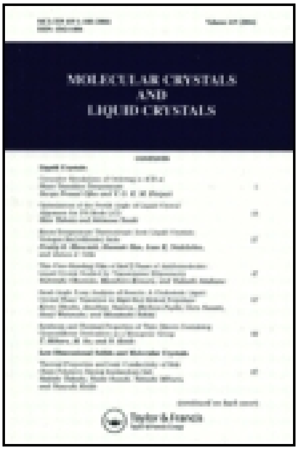

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# SMALL MOLECULES IN HOLE-BURNING SYSTEMS: A LOCAL ANTENNA FOR INFRARED-INDUCED SPECTRAL DIFFUSION PROCESSES

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Abstract Light-induced spectral diffusion in photochemical hole-burning systems is investigated with respect to its dependence on the frequency of the irradiated infrared light in the wavelength range between 2 µm and 11 µm. The investigated system is polymethylmethacrylate (PMMA) containing up to one volume percent water molecules and doped with free-base phthalocyanine ($H_2Pc$). Different resonant contributions to the infrared-induced spectral diffusion show that the microscopic origin of the observed diffusion process is a reorientation of $H_2O$ molecules. A simple kinetic model, based on the idea of two possible sites for each $H_2O$ molecule, allows to describe the dependence of the hole-broadening on infrared intensity and illumination time in a very good quantitative fashion.

## INTRODUCTION

In the past decade much experimental and theoretical work was done on spectral diffusion in amorphous solids. It turned out that at low temperatures optical dephasing phenomena[1] as well as the numerous caloric data[2] can be well described by assuming the presence of low-energy excitations, the so-called two-level systems (TLS). Photochemical hole-burning[3] and optical echo experiments[4]. have provided an experimental evidence for a different dynamics of optical transitions in glassy systems as compared to crystalline matrices. For glassy organic solids, the TLS concept was first proposed by Small and coworkers[5] and was later used by Reinecke[6] to explain low-temperature optical linewidths. At temperatures above 1 K not only tunneling transitions but also localized vibrations influence the physical properties. Both types of mechanisms have recently been incorporated in the soft potential model which contains the well-known tunneling model as a special case.

A microscopic interpretation of optical line-broadening phenomena in terms of e.g. local excitations of the matrix or switching of optically addressed chemical groups suffered from the lack of experimental data. In the past, several experimental techniques have been developed to shed light on the microscopic mechanism of the phenomena. The techniques are all based on the generation of phonons in the matrix material, expecially in the neighborhood of the spectral probe. Heat pulses from external heaters produce a broad distribution of phonon frequencies inside the chromophor-host system and permit the investigation of the dynamics of barrier crossings and of the coupling between the TLS and the dye molecules[7]. The IR-absorption method, on the other hand, in which the sample is illuminated with narrow-band IR-light, allows one to generate phonons with a comparatively small energy distribution in the direct neighborhood of the optical probe[8]. The contribution of the broadband black-body background radiation can be minimized by an appropriate intensity of a narrow-band IR-source.

The method of photochemical hole-burning (PHB)[3] is appropriate for detecting small perturbations in the matrix such as a transient change of the phonon distribution or permanent matrix rearrangements in the vicinity of the dye molecules. Such rearrangements can be due to a configurational change of parts of the polymer main chain or to a reorientation of small molecules (water), which may be embedded in the matrix in addition to the dye molecules.

## EXPERIMENTAL

The experimental setup for burning and detecting spectral holes with a narrow band laser has been described elsewhere[3]. The experiments were performed at 1.8 K in a bath cryostat in which the sample was immersed in superfluid helium. The sample was polymethylmethacrylate (PMMA), doped with free-base phthalocyanine ($H_2Pc$) at low concentration ($10^{-4}$ mol/mol). Because of its strong hydrophilic nature, PMMA has a high capacity of water absorption at atmospheric conditions. The optical windows of the cryostat consisted of crystalline $BaF_2$, which allowed the study of hole-burning spectra in the lowest vibrational band of the electronic $S_0$ - $S_1$ transition at about 0.69 μm as well as under IR-illumination between 2 μm and 11 μm. A globar was used as an IR-radiation source and frequency selection was performed by a monochromator and dielectric IR-filters. Typical IR-intensities at the location of the sample were some 100 μW/cm$^2$ with a bandwidth between 0.05 μm and 0.2 μm.

## INDUCED SPECTRAL DIFFUSION

The IR-induced spectral diffusion is caused by addressing specific moieties within the matrix via the excitation of local vibrations. In the following, weakly bound water molecules are studied. When a change in the spatial configuration takes place during the relaxation process of a water molecule, the optical transition of a neighbouring dye molecule will be affected. Optical absorbers in glasses are therefore very sensitive probes for local rearrangements and are suited for a microscopic study of this topic. Because of the low irradiation intensities the temperature of the matrix do not increase by more than 0.01 K and, hence, yield no measurable dephasing effect via a change of the phonon distribution.

