Probing properties of glassy water and other liquids with
site selective spectroscopies

by

Nhan Chuong Dang

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Physical Chemistry

Program of Study Committee:
Ryszard Jankowiak, Co-major Professor
Klaus Schmidt-Rohr, Co-major Professor
Mark Gordon
Xueyu Song
Victor S.-Y. Lin

Iowa State University

Ames, Iowa

2005

Copyright © Nhan Chuong Dang, 2005. All rights reserved.

Graduate College
Iowa State University

This is to certify that the doctoral dissertation of

Nhan Chuong Dang

has met the dissertation requirements of Iowa State University

Co-major Professor

Co-major Professor

For the Major Program

TABLE OF CONTENTS

CHAPTER 1. BACKGROUND ON SUPERCOOLED LIQUIDS, GLASSES AND HETEROGENEOUS DYNAMICS	1
1.1. Formations of Supercooled Liquids and Glasses	1
1.2. Dynamics, Thermodynamics, and Heterogeneous Dynamics of Supercooled Liquids and Glasses	3
1.3. Background on Supercooled and Glassy water	10
1.4. Remarks on Unsolved Problems Concerning Dynamics of Supercooled Liquids and Glasses and Proposals of Solving the Problems	14
1.5. Dissertation Organization	20
References	22
CHAPTER 2. OPTICAL SPECTROSCOPY OF IMPURITIES IN SOLIDS	27
2.1. Electronic Spectra of Single Impurities in Solids	27
2.2. Electron-Phonon Coupling	33
2.3. Single Site Absorption Line Shape	37
2.4. Inhomogeneous Broadening and Optical Bands of Impurities in Solids	38
2.5. Spectral Hole Burning	42
2.5.1. NPHB Mechanism	47
2.5.2. Dispersive Hole Growth Kinetics	53
2.5.3. Temperature Dependence of Zero-Phonon Hole	56

2.6. Introduction to Single-Molecule Spectroscopy in Solids	57
2.7. Single-Molecule Spectroscopy in	
Studying the Glass Transition and Rotational Dynamics	62
References	65
CHAPTER 3. NON-PHOTOCHEMICAL VERSUS PHOTOCHEMICAL HOLE BURNING IN HYPERQUENCHED GLASSY WATER AND CUBIC ICE	72
Abstract	72
1. Introduction	73
2. Experimental	76
3. Results and Discussion	76
References	86
CHAPTER 4. A MODEL FOR PERSISTENT HOLE BURNED SPECTRA AND HOLE GROWTH KINETICS THAT INCLUDES PHOTOPRODUCT ABSORPTION: APPLICATION TO FREE BASE PHTHALOCYANINE IN HYPERQUENCHED GLASSY ORTHO-DICHLOROBENZENE AT 5 K	88
Abstract	88
1. Introduction	90
2. Experimental	93
3. Model for Simulation of Hole Spectra and	
Dispersive Hole Growth Kinetics	95
4. Results and Discussion	103
References	121

CHAPTER 5. DISPERSIVE HOLE GROWTH KINETICS AND FLUENCE BROADENING OF ZERO-PHONON HOLE OF IMPURITIES IN AMORPHOUS SOLIDS	124
Abstract	124
1. Introduction	125
2. Calculation Methods	129
3. Results and Discussion	132
4. Concluding Remarks	144
References	146
CHAPTER 6. PROBING CONFINED WATER WITH NON- PHOTOCHEMICAL HOLE BURNING SPECTROSCOPY: ALUMINUM PHTHALOCYANINE TETRASULFONATE IN POLY(2-HYDROXYETHYL METHACRYLATE)	149
Abstract	149
1. Introduction	151
2. Experimental	153
3. Results	154
4. Discussion	164
5. Concluding Remarks	174
References	176
CHAPTER 7. TEMPERATURE DEPENDENCE OF DISPERSIVE HOLE GROWTH KINETICS OF ALUMINUM PHTHALOCYANINE TETRASULFONATE IN HYPERQUENCHED GLASSY WATER	179
Abstract	179
1. Introduction	180

2. Experimental	182
3. Standard Hole Growth Kinetics Model	184
4. Results	188
5. Discussion	194
6. Conclusions	200
References	201
CHAPTER 8. CONCLUDING REMARKS	203
APPENDIX. DYNAMICAL PROPERTIES OF GLASSY WATER AND ETHANOL STUDIED WITH POLARIZATION- RESOLVED SINGLE MOLECULE SPECTROSCOPY	208
1. Introduction	208
2. Experimental	211
3. Preliminary Results and Discussions	218
4. Conclusions	225
References	226
ACKNOWLEDGMENTS	227

CHAPTER 1.

