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13. ABSTRACT *(Maximum 200 words)*

This report focuses on organically doped sol-gel glasses as novel fast response photochromic materials. In particular, we discuss time-resolved spectroscopic measurements of: 1) nanosecond optical energy transfer in organically doped glasses; 2) investigation of the spatial distribution of chromophores within the porous sol-gel matrix; 3) homogeneous dephasing of optically excited states as a probe of chromophore-host interactions; 4) time-resolved anisotropy measurements as a probe of chromophore dynamics in porous sol-gel matrices; and 5) optical limiting based on fast photophysical processes of organic chromophores. Optical energy transfer in organically doped sol-gel glasses is investigated by time-resolved fluorescence depolarization measurements. We observe nanosecond optical energy transfer and analyze these results in terms of the spatial distribution of chromophores in doped porous xerogel glasses. Time-resolved polarized emission results are also used to probe the rotational dynamics of chromophores during the fabrication process from solution to gel to porous glass. Furthermore, picosecond photon echo measurements have been used to obtain the homogeneous dephasing rate of organic dopants in an inorganic sol-gel glass, as a means of probing chromophore-host environment.

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ULTRAFAST FREQUENCY AGILE OPTICAL MATERIALS: Organically Doped Sol-Gel Glasses

FINAL REPORT

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OCTOBER 13, 1992

U.S. ARMY RESEARCH OFFICE

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A. Statement of the Problem

The need for fast response optical material is illustrated by the recent and continuing progress in the development of high intensity ultrashort laser sources and the purpose of this project has been to develop and investigate "smart" optical materials based on optical energy transfer and relaxation processes in organically doped sol-gel glasses. Furthermore, a better understanding of the basic structure, chromophore dynamics, and photophysics of organically doped sol-gel glasses is desirable given the array of proposed applications for these novel materials (e.g. fluorescent planar concentrators [1] [2], solid state dye laser materials [3][4], optical data storage media [5], nonlinear optical materials [6], environmental impurity sensors [6], etc.). Sol-gel glasses hold promise as versatile nonlinear optical materials since they can solvate a wide variety of chromophores at high concentrations. These materials can be prepared chemically at room temperature by the hydrolysis of a variety of metal alkoxides, and thin films are easily produced by dip coating or spin casting [7]. Dried gels result in rigid xerogel glass matrix with considerable porosity(~50% void volume) depending on the sol-gel chemistry [8]. In addition, polarized optical response characteristics requires a knowledge of the rotational dynamics of organic dopants in metal alkoxide solutions, gels, and xerogel glasses.

B. Summary of Important Results

1. Fast Optical Energy Transfer in Organically Doped Sol-Gel Glasses

Sol-gel glasses can be doped at relatively high concentrations with minimal aggregation since gelation of the solution occurs before drying and shrinkage of the matrix. The resulting organically doped sol-gel glass films can have high chromophore concentrations with correspondingly fast optical energy transfer processes. Furthermore, time-resolved depolarization measurements have been used to probe the rate of electronic energy transfer and the spatial distribution of chromophores in organically doped sol-gel glasses. In the absence of rotational diffusion, fluorescence depolarization is a direct measure of electronic energy transfer between chromophores [9-11]. Since the rate of dipolar energy transfer is sensitive to the proximity of neighboring molecules (i.e. rate~r^{-6}), time-resolved fluorescence anisotropy measurements have been used to probe the spatial distribution of dopants [9] in silicate and aluminosilicate sol-gel glasses.

a. Nanosecond Optical Energy Transfer

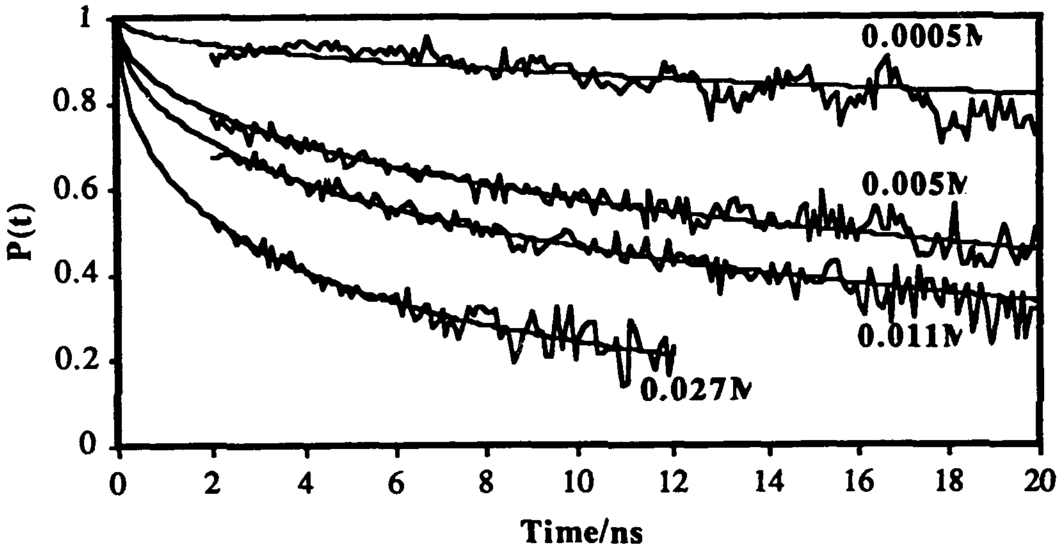
Nanosecond optical energy transfer rates have been measured in doped sol-gel glasses by time-resolved depolarization measurements. Since the time-resolved fluorescence polarization anisotropy (in the absence of rotational diffusion) is proportional to the probability that the electronic excitation still resides on the originally excited molecule, such measurements have been used to probe the rate of electronic energy transfer in organically doped sol-gel glasses. Furthermore, the large volume decrease that occurs in the gel to glass transition has been used to produce very highly doped glasses (i.e. above the maximum solution concentration) without aggregation effects. The highly doped solids result in very fast optical energy transfer rates and allow fabrication of thin glass coatings (~200nm) with high optical densities.