The experimental procedure is the following: A spectral hole is burnt and its spectrum is repeatedly recorded while the sample is being exposed to infrared radiation of a certain wavelength at a constant irradiation intensity. Figure 1 (left side) shows a typical increase of the hole-width and the strong dependence of this behaviour on the IR-wavelength.

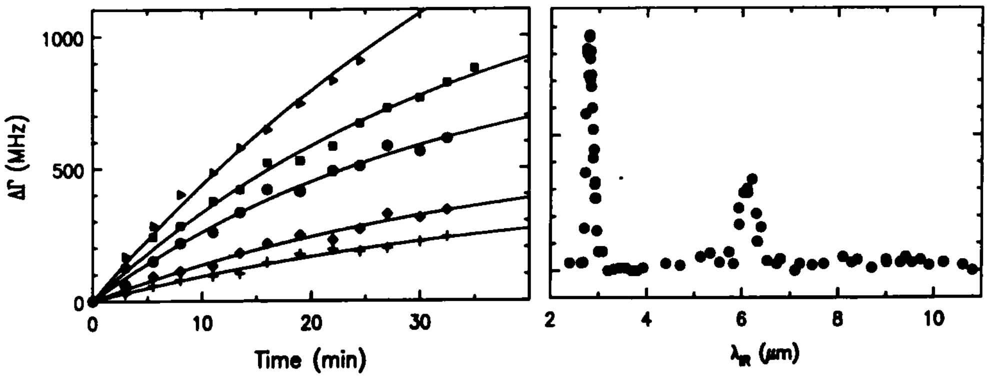

Figure 1 Left-side: Time evolution of the hole broadening by different IR-wavelengths. (from top to bottom: 2.80 μm, 2.86 μm, 2.90 μm, 2.96 μm, 3.04 μm)
Right-side: Dependence of the hole-broadening due to induced spectral diffusion on IR-wavelength after $t_0$ = 35 min.

To illustrate the pronounced spectral selectivity, one value of each hole-broadening curve at $t_0 = 35$ min is plotted in the right side of figure 1 versus the corresponding IR-wavelength. The data points do not simply reflect the absorption behaviour of the sample (curve B in figure 2). The small concentration of water molecules in the matrix gives rise to non-saturated absorption bands near 2.8 μm and 6.1 μm. They correspond to the fundamental stretching and bending vibrations of $H_2O$, respectively. The quotient spectrum (curve C in figure 2) of water-free and water saturated PMMA yields the exact position of the $H_2O$ absorption bands, which agree very well with the resonances found in our experiment.

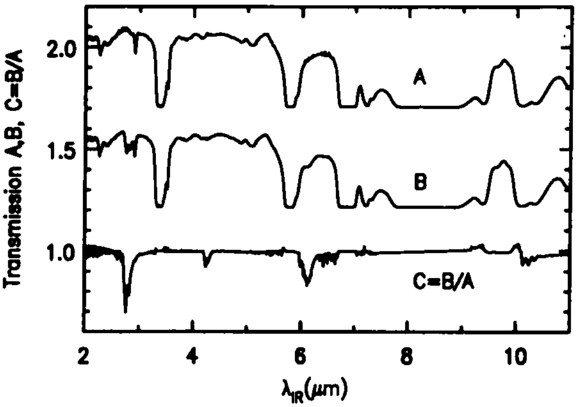

Figure 2 Transmission spectra of PMMA without (curve A) and with (curve B) natural water content. The quotient C=B/A reveals the $H_2O$ absorption.

Replacing protonated with deuterated water yields a red shift of the IR-resonances which also agrees very well with the corresponding absorption spectra of heavy water.

In analogy to the tunneling model, which is based on the assumption of two potential minima, we assume two stable sites for each water molecule (figure 3). Since the experimental results indicate that a permanent change in the matrix occurs, transitions between the two sites are only allowed via the first excited vibrational states. Using such a simple four-level model for the underlying kinetics, we are able to explain the temporal behaviour of the induced spectral diffusion in a quantitative fashion.

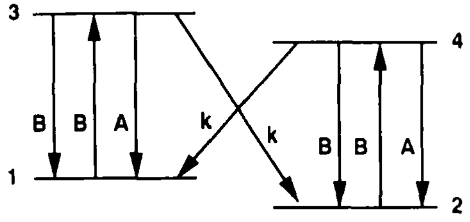

Figure 3 Energy level scheme of a $H_2O$ molecule in a two site model

The two ground states are labelled 1 and 2, the first vibrationally excited states 3 and 4, respectively. The IR-induced and the spontaneous transition rate for each site are denoted by B and A, respectively. In our notation, B is proportional to the irradiated IR-intensity. Transitions between the two sites are denoted by the conversion rate k. The transitions shown in figure 3 lead to a system of 4 coupled linear rate equations. Since we used very low intensities of the infrared light in our experiments, we consider only the limit $B << A$ so that the population of the excited levels 3 and 4 is negligible at all times. The result is a time-dependent number of flips between the two ground states $n_f = n_{1-2} + n_{2-1}$. Only those flips are taken into account which contribute to a change in the total configuration of all water molecules with respect to the time $t = 0$ of the hole-burning process.

