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Rotational relaxation of azobenzene in porous Vycor glass

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Abstract. Polarised picosecond transient grating experiments on azobenzene molecules doping a solution of 4.3 mol of methanol in toluene demonstrate that rotational relaxation is much faster in the bulk fluid than in the fluid embedded in Corning 7930 Vycor glass. As rotational and translational Brownian motions are related to each other, this proves a drastic change in the diffusion coefficients even on a microscopic length scale, which is in contradiction with a previously suggested fractal model. We interpret this feature in terms of sticking effects on porous walls. Since macroscopic and microscopic diffusion coefficients can be determined using the same transient grating experiment by looking at the long- and the short-time-scale behaviours, respectively, it is suggested these two techniques are used simultaneously in order to investigate the influence of pore tortuosity and connectivity on the diffusion properties.

1. Introduction

Nowadays, much interest has been devoted to the study of porous materials, and recent work (Kats and Thompson 1985) on rock structures seems to indicate that the geometry of some pore spaces is fractal (Mandelbrot 1975) (structures with a dilation symmetry). In contrast, one of the most intensively studied porous materials is Corning Vycor glass (PVG) (7930), the structure of which seems to be well represented through a compact packing of glass spheres of about 200 Å diameter so that the pore radius is about 20 Å and the porosity about 28% (Kadukora 1983); this is confirmed by electron microscopy photographs (Kadukora 1983). In the same way, this description agrees quite well with recent results on superfluid helium embedded in this porous material (Beamish *et al* 1983) and with x-ray scattering (Schaefer *et al* 1987).

However, different researchers have tentatively suggested a fractal structure for PVG in view of their recent results concerning one-step energy transfer (Even *et al* 1984) and diffusion of excited molecules (Dozier *et al* 1986) in this porous material. For instance, the time and concentration dependences of the energy transfer occurring between an excited donor molecule (rhodamine B) and a distribution of acceptor molecules (malachite green) have been determined by Even *et al* (1984) who have interpreted their results in the light of the Klafter–Blumen (1984) theory of a one-step trapping process due to a dipole–dipole interaction occurring on a fractal space of dimension $\bar{d}$. They concluded that the pore structure had a 1.75 fractal dimension. However, Yang *et al* (1985) have demonstrated that such a transfer strongly depends on the variations in the

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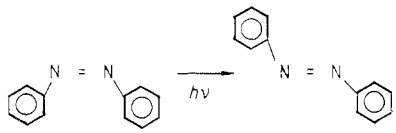
local environment on a typical length scale that this experimental set-up is unable to test real dilation symmetry and the fractal character of the space. Moreover, Yang *et al* (1985) have theoretically derived the main features of the experimental results, assuming only the previously mentioned structure which is made of a compact packing of spheres; this makes the fractal interpretation really doubtful.

Dozier *et al* (1986) have performed transient grating experiments on a solution of a dye molecule (azobenzene) which undergoes a photo-isomerisation:



cis-azobenzene *trans*-azobenzene

After much care has been taken in order to try to avoid any sticking of the azobenzene on the surface of the pores and after an index matching of the liquid embedding the Vycor, they could measure the diffusion coefficient in both the bulk solution and the solution in PVG and found that these two diffusion coefficients differ from each other by a factor of about 50. They interpreted this result by assuming a large tortuosity of the paths connecting the pores and a small connectivity of the pores at a small length scale compared with the interfringe of the gratings. On the assumption that these geometrical features can be mapped on a fractal or a percolation model, the diffusion coefficient can be calculated (Evesque *et al* 1985a, b); it depends not only on the fractal dimension but also on the spectral dimension (Alexander and Orbach 1983, Rammal and Toulouse 1983) so that a whole class of different fractal spaces with different fractal dimensions is possible (Dozier *et al* 1986) without taking into account any sticking effect.