b. Chromophore Environment within a Sol-Gel Matrix

Where spatial disorder exists, the probability P(t) that the excitation remains on the originally excited molecule at time t, for an arbitrary spatial distribution of chromophores u(r), can be obtained by integration of the following equation,[10,11]

$$\ln P(t) = -(\rho /\lambda) \int_0^\infty (1-\exp(-\lambda\omega t))\, u(r)dr \qquad (1)$$

Time-Resolved Fluorescence Depolarization of Q doped aluminosilica



Time-Resolved Fluorescence Depolarization of Q-Al in silica films

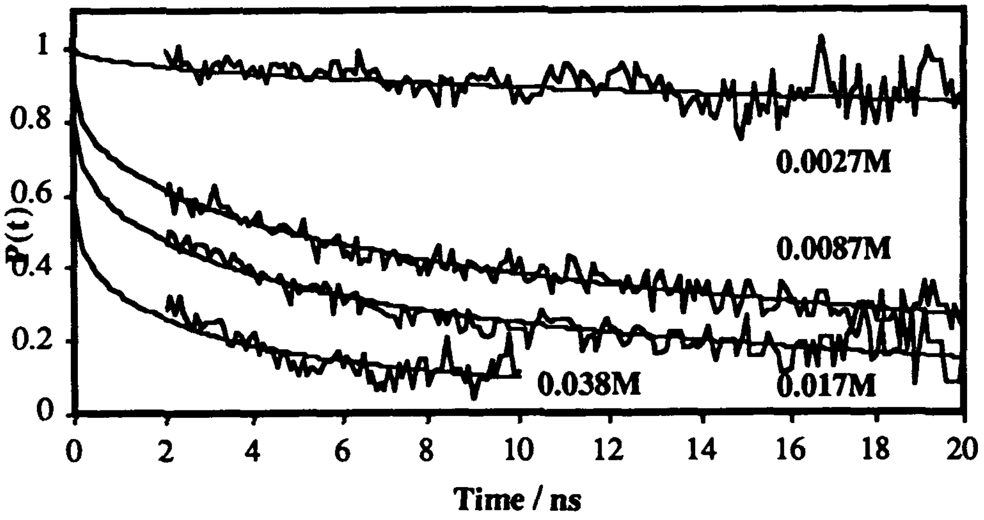


Fig. 1. Nanosecond optical energy transfer in quinizarin doped aluminosilicate and silicate sol-gel films (0.2 μm) observed by time-resolved fluorescence depolarization. In addition, the functional form of the depolarization decay has been used to investigate the spatial distribution of chromophores in these porous xerogel glass matrices. **a)** For the doped aluminosilicate glasses, the solid lines are fits to a random spatial distribution model, whereas in **b)** the doped silicate xerogels are fit by a distribution that indicates multiply occupied pores at higher concentrations.

where ρ is the number density of chromophores, $u(r)dr$ is the probability that a chromophore is located a distance r from any initially excited donor chromophore, and λ parametrizes donor-trap ($\lambda=1$) and donor-donor ($\lambda=2$) energy transfer mechanisms. Thus, an experimental measurement of P(t) can be used to evaluate a trial spatial distribution function u(r).

In an isotropic three dimensional solid (i.e. $u(r)dr = 4\pi r^2 dr$), the probability that an initially excited donor molecule remains excited a time t after excitation reduces to,[10,12]

$$P(t) = \exp(-\alpha t^{1/2}) \tag{2a}$$

where

$$\alpha = c\,\gamma\,\Gamma(1/2)\,(\lambda\tau_n)^{-1/2} \tag{2b}$$

and where c is a dimensionless concentration corresponding to the number of chromophores in a sphere of radius R_o [10]. For chromophores randomly distributed within a restricted geometry such as a zeolite or a bilayer, the time dependence of P(t) can be of a reduced exponent,

$$P(t) \sim \exp(-\beta t^{D/6}) \tag{3}$$

where D corresponds to the dimensionality of the restricted lattice and where β characterizes the energy transfer rate.[10][12][13] Thus, the time-dependence of P(t) resulting from energy transfer processes has provided a method for determining the spatial configuration of chromophores in a variety of well defined restricted geometries such as fractal lattices, finite spheres, and polymer chains.[9]

Time-resolved fluorescence depolarization measurements have been used to probe both the spatial distribution of dopant as well as the rates of electronic energy transfer in these novel solids. At high concentrations our depolarization results for quinizarin doped silicate glasses consisted of a fast unresolved component and a slowly decaying component to the fluorescence anisotropy. For the silicate glasses the depolarization results are fit by a spatial distribution consisting of a number of closely spaced neighbors in addition to an underlying random distribution. This suggests that some of the micropores within the xerogel solid appear to be multiply occupied by quinizarin molecules at high concentration.

Although an analysis of our time-resolved fluorescence depolarization data does not yield a unique determination of the chromophore distribution, the data is consistent with a fast energy transfer process within multiply occupied pores and a slower energy transfer process between randomly distributed chromophores. Thus, at high concentrations the chromophore distribution function for distances comparable to a pore radius (~30Å [14]) may increase due to multiply occupied pores. Our time-resolved fluorescence anisotropy results for Q in aluminosilica are consistent with a random distribution of dopants within the xerogel glass and our depolarization results on Q:Al doped silica at high concentrations provided evidence for energy transfer between chromophores in close contact. It is not unreasonable that different chromophore distributions exist in these two systems since Q chemically binds to the aluminosilicate glass, whereas the Q:Al complex simply becomes trapped within closed pores of the silica glass and is therefore more mobile during the gel drying process.

We conclude that in the silicate xerogels, the dopant molecules are most likely incorporated into a collection of randomly distributed micropores within the sol-gel glass, but that as the concentration is increased, a significant fraction of the molecules reside in multiply occupied micropores. The micropore diameters, r_c, for the samples in this study are on the order of 30Å, and the fast component of the anisotropy decay is due to the fast energy transfer between closely spaced molecules within multiply occupied micropores. The concentration dependence of the fluorescence depolarization for the aluminosilicate glass is fit well by a random distribution of chromophores, i.e. $P(t) = \exp(-\alpha t^{1/2})$. This indicates that the chromophores remain randomly distributed even at high concentrations, most likely due to a more restricted void volume geometry in the aluminosilicate xerogel versus the silicate glass.

c. Dispersive Energy Transfer in Low Temperature Glasses

Dispersive (i.e. frequency dependent) energy transfer [15] is observed in low temperature glasses and in glasses doped with multiple chromophores due to donor-trap processes. Such mechanisms are important for applications utilizing a light absorbing donor chromophore as an antenna and an optical trap as an actuator. Quinizarin doped aluminosilicate glasses have little dispersion in the rate of optical energy transfer at room temperature, however, dispersion is seen at 77K, as shown in Fig. 2. Energy transfer rates for 0.005M Q doped aluminosilica decrease as the excitation wavelength is moved to the red.