BACKGROUND ON SUPERCOOLED LIQUIDS, GLASSES AND HETEROGENEOUS DYNAMICS

1.1. Formation of Supercooled Liquids and Glasses

A glass-forming system in the liquid state has low viscosity, low density, and fast equilibrium relaxation time. The liquid may crystallize at the freezing/melting point, T_m . However, if the liquid is cooled so fast that it bypasses T_m without crystallizing, it will enter the supercooled liquid state. As the temperature of the supercooled liquid is further reduced, viscosity and density increase rapidly and molecular motion slows. With further cooling, the molecular motion becomes so slow that the molecules do not have enough time to relax to equilibrate the system. As a result, the system suddenly enters into a "dynamical arrest" state on the timescale of the laboratory experiment. This process is called the glass transition, and the corresponding temperature is called the glass transition temperature, T_g . At temperatures slightly lower than T_g , the system (glass) is considered "frozen." When the molecular motion of a system that is in a highly viscous state is suddenly halted, the system assumes a highly disordered structure as it does in the liquid phase. Fig. 1 shows such a response of the entropy of a typical liquid upon cooling. The exact value of T_g , as well as the properties of the glass, depends on the cooling rate. The faster the cooling rate, the faster the system enters into a "dynamical arrest" state and, consequently, the T_g of the system is higher. Thus, a glass can be produced from the liquid state if it is continuously cooled at rates that will

Figure 1. The temperature dependence of a glass forming system's entropy at constant pressure. T_m is the melting temperature. Dotted lines represent the glass transition for two different cooling rates. A slower cooling rate produces a glass transition at T'_g ; a faster cooling rate leads to a glass transition at T_g ($T_g > T'_g$).

bypass crystallization. Due to “dynamic arrest,” the structure of glassy materials lacks long-range order. It should be noted that amorphous solids that are produced directly from the vapor state lack the internal stability to form a supercooled liquid state and the glass transition.

1.2. Dynamics, Thermodynamics, and Heterogeneous Dynamics of Supercooled Liquids and Glasses

The relaxation processes (dynamics) and thermodynamics of supercooled liquids and glasses at temperatures above and close to T_g have been under intense study for more than 50 years [1-11]. Current challenges include understanding the dramatic slowing-down of the molecular dynamics as the temperature of a supercooled liquid approaches T_g , and the final kinetic events that lead to the glass. At present, there is no general agreement about what causes molecular slowdown, which is responsible for the glass transition from the view of a supercooled liquid. Also, there is no microscopic theory for temperatures between T_g and $\sim 1.2 T_g$ that captures all of the important features of the glass formation process. The freezing-in phenomenon might imply that the thermodynamic state of a glass can be viewed as unstable, and that of supercooled liquid state as metastable. Again, since the kinetic events at glass transition are considered a dynamical arrest on the timescale of the laboratory experiments, this does not imply that structural relaxation processes do not occur for $T < T_g$. It only suggests that, for all practical purposes, a molecule is unable to sample all of the configuration space. Below are brief descriptions of the phenomenological treatments of the dynamics and thermodynamics of supercooled liquids and glasses, which have been developed for this field.

At a sufficiently high temperature, most liquids show an Arrhenius viscosity, η , and dynamical relaxation times, τ . As the temperature of a supercooled liquid is lowered towards T_g , η and τ rapidly increase. At intermediate and low temperature limits, the temperature dependence of the glass-forming melt viscosity can be described using a modified Arrhenius equation known as the Vogel-Fulcher-Tammann (VFT) equation [12-14]

$$\log \frac{\eta}{\eta_{\infty}} = \frac{B}{T - T_0}, \quad (1.1 \text{ a})$$

where B and T_0 are constants, and also the Williams-Landel-Ferry (WLF) equation [15],

$$\log \left\{ \frac{\eta(T)}{\eta(T_0)} \right\} = \frac{[a_1(T - T_0)]}{[a_2 + (T - T_0)]} \left\{ \frac{T\rho}{T_0\rho_0} \right\}, \quad (1.1 \text{ b})$$

where ρ_0 is the density at a reference temperature T_0 , a_1 and a_2 are constants, and ρ is the density at T . The VFT and WLF laws are very useful because they allow for a simple parameterization of the data with quite good accuracy. Using these laws, the viscosity of nonpolymeric glass formers is found to be $\sim 10^{13}$ Poise at T_g compared to $\sim 10^{-2}$ Poise for liquids such as water and ethanol at room temperature. With the VFT equation expressed in $\log \eta$ - T relation, the molecular picture for dynamics or thermodynamics in the liquid can be interpreted using a parameter, which is called “fragility.” [16]. For $T = T_g$, fragility is expressed as a dimensionless “steepness index,” m , as in the following [16]:

$$m(T_g) = -\frac{d \log_{10} \eta}{d \ln T}, \quad (1.2a)$$

or in an equivalent form [8],

$$m(T_g) = -\frac{d \log_{10} \langle \tau \rangle}{d \log_{10} (T_g / T)}, \quad (1.2b)$$

