the origin along the z direction. The site density function $\rho(r)$ for this case is[16]

$$\rho(r)dr\,dz = 2r\rho\,\arccos(r/2R_p)dr\,dz. \qquad (4)$$

and

$$\Phi(t) = \exp[-pI(t)] \qquad (5)$$

with

$$I(t) = 4 \int_0^{2R_p} dr \int_0^{\infty} dz r\rho \arccos\left(\frac{r}{2R_p}\right)\{1-\exp[-t\alpha(r^2+z^2)^{-3/2}]\}. \tag{6}$$

and $\alpha = \frac{3}{2}\kappa^2 R_0^6 \tau_D^{-1}$. From Eqs. (5) and (6) we conclude that for short times, $t \ll R_p^6/\alpha$, one recovers a Förster type decay, where the donor sees only half-space occupied by the acceptors. For the long time decay, $t \gg R_p^6/\alpha$, Eq. (6) yields the Förster decay corresponding to one dimension

$$\Phi(t) = \exp[-p\rho\pi R_p^2 \Gamma(1-1/s)(t\alpha)^{1/6}] . \tag{7}$$

This crossover, typical to confined spaces, depends on the relationship between two lengths in the problem, R_0, the critical DET radius and R_p, the pore radius. The cylinder example can be generalized to more complex pore structures. We conclude then that DET provides a spectroscopic means to elucidate spatial organization of adsorbed molecules as determined by the local pore properties. DET is capable of sensing the location of acceptors relative to donors up to time t_{max}, or distance R_{max} (directly related to R_0. For more details see Ref. [14]) which depend on the experimental limitations of the detection systems. R_{max} also depends on the acceptor concentrations--the higher is the concentration the shorter is R_{max}. For $R_p \gg R_{max}$ one expects a two-dimensional DET on the time scale of the experiment. As R_p gets shorter more of the structure is being sensed, until a three-dimensional DET is to be observed when $R_p \ll R_{max}$.[14]

DONOR QUENCHING BY DIFFUSING ACCEPTORS

We now concentrate on the situation where acceptor *gas* molecules *move* within the spatial confinement of the pore network and quench the excited adsorbed donor upon encounter. We again follow the decay of the donor in time. In order for the geometry to play a role one has to make sure that it is not the gas phase molecule-molecule collisions among the quenchers that dominate the diffusion but rather the scattering of the individual quenchers by the pore boundaries. Such a behavior is expected for the quenchers in the gas phase at relatively low pressures in the Knudsen regime.[17] A criterion for Knudsen diffusion is that the mean free path due to molecule-molecule scattering, λ, is larger than the mean pore size, R_p,

$$\lambda >> R_p \tag{8}$$

where $\lambda = \frac{k_B T}{\sqrt{2}\pi\sigma^2 P}$, σ is the collision diameter of the molecules and P is the gas pressure. We are then in the limit of relatively small pores where the quenchers collide more often with the pore boundaries than with each other. The problem of donor quenching due to Knudsen diffusion is complementary to the direct energy transfer problem, discussed in the previous section. In the energy transfer case the boundaries restricted the *locations* of the adsorbed acceptors. Here the same boundaries restrict the *motion* of the acceptors. In both cases, it is possible to relate the morphology to the decay of the donor.

In order to calculate the survival probability of the excited donor due to acceptors in the Knudsen regime, we assume that the pore space in porous silicas can be viewed as a three-dimensional homogeneous, yet tortuous, network. THe leading term in the survival of the donor is an exponential given in terms of a Smoluchowski-type decay rate,[4]

$$\Phi(t) = \exp(-Kt) \tag{9}$$

with

$$K = K_q + \frac{1}{\tau_D} \tag{10}$$

Here τ_D^{-1} is the lifetime decay rate of the isolated donor and K_q is is the Smoluchowski-type expression for the donor annihilation by the quenchers. K_q has been shown to be

$$K_q \approx \frac{g \cdot v \cdot r_{AB}}{k_B T} \cdot R_p \cdot P \tag{11}$$

where r_{AB} is a reaction radius, v is the acceptor's mean velocity and g is structure factor which depends on porosity turtuosity and other structural details. The initial donor decay rate scales with the mean pore size of the silicas and with the gas pressure. Although the above model is somewhat oversimplified concerning the complexity of most porous systems, we believe that it still captures the basic physics of the process. Here again the mean pore size is the geometrical factor that directly enters the dynamical expression. Experimentally the quenching of benzophenone by oxygen molecules has been studied within various silica gels.[4] The findings confirm the predictions of Eqs. (9)-(11). As the pore size, R_p, increases and approaches λ, or as the pressure increases, one expects a crossover in the quenching rate. For the limit where $\lambda \ll R_p$, the rate should be independent of the pore size, and governed by the molecule-molecule scatterings.

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REFERENCES

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1. J. Klafter, R. Rubin and M. F. Shlesinger, Eds. Transport and Relaxation in Random Media, (World Scientific, Singapore, 1986).
2. J. Klafter and J. M. Drake, Eds. Molecular Dynamics in Restricted Geometries (John Wiley, NY, 1989).
3. R. Kopelman, Science, 241, 1620 (1988).
4. J. M. Drake, P. Levitz, N. J. Turro, K. Stephen Nitsche and K. F. Cassidy, J. Phys. Chem., 92, 4680 (1988).
5. W. D. Dozier, J. M. Drake and J. Klafter, Phys. Rev. Lett., 56, 197 (1986).
6. J. Warnock and D. D. Awschalom, Phys. Rev., B34, 475 (1986).
7. M. B. Ritter, D. D. Awschalom and M. W. Shafer, Phys. Rev. Lett., 61, 966 (1988).
8. G. Nimtz and W. Weiss, Z. Phys., B67, 483 (1987).
9. D. Ben-Amotz and J. M. Drake, J. Chem. Phys., 89, 1019 (1988).
10. F. Rondelez, H. Hervet and W. Urbach, Chem. Phys. Lett., 53, 138 (1983).
11. See Ref. [2].
12. J. M. Drake, P. Levitz and S. K. Sinha, in Better Ceramics

Through Chemistry II, Ed. C. J. Brinker, D. E. Clark and D. R. Ulrich (MRS, Pittsburgh, PA, 1986).

13. J. M. Drake, P. Levitz, S. K. Sinha and J. Klafter, Chem. Phys., 128, 188 (1988).
14. P. Levitz, J. M. Drake and J. Klafter, in ref. [2].
15. J. M. Drake, P. Levitz and J. Klafter, in Dynamical Processes in Condensed Molecular Systems, J. Klafter, J. Jortner and A. Blumen (World Scientific, Singapore, 1989).
16. A. Blumen, J. Klafter and G. Zumofen, in Optical Spectroscopy of Glasses, Ed. I, Zschokke (D. Reidel, Dordrecht, 1986).
17. E. L. Cussler, Diffusion: Mass Transfer in Fluid Systems (Cambridge University Press, Cambridge, 1984).