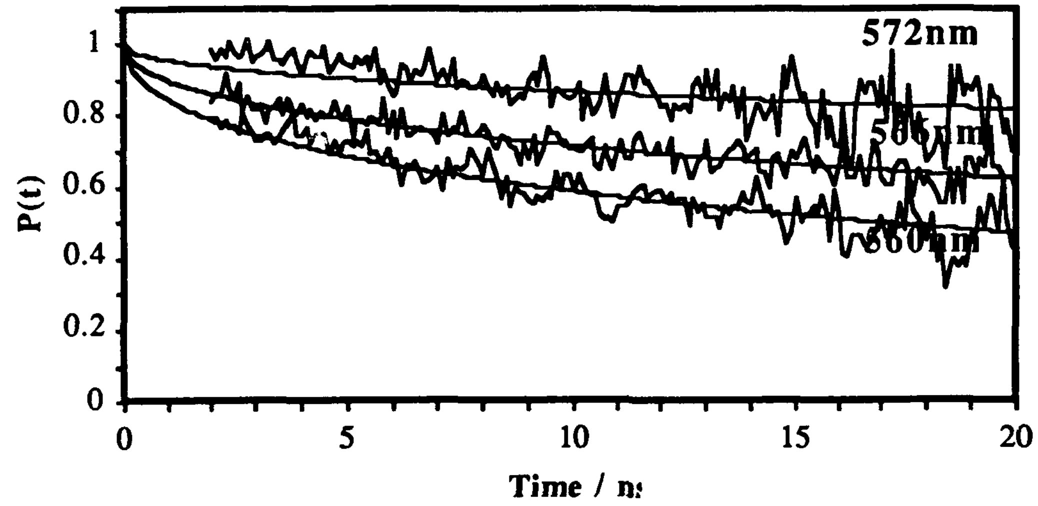


Figure 2. Dispersive energy transfer in Quinizarin doped aluminosilica at 77K. Increased energy transfer rates are observed as the excitation wavelength is lowered from 572nm, to 566nm, and 560nm.

2. Chromophore Dynamics within a Porous Sol-Gel Host

Time-resolved fluorescence depolarization measurements have been used to probe chromophore orientational dynamics in aluminosilicate and silicate solutions, gels, and porous xerogel glasses. Since orientational chromophore dynamics depend on the local viscosity, these measurements are used to probe the local chromophore environment along the solution/gel/xerogel transition. The ability of quinizarin to complex aluminum leads to different chromophore rotational dynamics in the silicate and aluminosilicate solutions and gels. However, we observe little chromophore orientational motion in either of the xerogel glasses, on a timescale of the fluorescence lifetime. In fact, rotational diffusion becomes frozen upon gelation of the monomer solution.

Time-dependent fluorescence anisotropy has been widely used for the study of orientational dynamics [16-19] and intermolecular electronic excitation transport [20-23] of probe molecules. Rotational diffusion of a chromophore is typically the dominant cause of fluorescence depolarization in low viscosity solutions. Following a polarized excitation pulse, the time-resolved fluorescence anisotropy decay for a spherical molecule is a single exponential,

$$r(t) = r_o \exp(-t/\phi) \qquad (4)$$

where the magnitude of the rotational correlation time of the chromophore (ϕ) can be calculated using the Debye-Stokes-Einstein hydrodynamic theory, which for a spherical molecule yields,