where τ is the glass relaxation time. Large values of $m(T_g)$ correspond to “fragile” liquids and small values to “strong” liquids. Typically, $m(T_g)$ ranges from about 15 for strong liquids and up to 200 for very fragile liquids. A glass-forming liquid, whose viscosity is low near the melting point, T_m , but exhibits highly non-Arrhenius behavior near the glass-transition temperature, T_g , is called “fragile.” A liquid whose viscosity shows Arrhenius-like behavior is called “strong.” For strong liquids, such as SiO_2 , $\log \eta$ approaches T^* (the temperature at which $\eta = 10^{12}$ poise) at a constant rate, i.e. the behavior is Arrhenius-like [2-5]. For fragile liquids, such as o-terphenyl, the rate of change of η is more pronounced as it approaches T^* , i.e. behavior is non-Arrhenius. Generally, fragile liquids are those that lack strong directional bonding, unlike the extended tetrahedral bonding network of SiO_2 . Although viscosity can be related to dynamics and thus defines the kinetic aspect of fragility, there is also a thermodynamic aspect. It has been shown that at T_g there is a distinct and abrupt decrease in the excess heat capacity (C_p (liquid)/ C_p (crystal)) near T_g , plotted as a function of T/T_g [8] – the more fragile the liquid, the larger the decrease. As explained in in Ref. 8, the freezing-in of a higher energy configuration is responsible for the decrease. It was thought that the behavior of observables reflects the stability of the short-and-medium range order against temperature degradation that suggested the terms of “strong” and “fragile” for the extremes of behavior [8]. For a fragile liquid, the structural changes produced by warming above T_g exhibit a stronger temperature dependence than those of a strong liquid. The degree of fragility can also be judged on the basis of the Kauzmann temperature, T_K , [1,17] or the temperature at which the liquid entropy equals that of the crystal (obtained by extrapolating higher temperature data). This “entropy crisis” for fragile liquids is avoided by the glass transition at $T_g > T_K$; the higher T_K , the more fragile the liquid.

In addition to the VFT and WLF laws, the T -dependence of the glass-forming melt viscosity can be described by a so-called mode-coupling theory of the glass transition, which is derived in Refs.18 and 19:

$$\eta(T) = \eta_0 (T - T_c)^{-\gamma}, \quad (1.3)$$

where T_c is the critical temperature and often found to be $\sim 20 - 30\%$ above T_g . The mode-coupling theory is a well-known method of describing the divergence of the viscosity of supercooled liquids at $T_c \geq T_g$ (where $10^{-1} \leq \eta \leq 10^2$ Poise). However, this functional form is valid only for the temperature far above T_g .

For the kinetic aspect in the time domain, relaxation kinetics associated with molecular rotation can be characterized using the Kohlrausch-Williams-Watts (KWW) function, which is given by [20, 21]:

$$\Phi(t) = A \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right], \quad (1.4)$$

where A is an amplitude, τ is defined as relaxation time, and $\beta \leq 1$ is the KWW or “stretch” exponent. For normal liquids at sufficiently high temperature, the exponent $\beta = 1$, thus yielding exponential decay. A distinctive feature of fragile supercooled liquids is their nonexponential relaxation kinetics. For fragile liquids near T_g , $\beta \leq 0.5$ [1-3], i.e. one has highly nonexponential decay. At T_g , rotational relaxation times (τ) of fragile liquids are hundreds of seconds; in normal liquids at room temperature they are in the ns-ps range. Thus, relaxation times as well as η increase by about twelve orders of magnitude during the transition from a normal liquid to a liquid near T_g . The reasons are unclear [2, 5, 22], although one possible explanation is that *structural heterogeneity* in supercooled (viscous)

liquids at temperatures above T_g (becoming more pronounced as $T \rightarrow T_g$) creates differences in the relaxation dynamics from particle to particle. Therefore, stretching is the cumulative effect of many different relaxation times. Another explanation (*homogeneity*) is that the presence of the disordered structure gives rise to inherently different relaxation dynamics. Given the nonexponential response of fragile supercooled liquids and glasses to perturbations, the question arises as to whether nonexponential kinetics are due to nearly exponential kinetics in different spatial regions (domains) with the domains consisting of several molecules and exhibiting different relaxation rates, or to the system being more or less homogeneous but in each region the dynamics are nonexponential. Recent “dynamic filtering” and single molecule spectroscopy experiments favor the former dynamic heterogeneity model (see below).

One class of theories on the viscous slowdown and glass transition of supercooled liquids deals with thermodynamic and environmental fluctuations. Most of these theories involve the concept of freezing-in of structural fluctuations, which is responsible for the slowing of relaxation processes and the glass transition. Free volume theories [5] fall into this category. Cohen and Grest [23], for example, theorized that with a two-phase (region) model, solid-like regions eventually percolate through the system, signaling the formation of glass that possesses an excess free volume as measured relative to the crystal. This excess free volume is required in order for limited molecular motion to occur. However, this theory supports the VFT law only if the excess free volume depends linearly on temperature. Alternatively, Adams and Gibbs [24] propose “cooperatively rearranging regions (CRRs),” which they define as “a subsystem which, upon a sufficient thermal fluctuation, can rearrange into another configuration independently of its environment.” The insight of

molecular cooperativity is that the local molecular motion is too slow to maintain molecular mobility for very low free volume in supercooled liquids; i.e. the motion of a particular molecule depends to some degree on that of its neighbors. This leads to the rearranging movement of one molecule being cooperative with a certain number of neighbor molecules. Therefore, the T -dependence of the number, size and relaxation dynamics of the CRRs are responsible for the slowdown in dynamics and the large apparent activation energies for fragile liquids as $T \rightarrow T_g$. By linking the temperature dependent configurational entropy, S_c , and the relaxation time, τ , Adams and Gibbs obtained the result:

$$\tau = \tau_0 \exp (C/T S_c), \quad (1.4)$$

where C is constant. With S_c vanishing at a finite temperature (T_K), this equation is equivalent to the VTF equation, $\tau = \tau_0 \exp [B/(T-T_\infty)]$ with T_∞ set equal to T_K . The divergence at T_K may be due to a second order phase transition [5].