This paper is aimed at detecting any sticking anomaly in these diffusion coefficients by performing transient grating experiments on a picosecond time scale and measuring typical reorientation times of the molecule using an analysis based on the effects of the electric field polarisation. The basic idea underlying this work can be summarised as follows: since the works of Lord Rayleigh, Einstein, Langevin and Perrin on Brownian motion, it is well established that rotational and translational diffusions are related to each other in a bulk liquid. (This is not true for adsorption processes.) So, the assumption that the translational diffusion coefficient measured by the transient grating method is not disturbed by sticking effects implies that the rotational relaxation time of the molecule is independent of whether the liquid is or is not embeded in PVG. On the contrary, if we find two different rotational relaxation times for the molecule in the bulk solution and in the liquid embedded in PVG, this will be induced by a very local change in the translational and rotational diffusion properties (i.e. on a much smaller length scale than the 40 Å diameter of the pore size since the hydrodynamic radius of azobenzene is about 6.5 Å, (Dozier *et al* 1986)). In turn, this will probably mean that the molecule sticks on the wall of the pores.

The goal of this paper is manifold.

(i) We present here an experimental method which uses the transient grating technique to determine molecular diffusion coefficients from a 1 nm scale to a 1 μm scale. This new method can be quite well adapted to the exploration and the determination of fractals (investigation over three orders of magnitude in length).

(ii) We determined the rotational relaxation time of azobenzene in a liquid embedded in PVG.

(iii) We studied the long-time (0.1 ms) dynamics of azobenzene excited states. We proved that our picosecond excitation does not yield the isomeric form which was observed by Dozier *et al* (1986).

(iv) We measured the optical density of the bulk solution and that of the solution embedded in PVG samples. Both solutions were in thermodynamic equilibrium. We found a strong increase in the effective concentration of azobenzene in PVG. We interpret these results by means of a model based on the physisorption of azobenzene on pore walls. We found a mean sticking time of about 0.5 ns. This simple model may include a large increase in the viscosity of the fluid inside the porous medium. We want to emphasise that our physisorption process is not related to the chemisorption reported by Dozier *et al* (1986) which lasts more than 1 s. They observed this phenomenon on some locations of underivatised samples. When this chemisorption was not observed in these samples, they found similar results to those obtained with derivatised samples. Our underivatised samples do not exhibit such chemisorption effects.

2. Experimental arrangement and detection

2.1. Optical arrangement

The transient grating is schematically shown in figure 1. A 1.06 μm infrared beam of an acousto-optically mode-locked and Q-switched neodymium-doped yttrium aluminium garnet laser is frequency doubled through a CD*A crystal. This 532 nm beam is then divided into two equal parts which are focused at the same point of the studied sample. Changing the focal length of this lens allowed us to vary the angle θ between the two excitation beams (wavevectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$) and then the inter-fringe spacing of the gratings.

A probe beam of wavevector $\boldsymbol{k}_3$ obeying the Bragg condition was focused on the excited region of the sample. Analysing the time dependence of the signal diffracted along the direction $\boldsymbol{k}_4 = \boldsymbol{k}_3 - \boldsymbol{k}_2 + \boldsymbol{k}_1$ allowed us to determine the evolution of the grating contrast. The 532 nm excitation beam consists of a repetitive series of some 40 pulses of 100 ps width and separated by 6 ns. These are emitted at a repetition rate equal to or less than 500 Hz (the Q-switch frequency). So, two time scales were investigated by this method: 0.1–6 ns and 0.3 μs–2 ms. This last range was investigated using a 0.1 mW

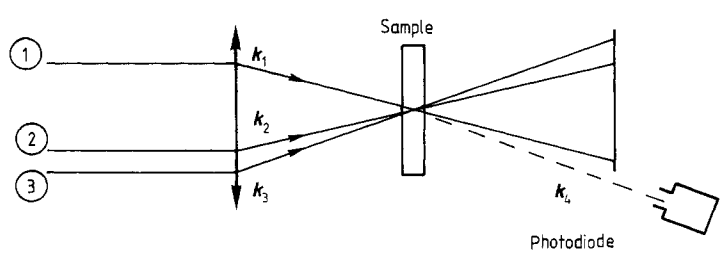


Figure 1. The experimental arrangement. Beams 1 and 2 are the excitation beams of a Q-switched mode-locked yttrium aluminium garnet laser which has been frequency doubled. Beam 3 is either a continuous-wave He–Ne laser for long-time-scale experiments (1 μs–2 ms) or a part of the frequency-doubled yttrium aluminium garnet laser excitation beam for short-time-scale experiments (0.1–6 ns).