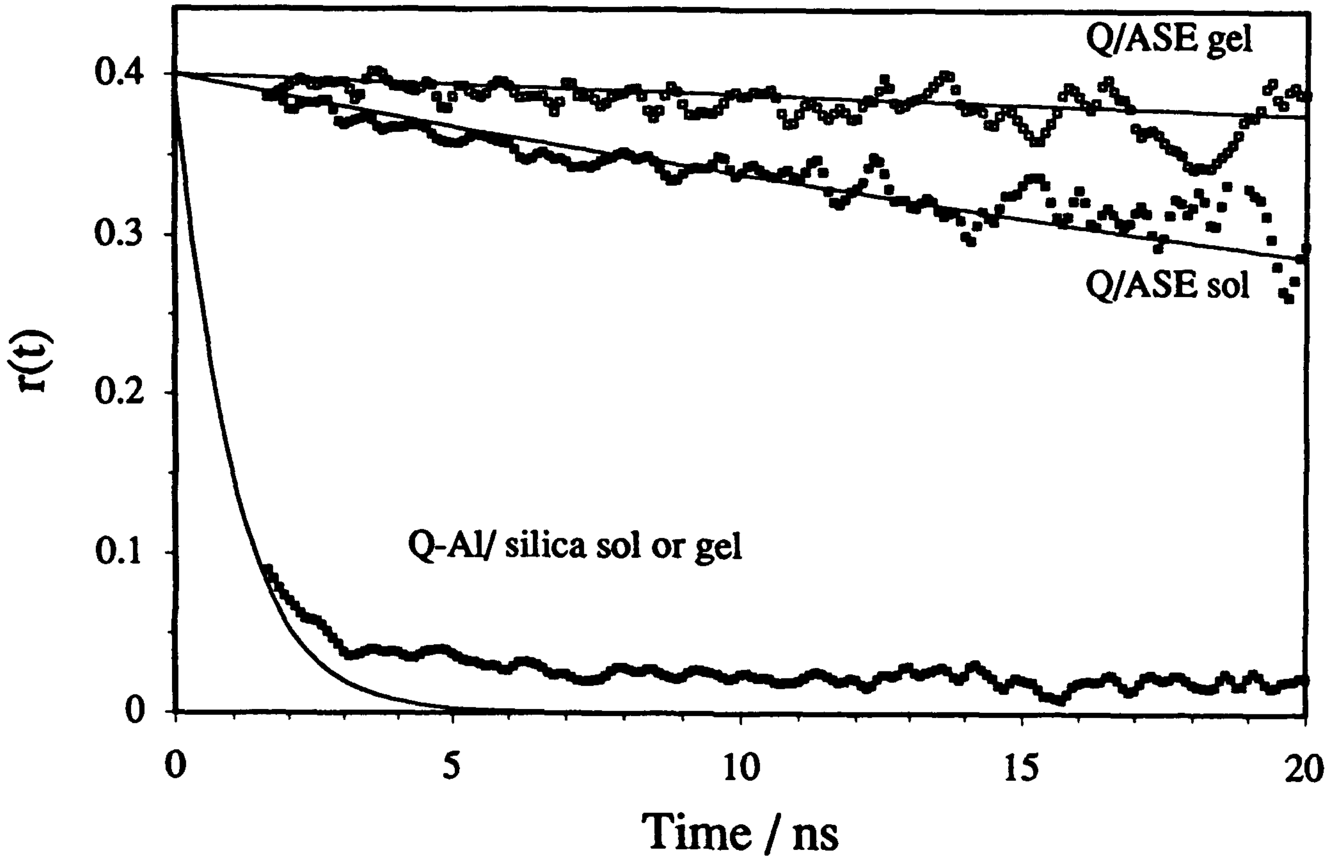


Figure 3. The time-resolved fluorescence anisotropy decay for the Q-Al chromophore in a tetraethoxysilane/isopropanol/water solution is labeled Q-Al/silica at the bottom of the figure. The solid curve is a fit of Eq (4) to the tail of the anisotropy decay, with a rotational correlation time of ϕ = 1ns. The data remains unchanged for the silica solution as the viscosity increases to form the gel (after 180 hrs). Although ϕ=1ns is close to the resolution of this instrument it represents an upper bound on the rotational diffusion time for the Q-Al complex, both in solution and in the silica gel. The middle data set is for quinizarin in an aluminosilica/isopropanol/water solution, labeled Q/ASE sol, while the upper data set is for the same sample after it has gelled (38hrs), and is labeled Q/ASE gel. The large difference in rotational diffusion times between the Q/ASE solution and the Q-Al/silica solution is due to the higher viscosity of the ASE solution and the increased volume of the chromophore upon complexation with ASE. The chromophore rotational correlation time in ASE solution increases gradually as it polymerizes. The smooth curves drawn through the anisotropy decays are fit to Eq (4) with rotational correlations times of ϕ = 70ns for the Q/ASE solution and ϕ = 300ns for the Q/ASE gel.

$$\phi = \frac{\eta V}{kT} \qquad (5)$$

where η is the viscosity of the solvent, V is the volume of the rotating molecule, and T is the temperature of the solution [29]. This theory is sometimes modified for ellipsoidal molecules [25][26] by including shape and friction factors, as well as an inertial correlation time [27], however, the complexity of the solutions and gels in this study (e.g. a mixture of several components, a polymerization reaction, and spatially inhomogeneous gels) precludes such refinements. When the local viscosity of the chromophore environment in a gel is very different from the bulk viscosity, rotational diffusion measurements can be used as a probe of the local environment of the chromophore.

The rotational correlation time of the Q-Al chromophore immediately after preparation of the silica solution is fast, and is close to the experimental resolution of the measurements (~1ns), as indicated by the lowest curve in Fig. 3. During the growth of the SiO_2 polymer, the viscosity increases until a wet gel is formed, however, no change in the rotational dynamics of the Q-Al chromophore is observed as the solution polymerizes into a gel. These results are consistent with spectroscopic studies utilizing the spectral shifts of probe molecules in silica and ASE solutions and gels, which concluded that the ASE matrix was confining, whereas the chromophore environment in the silica gel remained more open [28].

The chromophore rotational dynamics in the ASE gel are very different from the silica gel since quinizarin complexes with the ASE solution/gel. The curve labeled Q/ASE-sol in Fig. 3 shows the time-resolved fluorescence anisotropy for the aluminosilicate solution immediately after preparation. The rotational correlation time of the Q-Al chromophore is 70 ns for this solution (of 22% ASE, 67% isopropanol, 11% water). This relatively long rotational correlation time is due to the higher viscosity of the ASE monomer solution, as well as due to an increased chromophore volume due to complexation of quinizarin with the ASE monomer. This indicates that the quinizarin molecules are bound to the aluminosilicate polymer network as it is growing. The rotational correlation time gradually increased as the solution became more viscous. The solution gelled within 38 hours, resulting in a much longer rotational diffusion time, as shown by the upper curve in Fig. 3. Orientational motion of the Q-Al chromophore is nearly absent on the timescale of the fluorescence lifetime, indicating that the quinizarin molecules are closely associated with the aluminosilicate polymer network, and not free to rotate within liquid filled pores.

The orientational dynamics of the Q-Al chromophore in silicate and aluminosilicate xerogel glasses (obtained by slow drying of the doped gels) is negligible in both matrices, over a timescale longer than the fluorescence lifetime. The time-resolved anisotropy data for both of these doped xerogels consisted of a nondecaying value of 0.4 and these data sets have not been included in Fig. 3. These results indicate that the Q-Al chromophore is strongly associated with the matrix and not free to rotate in either xerogel. This is not surprising for the ASE xerogel since the chromophore is complexed with the matrix. However, the Q-Al chromophore also becomes orientationally immobilized in the Q-Al/silica xerogel when all of the solvent is removed. We conclude that Q-Al adsorbs to the surface of the dry silica xerogel. This result supports the conclusions of a previous study of spectral shifts in doped silica gels/xerogels [28].