Since the proposal of CRRs, various studies have been used to estimate the number of molecules within a CRR and the characteristic length scale, ξ_C , associated with cooperative molecular motion. Several theoretical and experimental studies reviewed in Ref. 22 have shown that length scales grow as the temperature is lowered towards the T_g . It is instructive to consider two of these studies

First, Donth [25] has proposed a model (called the “minimal coupling model”) in which different sub-ensembles are characterized by different frequencies, ω_i (or motilities of CRRs, $\log \omega_i$). This model assumes that a CRR (the smallest representative system for CRRs) can be partitioned into equivalent partial systems, which are statistically independent but cooperatively coupled by a balance condition for free volume redistribution. With this

condition, cooperativity is described by an exchange of free volume between statistically independent partial systems of a CRR and the fluctuating free volume, v_f , which regulates the change of local mobility with the change of locally available (or excess) free volume, Δv , inside the CRR. The fluctuating free volume can be expressed as [25]:

$$v_f = \frac{\Delta v}{\Delta \ln \omega}, \quad (1.5)$$

where ω is the common frequency of partial frequencies. Applying a Levy distribution for Eq. 1.5, the author of Ref. 5 has shown that

$$v_f \propto N_\alpha^{-1/\alpha}, \quad (1.6)$$

where α is the Levy exponent ($0 < \alpha < 1$), and the “cooperativity” (or the average sizes of the partial systems), N_α is given as

$$N_\alpha = \frac{\rho V_\alpha}{M_0}, \quad (1.7)$$

where ρ is the sample mass density, M_0 is molar mass of what is considered as a particle, and V_α is volume of one CRR. By linking the minimal coupling model and the WLF equation, the temperature dependence of the dispersion of the CRR size distribution far below the onset temperature, T_{on} , of the cooperativity (the temperature where molecular rearrangement becomes cooperative) is given by

$$\delta N_\alpha(T) \propto \frac{1}{(T - T_\infty)^2} \quad \text{and} \quad \frac{\delta N_\alpha(T)}{N_\alpha(T)} = \text{const.} \quad (1.8)$$

Whereas near T_{on} , the dispersion of the CRR size distribution is given by

$$\delta N_\alpha(T) \propto (T_{on} - T)^{1/2} \text{ and } \frac{\delta N_\alpha(T)}{N_\alpha(T)} = \frac{1}{(T_{on} - T)^{3/2}}, \quad (1.9)$$

where T_∞ is the Vogel temperature. The minimal coupling model for cooperativity gives a phenomenological description of dynamic heterogeneity and consequences of its vitrification. For example, using this model, a typical characteristic length scale, $\xi_c = V_\alpha^{1/3} = V_o N_\alpha$ is found to range from 0.7 nm near the T_{on} up to 3.5 nm at T_g [26], corresponding to the N_α ranging from 1 to 100.

Second, due to the freezing-in at T_g , it has been thought that without physical aging, ξ_c is temperature independent in the region below T_g . Considering each molecule as a solid sphere, Wolynes et al. [27, 28] have shown that ξ_c is proportional to $\log(\tau/\tau_0)$ (independent of molecular composition), and $\xi_c = N^{1/3}a$, where τ is quenching time, τ_0 is molecular relaxation time, N is number of solid spheres, and a is the molecular length scale. The authors have also shown that the number of particles in a rearranging region, N , remain constant as the temperature is lowered below T_g . Thus, for the common kinetic laboratory glass transition of silica glass, the value of $\log(\tau/\tau_0)$ is found to be ~ 17 ($\tau = 10^4$ s) and $\xi_c \sim 5.7$ molecular radii, which results in roughly 190 molecules per rearranging unit.

1.3. Background on Supercooled and Glassy water

Vitrifying liquid water by cooling at a rate sufficient to bypass crystallization is a challenging task. Rice and Sceats [29] were the first to succeed at it; in 1984 they accomplished the task by slowly depositing water vapor onto a cryogenic surface. This

material, originally referred to as amorphous solid water (ASW) and now often called vapor deposited water (VDW), can be produced in two different densities: low-density, $\rho = 0.94 \text{ g ml}^{-1}$ and high-density, $\rho = 1.07 \text{ g ml}^{-1}$. The morphology and physical properties of ASW depend on the growth angle, thermal history of the film, and substrate characteristics [29-32]. For example, the high-density form was produced when water was deposited onto an orientated single crystal copper substrate with a deposition temperature, T_D , of 10 K; at 160 K or on polycrystalline or sapphire substrates, only the low-density form was obtained [33]. Jenniskens et al. [34] also produced a high-density form by depositing a thin film onto an amorphous carbon surface at 15 K. This form converts to the low-density form in the temperature region from 38 to 68 K [34]. A high-density amorphous material can also be prepared by compression to 1 Gpa at 77 K of either VDW or hexagonal ice, I_h [35, 36]. With a density of 1.17 g ml^{-1} , this material transforms irreversibly to low-density amorphous material upon warming to 123 K at atmospheric pressure. These two materials are usually referred to as high-density amorphous ice (HDA) and low-density amorphous ice (LDA). Recovering HDA at 77 K and atmospheric pressure and then heating it isobarically under pressure recently produced a distinctive form of HDA with a density of 1.25 g ml^{-1} [37]. This material is called very high-density amorphous ice (VHDA). VHDA can be converted back to HDA upon isochoric heating from 77 K to 140 K starting from 2 kbar, and LDA upon heating from 77 K to 127 K at 1.1 kbar without intermediate formation of HDA.