continuous-wave He–Ne laser; the diffracted signal was detected using a photomultiplier and averaged on a Le Croy 9400 digital oscilloscope. In the shorter-line (0.1–6 ns) case, 20% of the excitation beam intensity was optically delayed and used as a probe beam; varying the delay allowed us to determine the time dependence of the grating contrast. In order to increase the signal-to-noise ratio, a mechanical chopper running at half the Q-switch frequency switched off the probe beam intensity every two emissions. The diffracted signal was detected using a Schottky barrier photodiode and a lock-in amplifier and then stored in a microcomputer which was also used to drive the optical delay time τ_D.

Excitation beams were polarised in order to create a spatial modulation of polarised excited states. These excitations then induce polarisation of the sample, the time dependence of which was measured by a third probe beam with different directions of polarisation.

2.2. *Sample preparation*

Our industrial porous Vycor glass (PVG) was obtained from Corning Glass Corporation and is made by the phase separation of boron in borosilicate glass. The phase-separated boron, which is removed by HF acid leaching, forms a connected path which produces the pore space. Its pore size diameter is sharply peaked at 42 ± 2 Å which is large compared with the typical hydrodynamic radius of an azobenzene molecule in ordinary fluid (6.5 Å) (Dozier *et al* 1986).

Such small fluctuations in the pore diameter are really compatible with the classical view of spinodal decomposition which gives rather regularly spaced concentration fluctuations (Schaefer *et al* 1987).

It is well known that much care has to be taken when doping a porous medium in order to obtain reproducible results. We used the well defined and studied experimental conditions determined by Dozier *et al* (1986). For instance, a binary solution of azobenzene consisting of a mixture of 4.3 mol of methanol in toluene was chosen; this leads to perfect index matching with PVG. Two different concentrations of azobenzene (8 mM and 48 mM) were used to study the azobenzene properties in the bulk fluid, but only the smaller concentrated solution was embedded in PVG, the second solution leading to too large an optical density in PVG for transient grating experiments.

Our experimental procedure for preparing the PVG sample was as described by Dozier *et al* (1986). First, PVG was immersed in methanol for 3 d; the methanol was then evaporated. The same procedure was repeated with the binary solvent alone (without azobenzene) (absorption and evaporation). Finally, PVG was embedded in the azobenzene solution for 3 d.

As has already been explained in § 1, we did not use the 'derivatisation' procedure which had been used for the second sample of Dozier *et al* since our sample does not exhibit any chemisorption effect; total rotational relaxation is achieved in a few nanoseconds whereas chemisorption leads to relaxation times of several seconds. Both the PVG and the bulk fluid samples were 4 mm thick.

Finally, we note that we obtained a permanent grating which is built up in a few seconds when we excite the sample at the same location. This is due to the high power (50 kW for each picosecond pulse) together with the high repetition rate which allows a multi-photon chemical reaction to take place, destroying the azobenzene molecule. This phenomenon was avoided by placing the sample in a rotating mount so that the impact point of the laser beam changed with time.

3. Optical density and interpretation

3.1. Optical density measurements

Index matching between the PVG and binary fluid was obtained to prevent light scattering. Moreover, we checked that the ratio of the optical densities of two different samples is nearly independent of the wavelength and can be used to determine the concentration of the samples. At 532 nm, the optical densities of the bulk fluid doped at 8 mM with azobenzene and of the PVG sample are respectively $d_B = 0.5$ and $d_p = 2.31$. The c_p/c_B ratio of the azobenzene concentration c_p contained in a pore of PVG to the azobenzene concentration c_B in the bulk fluid is given by

$$c_p/c_B = d_p/\varphi d_B = 16.5 \tag{1}$$

where φ (=0.28) is the PVG porosity.

These two samples are in equilibrium with each other, since they were prepared from the same solution, so that a c_p/c_B ratio of 16.5 clearly indicates that azobenzene much prefers to be in the PVG than to stay in the bulk fluid or, in other words, that its energy is less in PVG than in the bulk fluid. Different models can be used to explain this result.