A colorless ASE xerogel can also be irreversibly doped with quinizarin by immersion into a Q/alcohol solution. The quinizarin molecules diffuse into the porous ASE xerogel and complex irreversibly with the aluminosilicate polymer. The diffusively doped glasses were later soaked in hot ethanol, but quinizarin could not be leached from the glass. The ability to dope an ASE xerogel by these two very different methods provides us with a unique comparison of the chromophore environments. The absorption spectra of the diffusively doped Q/ASE xerogel were the same as for a Q/ASE xerogel grown from the monomer solution. A cross section of the soaked aluminosilica xerogel glasses showed that the quinizarin diffused equally throughout the xerogel. The ability to diffusively dope an ASE glass with quinizarin seems to indicate that the chromophore environment is rather open. Furthermore, the absorption spectrum and optical energy transfer measurements on diffusively doped samples are similar to xerogels formed from a quinizarin containing monomer solution.

3. Novel Organically Doped Glasses and Coatings

Quinizarin doped aluminosilicate sol-gel glasses for energy transfer and rotational diffusion studies were produced by mixing diisobutoxyaluminoxy-triethoxysilane (ASE), water, and an isopropanol solution of quinizarin [29]. The quantities of materials used for each experiment are given in Table I. The mixture was sonicated until it turned clear due to hydrolysis of the ASE monomer, then poured into a polystyrene mold where the solution was covered but not sealed. The solutions gelled within one to two days as the hydrolyzed aluminosilica polymerized. Water and alcohol evaporated from the gel for two to three weeks, causing it to shrink and trap the dopant Q within the glass. These glasses were baked at 110°C to remove traces of water, but no attempt was made to densify the glass at higher temperature. The resulting *xerogel* glasses had a density of 1.7 g/cm^3. In these glasses, the quinizarin is covalently bound to the aluminoxy groups of the glass, forming a quinizarin-aluminum complex (Q-Al).

Table I: Recipes for aluminosilicate glasses (xerogels)

ASE	iPrOH	Water	Shrinkage	Use
3 ml	10 ml	1 ml	20	Thin discs for ET studies
2 ml	4 ml	1 ml	8	Gels for rotational diffusion

Q-Al doped silicate sol-gel glass films were prepared by adding quinizarin and aluminum nitrate hemihydrate to a 6:17:2:1 solution of tetraethoxysilane (TEOS), ethanol, 0.01N HNO_3, and Triton-X-100 after which the solution was warmed at *40°C for 24 hours* [30]. The optimum concentration of aluminum nitrate in the solution was 0.05M. Bulk samples were prepared by pouring the solution into polystyrene molds, and allowing the water and alcohol to evaporate, which took about one week [29]. Thin films were made by dipping glass microscope slides in the solution and withdrawing them at a rate of 2 mm/s. Films gelled in 5 minutes and dried within 2 hours. The silicate films were air dried to minimize dissociation of the Q-Al complex that occurred upon loss of water from the gel. Film thicknesses and densities were estimated by elipsometry and weighing. The thickness of the films was 0.8 mm (±25%). In these films the Q-Al complex is not bound to the glass, and is free to migrate into pores during gelation and shrinking.

Aluminum phthalocyanine chloride (CAP) doped buffered silicate sol-gel glasses were prepared by mixing 15ml TEOS, 5ml ethanol with CAP as dopant, and 5 ml 0.01N HCl in water. This solution was mixed by sonicating, then 2.5 ml of 0.05M sodium phosphate solution was added to buffer it. Next, the solution was poured into an unsealed polystyrene mold and the water and alcohol were allowed to evaporate, which took about two and a half weeks. Buffering is necessary since CAP in unbuffered silica faded as the final traces of water evaporated from the gel, possibly due to protonation of CAP in the highly acidic glass.

Both aluminosilicate and silicate gels shrank and hardened as water and alcohol evaporated. The volume of the aluminosilicate glasses shrank by a factor of 20 from the original solution while the silicate glasses shrank by a factor of 15, in each case yielding a final density of 1.7 g/cm^3. The shrinkage factors are large since increased solvent was used to adjust the solution viscosity for dipcoating. The shrinkage of the glass was used to estimate the final concentration and confirmed with optical absorption measurements of the doped solids. Aluminosilicate glasses were baked at 110°C to remove traces of water while the silicate glasses were merely air dried to minimize dissociation of the Q:Al complex. Film thicknesses and densities were estimated by elipsometry and weighing. The thickness of the silicate and aluminosilicate films were 0.8 µm and 0.2 µm (±25%) respectively.