In 1985, Mayer successfully vitrified small aerosolized droplets ($3 \mu\text{m} \leq d \leq 25 \mu\text{m}$) of liquid water onto a metal cryoplate ($15 \text{ K} \leq T \leq 77 \text{ K}$) with cooling rates of $\sim 10^6 \text{ K/s}$ [38]. This material is referred to as hyperquenched glassy water (HGW). In 1987, the glass

transition of HGW was first reported [39]. The report was based on differential scanning calorimetry (DSC) experiments for HGW in which samples of HGW annealed at 130 K for 95 min showed an endotherm in the temperature range 134 to 152 K, characteristic of the glass transition. The glass transition temperature of HGW was then assigned as 136 K. Further heating caused a large exotherm due to conversion of the sample to I_c . Although it has been suggested that HGW and annealed ASW are different materials [40], it is now widely accepted that HGW, LDA and annealed ASW are structurally similar [41-44] since they all require cooling rates of $\sim 10^6$ K/s to circumvent crystallization and crystallize to cubic ice I_c when they are heated to about 150 K.

As is well known, at sufficiently low temperatures water becomes more compressible and less dense when cooled, and more fluid when compressed. Below T_m , even more complex properties are observed for supercooled water. The minimum temperature at which bulk water becomes supercooled liquid water, without crystallization occurring, is 243 K [45]. It has been known that lower temperatures are attainable for samples with at least one microscopic dimension. The lowest temperature reported is 234 K [45]. For $T_g = 136$ K, it is reasonable to speculate that at temperatures ranging from 136 to 150 K, non-crystalline water would appear to be a highly viscous liquid slightly above its glass transition. Indeed, it has been shown that LDA deforms under load and behaves like a liquid near 143 K [46]. The results from the studies of ASW films also confirms that it behaves like liquid water in the 140 – 210 K range [47] or ultraviscous liquid water in the vicinity of 150 K [48 - 51]. This behavior has been attributed to rotational diffusion but not translational diffusion [52].

However, Velikov et. al. have recently proposed that T_g of HGW is considerably higher than 136 K [53]. This conclusion is based on a comparison of differential scanning

calorimetry (DSC) experiments for HGW and other hyperquenched materials. The comparison shows that HGW does not seem to follow the behavior observed for other hyperquenched materials on a scaled heat capacity plot. Studies of the other hyperquenched materials show that the excess enthalpy associated with being trapped in a high-energy configuration upon rapid cooling is completely relaxed at $1.1 T_g$. However, for $T_g = 136$ K, the excess enthalpy of HGW is still unrelaxed at 150 K when crystallization to I_c begins. This contradicts predictions that the frozen-in excess enthalpy of HGW should relax completely at 149 K. If T_g is revised to ~ 165 K, water's enthalpy recovery exotherm exhibits behavior similar to that of other hyperquenched materials. From this comparison, Velikov et al. conclude that T_g for water should be 165 K, i.e. above the glass to I_c transition.

In addition to the controversy of the glass transition temperature of water, its fragility is still a matter of debate (see below). At first, water was concluded to be a very fragile liquid, not only near its melting point but also near the glass transition temperature. This conclusion resulted from the observation of a weak endothermic effect at 136 K attributed to a glass transition [46], penetration of millimeters-thick samples of LDA by a blunt probe at a temperature 14 K above the LDA glass transition temperature T_g of 129 K [47], and liquid-like diffusion at 150 K [48 – 51]. In addition, Kivelson and Tarjus proposed that water II, which they refer to as twice-supercooled water, is a fragile liquid [54]. Most recently, by studying the dielectric relaxation time of bulk water at temperatures ranging from 136 to 155 K, Johari has shown that water is a liquid over the studied temperature range [55].

However, Angell argued that water II is a strong liquid [56] and later concluded that it undergoes a transition from extreme fragility in the 240 – 273 K range to strong liquid character in the range where crystallization is very probable [57]. Starr et al. confirmed this

by using computer simulations to study the Adam-Gibbs relation between entropy and the dynamic properties of water [58]. As a result, water shows the super-Arrhenius behavior for $T \geq 230$ K and the Arrhenius behavior for $T \leq 190$ K. The corresponding fragility index, $m(T_g)$ of the Arrhenius behavior is 24 for $T_g = 136$ K and 28 for $T_g = 160$ K, comparable to $m(T_g)$ of a very strong liquid. This led Stare et al. to conclude that water undergoes an unusual fragile-to-strong crossover. More recently, by comparing the properties of dielectric loss tangent of water-like aqueous solutions, $\text{H}_2\text{O}-\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}-\text{N}_2\text{H}_4$, to those of water in the temperature range 136 – 140 K, Angell and co-workers denied the existence of ultraviscous fragile water and confirmed its fragile-to-strong transition [59].