3.2. Models

The first simplest model—model a—considers that the fluid in the pore has the same azobenzene concentration as in the bulk fluid but that the average concentration of azobenzene in PVG is increased owing to sticking effects on the walls of the pores. If c_w is the azobenzene concentration on the walls and $c_p = c_w + c_B$, 94% of the azobenzene contained in PVG sticks on the walls; this enables us to compute the coverage of the pore surface by azobenzene molecules.

As a simple model of the porous medium, let us consider a compact packing of monodispersed glass spheres, the pores being the space which is left free between these spheres. If ($\approx$100 Å) R is the radius of a glass sphere and we consider a cubic face-centred compact packing model which can explain the value of 0.28 for the porosity φ, the total surface area S of the spheres in a volume V is $\pi V/(\sqrt{2}R) \simeq 2V/R$ which is about $2 \times 10^5\ \mathrm{m^2\,l^{-1}}$. S is not very different from the actual measured value of $1.33 \times 10^5\ \mathrm{m^2\,l^{-1}}$ (Even *et al* 1984). When the typical radius R_0 of the azobenzene molecule of about 4.5 Å and the concentration of the stuck azobenzene are taken into account, the surface coverage of pore walls in PVG samples is $\pi R_0^2 N_A \varphi c_w$ (N_A is the Avogadro number). This leads to an experimental estimate of the surface coverage of the order of unity, which indicates a strong azobenzene–glass interaction. It should be noted that R_0 is smaller than the hydrodynamic radius (6.5 Å) since this latter value is increased as a result of some solvent molecules which are stuck to azobenzene.

Model a is obviously based on crude approximations and one should introduce other parameters to give model b; for instance since the fluid spontaneously wets PVG and as there is a large surface area of PVG, it is highly probable that the chemical properties (and also the real concentrations of azobenzene) inside and outside the porous material are different.

Moreover (model c), it is possible that, instead of the two types of azobenzene molecule—stuck and not stuck on the walls of the pores—there could exist a concentration gradient of azobenzene along the perpendicular to the surface of the walls.

The surface itself could also be made up of a distribution of sites with different sticking probabilities, especially near the contact point between two glass spheres. Finally, instead of the fact that the walls are covered by a monolayer of azobenzene, in some locations a distribution of superimposed two or three layers might exist; this will change the time behaviour of the sticking–unsticking phenomenon drastically.

We shall now discuss the implications that these different models have on translational and rotational diffusion coefficients.

3.3. Influence of sticking on diffusion coefficients

For simplicity, in model a, we assume that, during sticking, the molecules do not move and rotate. Each molecule has a probability $c_B/(c_w + c_B)$ of being in the bulk and a probability $c_w/(c_w + c_B)$ of being stuck on the wall. So, as far as the ergodic principle is satisfied (no chemisorption), the average time spent by each molecule in the bulk solution is reduced by a factor $c_B/(c_w + c_B)$. This average time is the effective time for translation diffusion. If D_B is the translation diffusion coefficient in the bulk fluid, the average diffusion coefficient $\langle D_B \rangle$ is reduced by the factor $c_B/(c_w + c_B)$:

$$\langle D_B \rangle = D_B c_B/(c_B + c_w). \tag{2}$$

This $\langle D_B \rangle$ value does not take into account possible tortuosity.

We note that $\langle D_B \rangle$ is independent of the sticking time τ_s and unsticking time τ_u. In this model the rate equations are

$$\mathrm{d}c_B/\mathrm{d}t = c_B/\tau_u - c_w/\tau_s = -\mathrm{d}c_w/\mathrm{d}t.$$

They give at equilibrium

$$\tau_u/c_B = \tau_s/c_w.$$

On the contrary, τ_u will appear in the rotation characteristics; when τ_u is long compared with the rotation time τ_r of the molecule which is free in the bulk fluid, the rotation of the molecule has two components: one fast (τ_r) which corresponds to rotations of already free molecules and the other is $\tau_r' \simeq \tau_s + \tau_r$ for the stuck molecules.

These expressions of rotation time are only valid when most of the unstuck molecules rotate freely in the pores. This condition requires the pore size to be much larger than that of the molecules; which is effectively so in our case.

In model b, the expressions have to be modified to take into account the increase (or decrease) in the viscosity; rotational relaxation time increases (or decreases) and translational diffusion coefficients decreases (or increases).