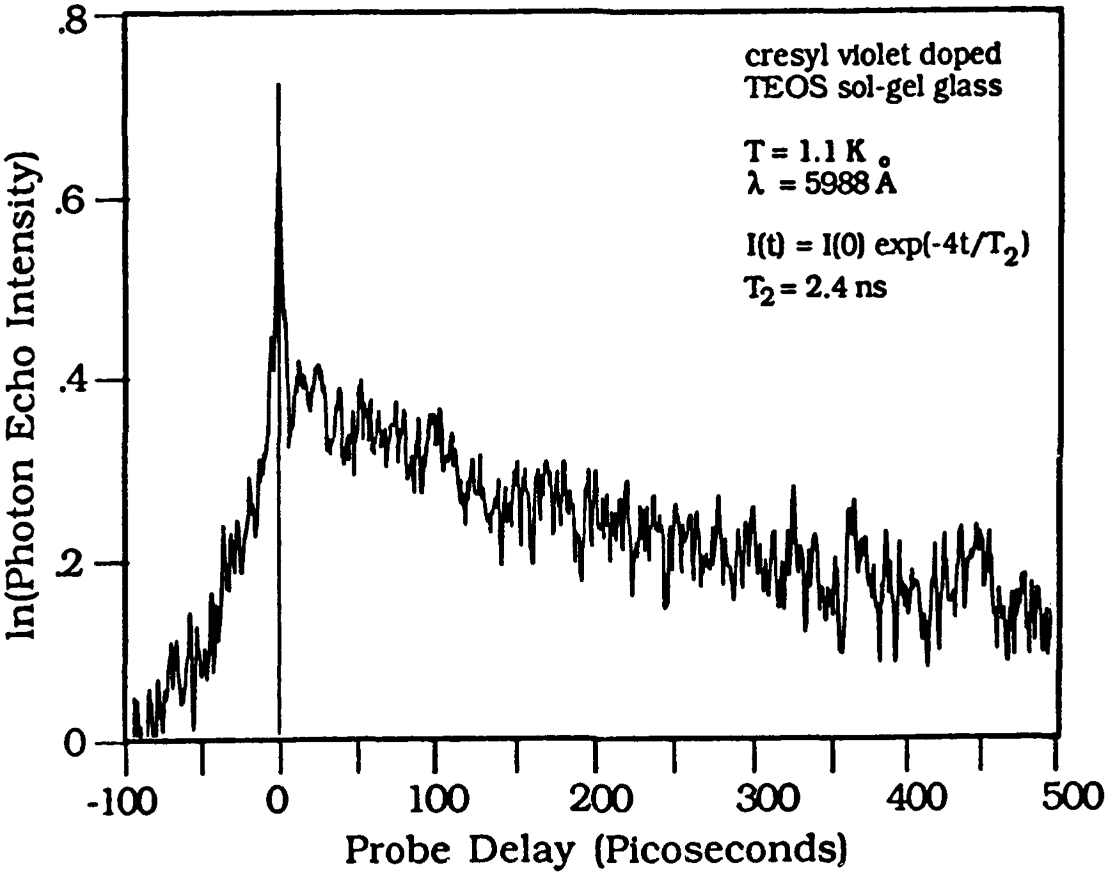


Fig. 4. A semilog plot of a photon echo decay yields an exponential coherence decay time of T2 = 2.4 ns for a cresyl violet doped silicate (TEOS) sol-gel glass at a temperature of 1.1 K. A similar measurement at T = 1.5 K yielded a homogeneous dephasing time of T_2 = 800 ps. The temperature dependence of the homogeneous dephasing at such low temperatures is reflects the density of states of the glassy TLSs. The measured dephasing rates $1/T_2$, include population relaxation (i.e. $1/T_2 = 1/2T_1 + 1/T_2^*$), where the fluorescence lifetime T_1 = 3 ns.

4. Photon Echo Measurements of Homogeneous Dephasing in Amorphous Glasses

Picosecond photon echo measurements on homogeneous dephasing of organically doped inorganic sol-gel glasses at low temperature (1.5K) have been used to obtain the homogeneous dephasing rate of the chromophore. These results are contrasted with recent hole-burning experiments on doped sol-gel glasses. Cresyl violet doped aluminosilicate (ASE) and silicate (TEOS) glasses were selected due to the extensive photon echo work on cresyl violet doped ethanol glasses [31-33] and the spectral hole-burning experiments on quinizarin doped sol-gel glasses.[34]

Thermally activated dephasing of chromophores in glassy matrices arises due to coupling of the transition dipole to the dynamics of two-level systems (TLSs) as well as low frequency modes (e.g. optical phonons) of the solid. Thus, temperature dependent photon echo spectroscopy provides a sensitive probe of how organic chromophores interact with the dynamics of inorganic sol-gel hosts.[31,32,35] A distribution of two-level systems (TLSs) is often used to model the local fluctuations inherent to a non-equilibrium glassy environment. In addition, temperature dependent photon echo measurements on doped glasses can be used to probe the dynamics of the TLSs as well as other low frequency modes of the host glass. For example, the thermally induced homogeneous dephasing rate for a doped glass can be given by,[36]

$$1/T_2^* = aT^\alpha + be^{-\Delta E/kT}/(1- e^{-\Delta E/kT}) \qquad (6)$$

The power law term is due to coupling of the optical transition dipole to the TLSs, and the exponential activation term arises from an optical phonon mode of the glass of energy ΔE. [36,37] Since the temperature dependent multiplier to the activated process is simply the thermal occupation number for phonons of energy ΔE, at low temperatures (i.e. $kT<\Delta E$) this term reduces to a simple Arrhenius activation process. This is in contrast to crystalline systems for which exponential activated dephasing occurs due to hindered librational motions of the guest chromophore.[38]

The comparatively large homogeneous dephasing rates obtained by hole-burning measurements in glasses have been attributed to spectral diffusion, and must be taken into account when making comparisons with photon echo measurements.[32] For example, photon echo measurements on cresyl violet doped ethanol glass at a temperature of 1.1 K yield a value of T_2 = 2.2ns (including a lifetime contribution of T_1 = 5.5ns) [31,32,35], while a spectral hole-burning experiment on the same sample yields a value of T_2 = 0.3 ns [32,33]. For comparison, our photon echo data for cresyl violet doped TEOS sol-gel glass yielded a T_2 value of 2.4 ns at a temperature of 1.1 K and a value of 0.8 ns at T = 1.5 K. The similarity between our measured homogeneous dephasing time for cresyl violet doped TEOS (2.4ns) and the results for cresyl violet doped ethanol glass (2.2 ns) may indicate similar environments. These results can also be compared to spectral hole-burning data reported for cresyl violet adsorbed onto porous Vycor glass at 1.7 K, which yielded T_2 = 40 ps (i.e. a holewidth of 8GHz) [34]. This T_2 value is over an order of magnitude shorter than our results for cresyl violet doped sol-gel glasses which may indicate that a reasonable amount of cresyl violet dopants do not reside in an environment similar to the surface adsorbed species on Vycor. However, at this time we cannot rule out spectral diffusion as the source of the large discrepancy between our photon echo data and the spectral hole-burning results for cresyl violet adsorbed onto Vycor glass.

5. Fast Response Optical Limiting in Doped Sol-Gel Glasses

Fast photochromic glasses have been produced by doping sol-gel glasses with molecules that posses fast photophysical induced absorption processes. For example, the excited state absorption of chloroaluminumphthalocyanine (CAP) molecules doped into a sol-gel glass exhibits fast optical limiting behavior, similar to that in CAP/alcohol solution [39]. Fig. 5 shows optical limiting behavior of buffered silica doped with CAP. The sample was approximately 1 mm thick. The straight line is a fit to Beer's Law corresponding to an absorbance of 0.48. The data shows a threshold fluence near 0.6 J/cm^2, and more significant optical limiting at higher fluences. Note, however, that the optical limiting characteristics are different from CAP in ethanol because the ground state absorption at 532nm in the sol-gel glass is greater than that in ethanol. The non-linear response of these molecular dopants compliments our continuing efforts to develop fast photochromic host materials (e.g. transition metal oxides).