1.4. Remarks on Unsolved Problems Concerning Dynamics of Supercooled Liquids and Glasses and Proposals of Solving the Problems

Although a number of theoretical studies have been proposed to explain the dynamics of supercooled liquids and glasses, at this time there is no direct evidence for diverging τ and η behavior or the divergence in the characteristic length scale. This is a difficult experimental problem since all dynamical processes slow down markedly at temperatures well above T_K . For glasses and amorphous solids, understanding their structural and physical properties and all dynamical processes remain an important and challenging scientific dilemma. This is especially true for polymers, proteins, and other biological systems at cryogenic temperatures; knowledge of the interrelation between structural and physical properties as well as the dynamics of the glass transition of these systems is necessary, for example, in glass, plastic and biomedical technologies (see Ref. 60 for examples).

Since glasses and amorphous solids possess disordered structure, the random character of the atomic positions enables some atoms or groups of atoms to move between two preferable energy states. Such behavior is treated as tunneling in a two-level system (TLS). [61, 62] TLS are asymmetric interatomic (molecular) double well potentials, which are separated by a barrier height V (see Fig. 1.2). In this figure, the energy difference between the minima of the double well potentials is characterized by an asymmetrical parameter, Δ . W is the tunneling frequency and is given by [63]

$$W = \omega_0 \exp(-\lambda). \quad (1.1)$$

In Eq. 1.1, ω_0 is the harmonic frequency of the wells of the TLS, and $\lambda = d(2mV)^{1/2}/\hbar$ is the tunneling parameter, where m is the effective mass of the tunneling entity and d is the displacement between the two potential energy minima. The random nature of glass also causes the “ruggedness” of the potential energy surface. Therefore, it leads to the treatment of the density of states for the TLS in term of phenomenological distribution functions (see [63] for detail reviews). For the scope of this dissertation, two of such proposed distribution functions are discussed. Originally, the TLS were proposed to explain the near linear and quadratic temperature dependencies (below 2 K) of the specific heat and thermal conductivity of non-doped glasses, respectively [61, 62]. Anderson et al. [61] and Phillips [62] have shown that the TLS density of states is constant in terms of the parameters Δ and λ (i. e. $P(\Delta, \lambda) = \bar{P}(\text{constant})$ for $\lambda_{\max} \leq \lambda \leq \lambda_{\min}$ and $\Delta_{\max} \leq \Delta \leq \Delta_{\min}$, Δ and λ are assumed to be uncorrelated). As a consequence, this distribution function leads to a density of states $\rho(E) \approx \rho_0$ (constant), where E is the tunnel state splitting and defined as $E = (W^2 + \Delta^2)^{1/2}$ [63]. Later, Jankowiak et al. [64, 65] argued that modeling the parameters Δ and λ (Δ and λ are still

Figure 1.2. The double well potential of a two-level system (TLS). V is the barrier height, Δ is asymmetry parameter, d is the displacement between the two potential energy minima, and W is the tunneling frequency.

assumed to be uncorrelated) as Gaussian distribution functions is physically reasonable. Using these distribution functions with the Monte Carlo simulation technique, it has been shown that $\rho(E)$ is slowly increasing function of the tunnel splitting E ($\propto E^\mu$) with $\mu \approx 0.3$ over a broad energy range [66]. In addition, these distribution functions have been successfully used to explain a number of problems including the temperature and time dependence of the specific heat of SiO_2 glasses with different $-\text{OH}$ (impurity) content [67]. Since then, Gaussian distribution functions of TLS parameters have been widely used.

Based on the nature of amorphous and glassy solids discussed above, it is obvious that configurational tunneling dynamics in these solids is different for each particular material. Using optical spectroscopy of impurities in solids (e. g. non-photochemical hole burning (NPHB) [63], which uses impurity centers as probes for dynamical processes taking place in their surrounding matrix), it is possible to investigate configurational tunneling dynamics in the solids and consequently, the degree of structural disorder of the solids.

In recent years dynamic hole-burning experiments on bulk supercooled molecular liquids and polymers at temperatures above T_g have yielded results that indicate heterogeneous dynamics (for reviews see [2, 5]). These results have also been verified by four-dimensional NMR experiments [68 - 72] and optical-hole burning experiments [2, 73-76]. In these experiments, a slowly relaxing subset of the ensemble is selected and the time it takes (τ_{ex}) for that subset to achieve bulk-like behavior is determined. In the optical experiments, photochemistry of the probe molecule tetracene in o-terphenyl was used to burn a spectral hole in the origin band of the most mobile tetracene molecules. The hole-filling time (τ_{ex}) as well as the average rotation time (τ_c) were determined. For the fragile glass

former o-terphenyl it was found that at $T_g + 4$ K, $\tau_{ex} \sim 10 \tau_c$ while at $T_g + 1$ K $\tau_{ex} \sim 10^4 \tau_c$. These findings indicate that the randomization of dynamic environments is strongly dependent at temperatures close to T_g . At least qualitatively, they are consistent with cooperatively rearranging regions (CRRs) whose size and inability of changing dynamics increase as $T \rightarrow T_g$ from above. A molecular view of the diffusion processes associated with τ_{ex} remains to be attained. Although it is not yet clear that heterogeneous dynamics are responsible for the glass transition rather than being a byproduct of it, the results of the experiments described above as well as dielectric dynamic hole burning [77] and time- and spectrally resolved phosphorescence [78] experiments offer much hope for achieving a better understanding of the glass transition.