The assumptions made in model c lead to a distribution of rotation times and to intricate decay shapes of rotational relaxation which are no longer pure exponentials.

4. Time-resolved results and discussion

When two coherent light beams of wavelength λ_0 are time coincident, are polarised along the same axis and cross each other at an angle θ in a sample, their electric fields interfere. In some cases, these interferences can be transferred to the sample so that one obtains spatially modulated gratings of inter-fringe spacing $\Lambda = \lambda_0/2 \sin(\theta/2)$ for a given time. These gratings can then be read during this time using the diffracted signal from a third incident beam. This is the transient grating technique.

In an absorbing medium, this intensity modulation generates spatial modulation of the electronic excited- and ground-state populations so that the complex index of refraction also becomes spatially modulated for a characteristic time equal to the lifetime of the excited states. This light modulation can also produce a local heating or an electrostriction effect, inducing phonon generation which, in turn, is dissipated through either a coherent propagation or an incoherent diffusion process (Fayer 1986); this dissipation occurs within a characteristic time which depends on the inter-fringe spacing, on the velocity of sound or on the diffusion coefficient. Moreover, when the excited states are mobile (i.e. when the sample is made up of absorbing molecules in solution), migration of electronic states (or molecules) can occur and leads to processes of modulation fading similar to the coherent or incoherent migrations which occur in the phonon case. It also leads to a new phenomenon; owing to optical selection rules, the molecules which are excited by the two excitation beams have a preferential orientation so that the intensity of the diffracted signal depends on the probe beam polarisation. After excitation, molecular orientational relaxation occurs. When the probe beam polarisation is parallel to the pump beam polarisation, molecular reorientation leads to a decrease in the diffracted signal; on the contrary, when the probe beam polarisation is perpendicular to the pump beam polarisation, reorientation leads to a rapid increase in the signal. It can be proved that the diffracted signal is independent of these reorientation processes when the probe beam polarisation is oriented at an orientation angle θ_m of 54°7′ (Fayer 1986). This angle, called the magic angle, does not depend on the intimate details of the relaxation processes (multi-exponentials, etc). Therefore the behaviour of the diffracted beam reflects the pure time dependence $I_e(t)$ of the average excited- and ground-state populations. It can also be shown (Tao 1969) that the time dependence of the molecular reorientation $r(t)$ can be obtained from the experimental dependences of the intensities $I_{\parallel}/(t)$ and $I_{\perp}(t)$ of the diffracted signals arising from probe beams polarised parallel and perpendicular, respectively, to the excitation beams. According to Tao (1969),

$$r(t) = (I_{\parallel}(t) - I_{\perp}(t))/(I_{\parallel}(t) + 2I_{\perp}(t)). \tag{3}$$

In the most general case, $r(t)$ is the sum of three exponential decays since the three principal axes of a molecule are not equivalent and correspond to three different coefficients of rotational diffusion (Perrin 1934). However, for a spherical molecule of hydrodynamic volume V_H in a liquid of viscosity η, $r(t)$ turns out to be a pure exponential of time constant $\tau_r = V_H\eta/kT$ (where T is the temperature and k the Boltzmann constant). In fact, the azobenzene molecule is not spherical, but our experimental accuracy does not allow us to extract more than one typical reorientation time (figure 2(*a*)), since this process is already convoluted with the spontaneous decay of the excited-state population.

Accordingly, we performed transient grating experiments on the three samples under three different probe beam polarisations (parallel to the excitation polarisation, perpendicular to the excitation polarisation, and oriented at the magic angle), with different inter-fringe spacings Λ varying from 4 to 13 μm and with different excitation powers ranging from 5 to 50 MW cm^{-2}.

We could no longer detect any difference between the behaviours of the 8 mM and the 48 mM solutions of azobenzene, in either the short- or the long-time range, so that we report here only the experimental result on the 8 mM solution of azobenzene as a bulk fluid or in PVG.