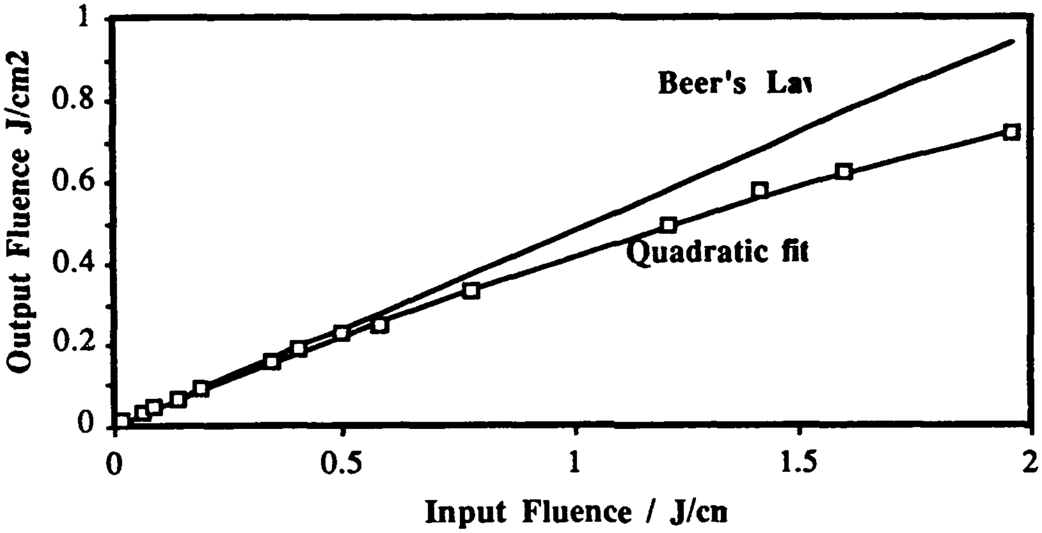


Figure 5: Output vs Input fluences for chloroaluminum phthalocyanine (CAP) doped into a buffered silica sol-gel glass. Optical limiting occurs due to induced excited state absorption by CAP. The rigid sol-gel glass is environmentally tough, has a relatively high optical damage threshold, and can increase the photochemical stability of organic dopants.

A competition between ground state and excited state absorption results in a nonlinear absorption and gives rise to optical limiting characteristics if the excited state absorption cross section is much greater than the ground state cross section. In addition, a fast initial response is facilitated by a singlet-singlet excited state absorption since intersystem crossing is not necessary. Similarly, the ground state recovery is typically much faster if intersystem crossing (ISC) is not significant. The equations which describe the nonlinear absorption for a molecule with a weak S_0-S_1 transition (with cross-section $\sigma_{0\text{-}1}$) and a strong S_1-S_n excited state absorption (with $\sigma_{1\text{-}n}$) are discussed below. Given the linear absorption coefficient for the weak transition ($\alpha_{0\text{-}1} = \varepsilon_{0\text{-}1}$ x conc.), the equation for generating N excited state molecules per unit volume is,

$$\frac{dN}{dt} = \frac{\alpha I}{h\omega} \qquad (7)$$

where I is the light intensity and $h\omega$ is the photon energy. The resulting intensity as a function of the propagation distance z through the sample,

$$\frac{dI}{dz} = -\alpha_{0\text{-}1} I - \sigma N I \qquad (8)$$

where σ is the excited singlet-singlet absorption cross-section. Clearly the intensity dependent number of excited state molecules N will give rise to an induced absorption if $\sigma_{1\text{-}n} >> \sigma_{0\text{-}1}$. For the results obtained for a chloroaluminumphthalocyanine doped sol-gel glass we find that the excited state extinction coefficient (@ $\lambda = 532$nm) is an order of magnitude larger than the ground state transition, i.e.

$$\frac{\varepsilon_{1-n}}{\varepsilon_{0-1}} = \frac{6000\ \mathrm{M^{-1}cm^{-1}}}{600\ \mathrm{M^{-1}cm^{-1}}} = 10.$$