Optical spectroscopy of single molecules in solids [79, 80] is another powerful tool to probe impurity-host interaction in the truly local “nano-environment.” Unlike other low temperature site selective spectroscopies, single-molecule spectroscopy (SMS) uses tunable optical radiation to select exactly one molecule within a solid matrix. By providing the combination of high spectral resolution and high spatial resolution, detected signals are not affected by any kind of ensemble averaging. For example, SMS allows one to construct a frequency histogram of the actual distribution of the spectral line shape of a heterogeneous system, or to study the energy change or spectral shift of individual molecules due to configurational changes in the nearby host, which influence the electronic transition via guest-host interactions. With polarized excitation and/or emission detection, the orientation and rotational motion of single molecules can be studied. These features are usually obscured by isotropy of the bulk sample.

The above optical dynamic hole burning experiments along with feasible single-molecule fluorescence studies of molecular orientation of probe molecules at room temperature [81, 82] set the stage for the recent single molecule spectroscopic experiments of Deschenes and Vanden Bout [11, 83]. In those works, the rotations of a fluorescent probe (Rhodamine 6G) in two polymers, were studied at $T_g + 5, 10$ and 15 K. The time period covered was $\sim 1-4000$ s. For both polymers, the results revealed heterogeneous dynamics. Interestingly, it was found that single molecules retain well-defined dynamics for a long period of time, $\sim 10 - 25 \tau_c$, before suddenly assuming a different set of dynamics. After a sufficient number of switches, the time-averaged dynamics approached ensemble average behavior. Roughly, $\tau(\text{ensemble}) = 125 \tau_c$ with a weak dependence on T . This unexpected weak dependence may result from the probe altering the dynamics of small domains, although that has yet to be conclusively determined. Nevertheless, SMS shows much promise for identifying T_g for fragile liquids and providing further insights on heterogeneous dynamics in supercooled liquids. In particular, the polarization-resolved SMS [11, 83] of single fluorophores in hyperquenched glassy and supercooled water has much potential to answer the questions arisen from the debates for the glass transition and fragility of water (see above). Two questions are: 1) What is the value of water T_g and, 2) if $T_g \sim 136$ K, is the substance above T_g a strong or fragile liquid. If one accepts that T_g is close to 136 K, the question arises as to the nature of the substance that exists between 136 K and the I_c transition temperature, referred to as water II (based on arguments that suggest there is not a reversible thermodynamic path between it and supercooled water (water I) [84]).

1.5. Dissertation Organization

A general introduction to the optical spectroscopy of impurities in solids, particularly non-photochemical hole burning (NPHB) and single molecule spectroscopy (SMS), is presented in Chapter 2. Although many studies have been undertaken over the past three decades to explain the physics of the NPHB mechanism, there is no general agreement on its mechanism [85-89]. A theory for NPHB has been proposed, developed, and firmly established in our research group. An important prediction of our NPHB mechanism is that NPHB should cease as soon as a crystalline phase is produced. The evidence for and experimental verification of this prediction is presented in Chapter 3 [Reinot, T., Dang, N. C. and G. J. Small, *J. Lumines*, 2002, **98**, 183]. The systems studied in these experiments are aluminum phthalocyanine tetrasulphonate (APT) and free base phthalocyanine tetrasulphonate (PcT) in hyperquenched glassy films of water (HGW) and cubic ice (I_c). In general, the persistent hole-burning mechanisms for these two molecular derivatives embedded in the same solid host matrix were expected to be different. Surprisingly, though, the hole growth kinetics in these two systems was so intriguingly similar that it led to another set of experimental studies, which are presented in Chapter 4. Chapter 4 presents a novel 2-D hole burning model that, for the first time, takes into account photoproduct absorption known to interfere with hole burned spectra [Reinot, T., Dang, N. C. and G. J. Small, *J. Chem. Phys.*, 2003, **119**, 10404]. The development of this model was instigated by the results provided in Chapter 3 that raise the fundamental question of how the disordered structure of the host couples to the guest chromophores. In this chapter, hole growth kinetics of free base phthalocyanine (Pc) in ortho-dichlorobenzene (DCB) is studied to address the question mentioned above. In addition, it has been shown that the hole evolution is affected

by burn fluence and that dispersive hole growth kinetics is a signature of NPHB for a chromophore in an amorphous host, a consequence of its structural disorder. Therefore, it is important to study the relationship between fluence broadening and dispersive hole growth kinetics, for which scant attention had been paid. Chapter 5 provides such a study [Dang, N. C., Reinot, T., Hayes, J. M. and G. J. Small, *Chem. Phys.*, 2004, **297**, 187], in which all the major factors (e.g. fluence, laser linewidth) affecting the hole evolution are considered. This study revealed the essential requirements for determining the experimental conditions to adequately reflect the dynamics of a hole-burning system. Besides the above validation of our theory for NPHB, NPHB has successfully demonstrated to be a powerful tool to probe properties of disordered structure of glasses. Chapter 6 presents a published paper [Dang, N. C., Reinot, T., Hayes, J. M. and G. J. Small, *J. Phys. Chem. A*, 2003, **107**, 10514] on the use of NPHB to probe the structural and dynamical properties of aluminum phthalocyanine tetrasulfonated (APT) in polymer-cage confined water. The results of this study were compared with those of a similar study done in hyperquenched glassy water (HGW). Differences between hole-burning properties are discussed in terms of the interaction of APT with bound (non-freezable) water - water bonded with the hydroxyl groups of the polymer, and the hydroxyethyl groups of the polymer. Chapter 7 describes temperature dependence of the hole growth kinetics of APT in HGW, from which the structural and physical properties of HGW were analyzed in detail. Chapter 8 summarizes the findings and presents a general conclusion for this dissertation. The dissertation ends with an Appendix. In this appendix, preliminary SMS data concerning the nature of hyperquenched glassy water and ethanol below and above its glass transition temperature are discussed.