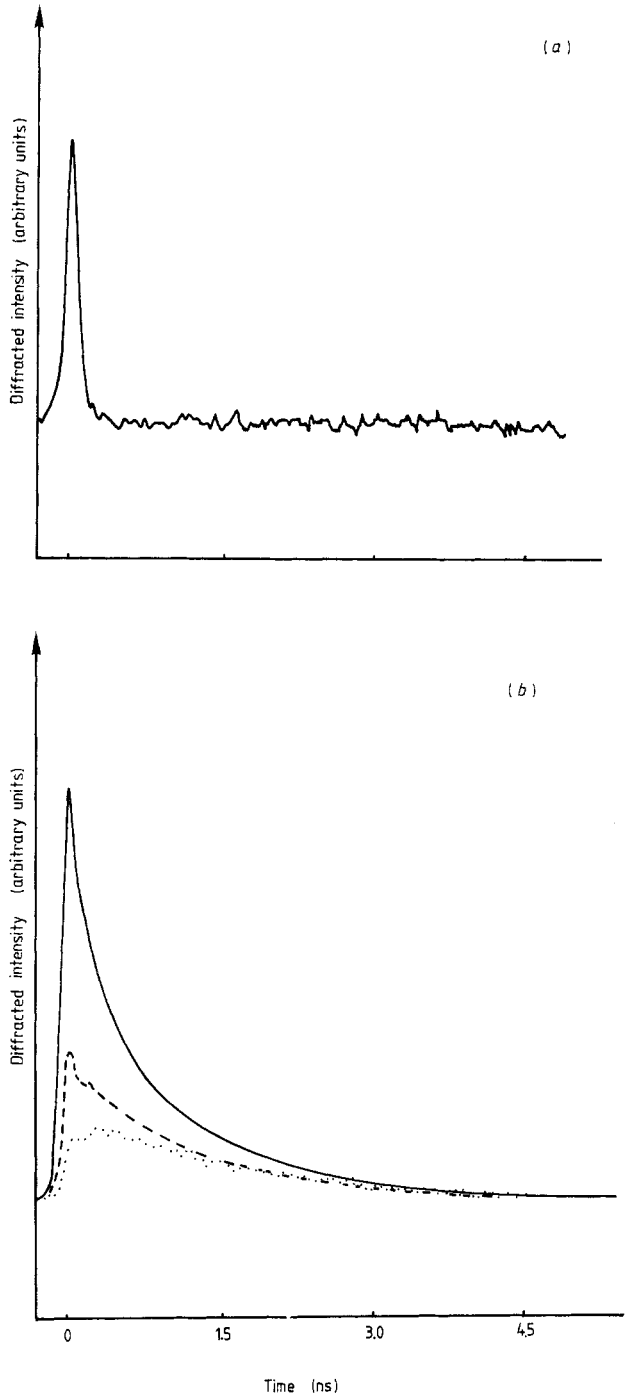


Figure 2. Short-time response of a transient grating experiment. (*a*) for an 8 mM azobenzene bulk solution; (*b*) for an 8 mM azobenzene solution in a porous Vycor glass at three different probe beam polarisations (——, polarisation parallel to the excitation beam polarisation; · · · · ·, polarisation perpendicular to the excitation beam polarisation; – – –, polarisation at the magic angle (see text)).

4.1. Short-time behaviour (figure 2)

We show in figure 2(*a*) the first 6 ns of the time dependence of the diffracted signal arising from the 8 mM solution of azobenzene using a probe beam polarised parallel to the excitation beam polarisation. It consists of a rather constant signal superimposed on a sharp peak of 100 ps width which is the coherence spike (Wherrett *et al* 1983), since it is not observed when the probe beam is polarised perpendicular to the excitation beam. Moreover, as the constant signal intensity does not depend on the probe beam polarisation, one is led to conclude that azobenzene rotational relaxation occurs in a time shorter than 100 ps (the width of the coherence spike) and that the excited state of azobenzene has a lifetime much longer than 6 ns.

Figure 2(*b*) shows the short-time dependence of the signal diffracted from the PVG sample with different probe beam polarisations (at the magic angle, and parallel and perpendicular to the excitation polarisation). We should remark first that the long-time (about 6 ns) behaviour tends to a constant which is independent of the probe beam polarisation so that each molecule has in fact rotated; this implies there is no chemical adsorption. The experimental result obtained at the magic angle provides a 2.2 ns lifetime for the excited state of azobenzene. Combining the results on the two other excitation polarisations in equation (3) allows us to compute the time dependence $r(t)$ of the rotational relaxation. For simplicity, we assumed a unique rotational relaxation time τ_r. The best fit gives $\tau_r = 450$ ps. This unique relaxation time τ_r implies a spherical shape for the azobenzene molecule. This crude approximation is only valid because of the lack of accuracy in the experimental results.