According to Reinecke[6], the width of the spectral-diffusion kernel $\Delta\omega$ is proportional to the number of flips $n_f$. Using the approximation that each flip yields the same contribution to $\Delta\omega$ and taking into account the decrease of the IR-intensity across the sample thickness as well as a random orientation of the $H_2O$ molecules, the result for $\Delta\omega$ can only calculated numerically. Using taylor expansion, however, a very good analytical approximation of the width of the induced spectral diffusion is given by the equation

$$\Delta\omega(t) = G\frac{N_0}{4\pi\hbar}\left(1-\left(1+\frac{2Bp_f t}{b}\right)^{-b}\right)$$

The difference between this analytical formula to the exact mathematical results is less than 5 %. $p_f$ is the flip probability of a single $H_2O$ molecule as defined by $p_f = k/(A+k)$, b is a dimensionless geometry parameter of about 2, $N_0$ is the density of the $H_2O$ molecules and G is the coupling constant between dye and water molecules. The above formula describes the dependence of the broadening of a spectral hole with respect on the number of absorbed IR-photons very well.

Moreover, it is possible to perform a test of the model. The above equation contains only two fitting parameters, the flip probability $p_f$ and the coupling constant G. These two parameters can be obtained from one single experiment.

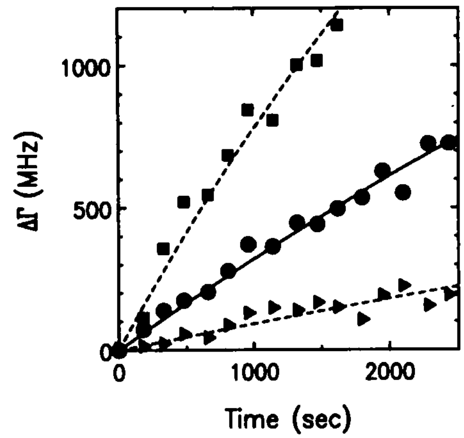

Figure 4 Test of the model. Hole broadening versus IR-irradiation time for three different IR-intensities (see text).

An example is given in figure 4. One set of experimental data (filled circles) is obtained at an IR-intensity of 80 $\mu W/cm^2$. The solid line is a fit according to the above equation and yields a flip-probability of 18 % and a coupling constant of $G = 3.6 \cdot 10^{-44}$ $Jcm^3$. (Note: The slight difference with respect to the data given in reference 9 is due to the extension of the model including the random orientation of the water molecules and the decrease of the IR-intensity according to Beer's law). With these two values it is possible to calculate the time dependence of the induced spectral diffusion for any irradition intensity. The dotted lines in figure 4 are calculated with the above equation for the intensities 230 $\mu W/cm^2$ and 20 $\mu W/cm^2$. The experimental results obtained under these conditions, represented by the squares and triangles, are in very good agreement with the theoretical predictions.

The high quantum yield of 18 % for the flip of a single water molecule becomes obvious by a comparison of the number of absorbed IR-photons (typically $10^{14}$/s) with the total number of water molecules in the sample volume (about $10^{18}$). Since a strong induced spectral diffusion is observed within several minutes, a local reorientation process with a high quantum yield must be involved.

The coupling strength between water and dye molecules can be estimated, by taking the static dipole moment of a $H_20$ molecule into account. A reorientation of $H_20$ molecules affects the dye molecules by the concomitant change in the local electric field at the location of the chromophores. Assuming a mean distance of 15 Å, and inserting data from Stark effect experiments one obtains a value of approximately $2 \cdot 10^{-44}$ $Jcm^3$ for the coupling constant which is very close to our fitted value. Together with the resonant phenomena discussed above, this yields a detailed microscopic understanding of this special kind of interaction.

## CONCLUSION

We can conclude, that spectral diffusion induced by the absorption of IR-photons in the frequency interval between 2 μm and 11 μm is found to be a resonant process. Its microscopic origin is a spatial rearrangement of weakly bound water molecules after vibrational excitation. Assuming a configurational model with only two possible sites for each water molecule and applying the theoretical model of spectral diffusion of Reinecke[6], an analytical description of the resonant hole broadening behaviour can be obtained. A variation of the IR-irradiation intensity shows that the model description yields excellent agreement with the experimental data.

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