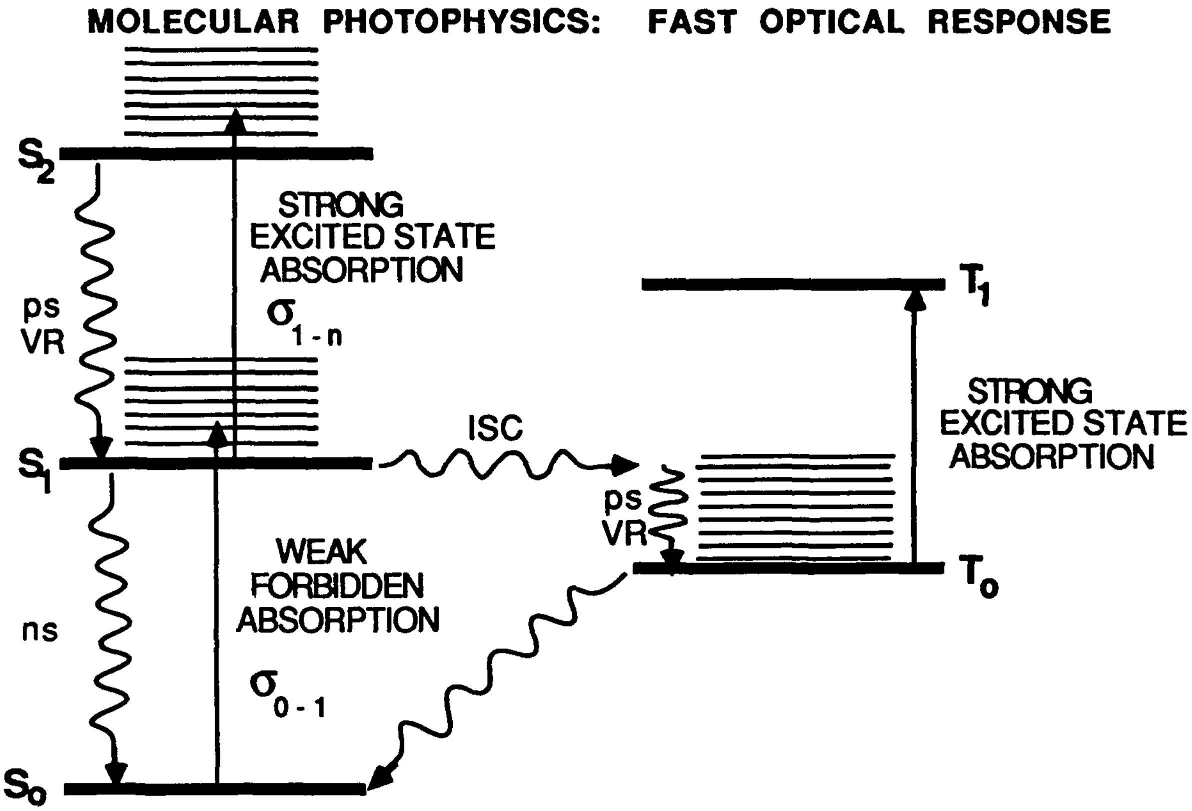


Fig. 6. A schematic diagram of the energy levels and photophysical processes relevant to nonlinear absorption.

The absorption spectrum of CAP changes considerably upon gelation and drying of the a silica sol-gel host. The absorption spectrum of CAP in ethanol is given in Fig. 7. The CAP absorption spectrum in buffered silicate solution resembles that in ethanol, but the spectrum broadens after solvent evaporation.

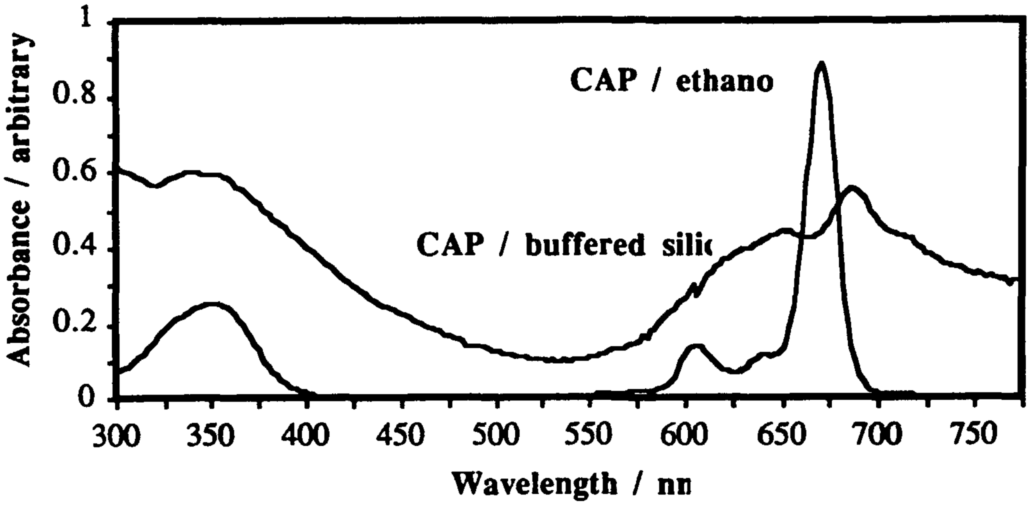


Figure 7: CAP in ethanol and doped into a buffered silica glass

6. Spectral Hole Burning in High Temperature Glasses

The local environment of organic dopants in porous xerogel glasses can result in unique optical properties. For example, the relatively narrow high temperature persistent spectral holes observed for quinizarin in silica xerogels (≤30K) and for quinizarin adsorbed onto γ-alumina (77K) [40] are attributed to reduced electron-phonon coupling of the chromophore to the host matrix. Hole-burning in quinizarin doped sol-gel silica glass is believed to be photochemical, due to an excited state proton transfer reaction which breaks an internal hydrogen bond and forms an external hydrogen bond with the host environment [41,42]. The similar homogeneous linewidths obtained for quinizarin in low temperature ethanol and silica sol-gel glasses (~1cm^{-1}) [41] suggests that the nearest neighbor environment of quinizarin may be similar in these two matrices, however, the different temperature dependences indicate that the dynamics are very different. We have observed reasonably narrow spectral holes in quinizarin doped aluminosilicate xerogels at a temperature of 77K and attribute the burning mechanism to hydrogen bond rearrangement. Similarly, spectral holeburning results have recently been reported for quinizarin adsorbed onto aluminum oxide powders, indicating that some of the molecules may be chemically adsorbed onto the inner surface of xerogel micropores. It is interesting to speculate whether the environment of the Q-Al complex formed in the ASE xerogel resembles the surface adsorbed species of the Q/alumina system.

C. Publications Acknowledging ARO Support

1. E. L. Chronister, "Doped Sol-Gel Glasses as Ultrafast Frequency Agile Optical Materials." Smart/Intelligent Materials and Systems (Technomic Press, Lancaster, PA, 1990) 294-308.
2. E. L. Chronister, D. M. L'Espérance, J.M. Pelo, J.S. Middleton and R. A. Crowell, "Time-Resolved Photon Echo Measurements of Organically Doped Inorganic Sol-Gel Glasses." Proc. SPIE - Photopolymer Device Physics, Chemistry and Applications II, vol. 1559 56-64 (1991).
3. D. L'Espérance and Eric L. Chronister, "Nanosecond Optical Energy Transfer in Quinizarin Doped Sol-Gel Glasses," Active Materials and Adaptive Structures (IOP publishing, Bristol, 1992) in press 1/92.
4. R. A. Crowell and Eric L. Chronister, "A Time-Resolved Study of Inhomogeneous Dephasing in High Pressure Molecular Crystals, Chemical Physics Letters (1992), in press 5/92.
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6. D. L'Espérance, J. M. Pelo, and Eric L. Chronister, "Optical Energy Transfer and Photochromism in Doped Sol-Gel Glasses," MRS Proceedings on "Smart" Materials Fabrication/Materials for Micro-Electro-Mechanical Systems, Volume 276-F2, A.P. Jardine, A. Crowson, and R.D. Beta Eds. (Materials Research Society, Pittsburgh, PA, 1992).
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