According to model a developed in § 3.3, and as we could not measure the rotational relaxation time of the free molecule (since the process is too fast), the time $\tau_r' = 450$ ps is the slow component; it is a measure of the sticking time. We can also interpret this result with models b and c developed in § 3.3. For instance, this increase in rotation time could arise from a large increase in the viscosity coefficient.

However, since we have established a large increase in the optical density and a large variation in the Browning rotation time, we think that the simplest model is to assume a physical adsorption process. According to equation (2) this model predicts a large decrease in the effective translational diffusion coefficient (equation (1)). This experimental fact has actually been found by Dozier *et al* (1986) who have measured the macroscopic diffusion coefficients (D_B in the bulk solution and D in PVG). They obtained $D_B = 2.4 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ and $D = 3.6 \times 10^{-8}\,\mathrm{cm^2\,s^{-1}}$. The ratio of these experimental values is 66.6, which is four times larger than our value of 16.5. This factor of 4 could be attributed to a pure tortuosity effect. In this case, it is not far from the value of 5.6 found by Smith (1981).

The interpretation of Dozier *et al* is rather different from ours since they attributed this change to a large increase in the path tortuosity together with a lack of connectivity of the pores, leading also to the emergence of dead-end channels. In order to compute the scale on which this material seems to be disordered, they mapped the diffusion problem and the path structure on a fractal space, characterised by its fractal dimension $\bar{d}$ and spectral dimension $\bar{\bar{d}}$ (Alexander and Orbach 1983, Rammal and Toulouse 1983), on a length scale larger than the pore size ($l_1 = 30$ Å) but smaller than a typical length ($l_2 > l_1$). According to the transient grating theory on a fractal space (Dozier *et al* 1986, Evesque *et al* 1985a, b) the ratio of the macroscopic to microscopic diffusion coefficient can be expressed as

$$D/D_B = (l_1/l_2)^{2(\bar{d}-\bar{\bar{d}})/\bar{\bar{d}}}. \tag{4}$$

An infinity of different fractal spaces exists for which the experimental results are satisfied. For instance, Dozier *et al* (1986) have obtained $l_2 = 300$ Å and $l_1 = 30$ Å when assuming a percolation network.

It seems to us that our result casts serious doubt on the interpretation of Dozier *et al* (1986). However, it is well known that porous media lead to irreproducible experimental results which are induced by the great sensitivity of these experimental results to the conditions of the sample preparation, as shown by Dozier *et al* (1986, figure 2). Moreover it is worth noting that our excitation conditions are different from theirs so that the excited states and molecules which are studied here are probably not the isomeric form the diffusion properties of which have been already investigated by Dozier *et al* (1986). We then investigated the long-time behaviour of the diffracted signal intensity in order to prove that this feature exists.

4.2. Long-time behaviour (figure 3)

The long-time behaviour of the diffracted signals which are given in figure 3 depends neither on the probe beam polarisation nor on the inter-fringe spacing. These data establish clearly that the gratings decay much faster in PVG than in the bulk solution and the two respective decay times are 5 μs and 50 μs. As they are both several orders of magnitude shorter than the *cis*-to-*trans*-azobenzene relaxation time (Dozier *et al* 1986), these lifetimes must concern the triplet ground state of the *trans*-azobenzene. It definitely proves that our experiments deal with states different from the isomeric form studied by Dozier *et al*. This is in agreement with the well known result that efficient photo-isomerisation is only performed when using light pulses longer than 1 μs.

The relaxation times which have been measured are much shorter for the azobenzene in PVG than for this molecule in the bulk fluid. This may arise from an enhancement of

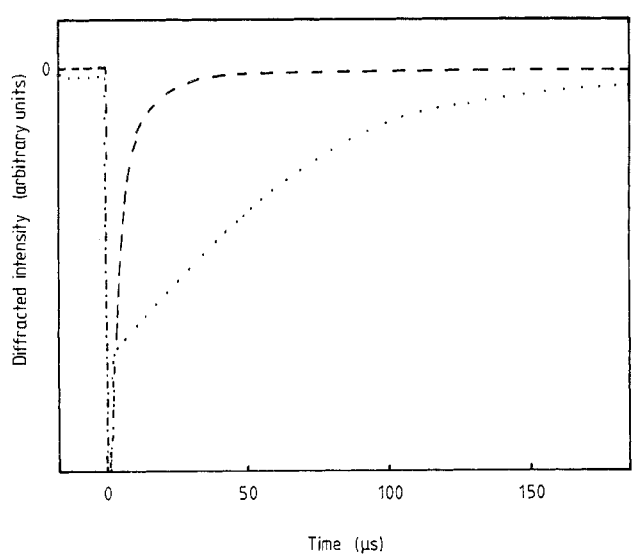


Figure 3. Long-time behaviour of the transient grating response: ·····, in a bulk solution doped with 8 mM of azobenzene; ---, in an 8 mM azobenzene solution in porous Vycor glass.

non-radiative de-excitation processes which is probably induced by repetitive collisions of azobenzene on the porous walls; in other words, this is related to repetitive sticking-unsticking processes on the PVG surface.

5. Conclusion

Optical density measurements on azobenzene in a solution of 4.3 mol of methanol in toluene have clearly demonstrated that the azobenzene concentration in the bulk fluid is 16 times smaller than that of the fluid embedded in a porous Vycor glass. This result together with the large change in the rotational relaxation time measured by picosecond transient grating experiment is consistent with an interpretation assuming a physisorption mechanism of azobenzene on the walls of the pores; in this case the average sticking time would be equal to the measured rotational relaxation time (450 ps). In contrast, we did not detect any chemisorption effect.

These results seem to be in contradiction with the hypothesis relating the large decrease in the macroscopic diffusion coefficient of the *cis*-azobenzene to the existence of a huge pore tortuosity and to a fractal structure of the pore space (Dozier *et al* 1986). Our results, on the contrary, indicate that most of the observed features arise from the sticking effect of molecules on the pore surface. *Our interpretation is compatible with the full range of observed phenomena.*

However, since our experiment, which was performed on a time scale longer than 1 μs, measures an excited-state lifetime which is much smaller than that determined by Dozier *et al* (1986), it definitely proves that our experimental set-up does not test exactly the same diffusion problem. Moreover, in this special case, as it is well known that an experimental measurement performed on porous materials depends drastically on the preparation condition of the sample, it might be that our results and theirs are not measured on identical samples.

In any case, we want to emphasise that, if one can find a molecule which exhibits a long-lifetime greater than (1s) excited state which can be excited by a picosecond laser, the transient grating experiment is a well suited technique which gives information about diffusion properties over a wide range of lengths. For instance, when this molecule is embedded in a porous medium, the experiment can first test whether the molecule sticks to the pore walls or not. If it does not stick, the short-time measurement, using polarised lasers, allows us to determine the rotational relaxation time which is induced by Brownian motion. This then determines the microscopic diffusion coefficients. The analysis of the long-time response as a function of the inter-fringe spacing determines the macroscopic diffusion coefficients. On the contrary, when a large number of molecules stick to the walls of the pore, the rotational reorientation time corresponds to the average time during which the molecules stay stuck on a wall (since rotation and migration are unlikely to occur when a molecule is stuck); under these circumstances, the rotational relaxation time can no longer be related to the microscopic diffusion coefficient. Then, determining the average ratio of the stuck to unstuck molecules through an optical absorption measurement allows us to compute, with a few assumptions, the macroscopic diffusion coefficient in porous material. On these assumptions, the calculated diffusion coefficient will only concern a material which does not present any tortuosity or lack of connectivity. So, the ratio of the computed to measured macroscopic diffusion coefficient will determine, at least in principle, the tortuosity of the paths and the fractal nature of the pore spaces.

Thus, it seems to us that the transient grating experiment can be an efficient tool for investigating the diffusion properties of disordered materials. This is so because one can perform such an experiment over quite a large range of time scales. This last condition is unfortunately difficult to achieve experimentally, but it is realised when dealing with a photo-isomerisation process.

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