References

1. Angell, C. A., Ngai, K. L., McKenna, G. B. and Martin, S. W., *J. Appl. Phys.* 2000, **88**, 3114.
2. Ediger, M. D., *Annu. Rev. Phys. Chem.* 2000, **51**, 99.
3. Ediger, M. D., Angell C. A., and Nagel, S. R., *J. Phys. Chem.*, 1996, **100**, 13200.
4. Bohmer, R., *Curr. Opin. Solid State Mat. Sci*, 1998, **3**, 378.
5. Sillescu, H., *J. Non-Cryst. Solids*, 1999, **243**, 81.
6. Debenedetti, P. G. and Stillinger, F. H. *Nature*, 2001, **410**, 259.
7. Wang, C.-Y., Ediger, M. D. *J. Phys. Chem. B*, 2000, **104**, 1724.
8. Angell, C. A., *J. Non-Cryst. Solids*, 1991, **131-133**, 13.
9. Bohmer, R. J., et. al., *J. Non-Cryst. Solids*, 1998, **235-237**, 1.
10. Ediger, M. D. and Skinner, J. L., *Science*, 2001, **292**, 233.
11. Deschenes, L. A. and Vanden Bout, D. A., *Science*, 2001, **292**, 255.
12. Vogel, H., *Phys. Z.*, 1921, **22**, 645.
13. Fulcher, G. S., *J. Amer. Ceram. Soc.*, 1925, **8**, 339.
14. Tammann, G., Hess, G., *Z. Anorg. Allg. Chem.*, 1926, **156**, 245.
15. Williams, M. L., Landel, R. F. and Ferry, J. D., *J. Amer. Chem. Soc.*, 1955, **77**, 3701.
16. Angell, C. A., in: *Relaxation in Complex Systems*, Eds.: Ngai, K. L. and Wright, G. B., National Technical Information Service, Springfield 1985, p. 3.
17. Kauzmann, W., *Chem. Rev.*, 1948, **43**, 219.
18. Gotze, W., in: *Liquids, Freezing and the Glass Transitions*, Eds.: Hansen, J. P., Levesque and Zinn-Justin, J., Les Houches. Section LI, 1989, North Holland, Amsterdam, 1991, p. 287.

19. Gotze, W. and Sjogren, L., *Rep. Prog. Phys.*, 1992, **55**, 241.
20. Kohlrausch, R., *Ann. Phys. (Leipzig)*, 1847, **12**, 393.
21. Williams, G., and Watts, D. C., *Trans. Faraday Soc.*, 1980, **66**, 80.
22. Richert, R., *J. Phys.: Condens. Matter*, 2002, **14**, R703.
23. Cohen, M. H. and Grest, G. S., *Phys. Rev. B*, 1979, **20**, 1077.
24. Adam, G. and Gibbs, J. H., *J. Chem. Phys.*, 1965, **43**, 139.
25. Donth, E., *Acta Polym.*, 1999, **50**, 240.
26. Donth, E., *J. Polym. Sci. B: Polym. Phys.*, 1996, **34**, 2881.
27. Lubchenko, V. and Wolynes, P. G., *Phys. Rev. Lett*, 2001, **87**, 195901.
28. Xia, X. and Wolynes, P. G., *PNAS*, 2000, **97**, 2990.
29. Sceats, M., G. and Rice, S. A., in: *Water, A Comprehensive Treatise*, Ed.: Franks, F., Plenum: New York, 1982, **7**, Chapter 2.
30. Stirniman, M. J., Huang, C., Smith, R. S., Joyce, S. A. and Kay, B. D., *J. Chem. Phys.*, 1996, **105**, 1295.
31. Kimmel, G. A., Stevenson, K. B., Dohnalek, Z., Smith, R. S., and Kay, B. D., *J. Chem. Phys.*, 2001, **114**, 5284.
32. Safarik D. J., Meyer, R. J., and Mullins C. B., *J. Chem. Phys.*, 2003, **118**, 4660.
33. Narten, A. H., Venkatesh, C. G., Rice, S. A., *J. Chem. Phys.* **1976**, **64**, 1106.
34. Jenniskens, P., and Blake, D. F., *Science*, **1994**, **265**, 73.
35. Mishima, O., Calvert, L. D., and Whalley, E., *Nature*, **1984**, **310**, 393.
36. Mishima, O., Calvert, L. D., and Whalley, E., *Nature*, **1985**, **314**, 76.
37. Loerting, T. Salzmann, C., Kohl, I., Mayer, E. and Hallbrucker A., *Phys. Chem. Chem. Phys.*, **2001**, **3** 5355.

38. Mayer, E., *J. Appl. Phys.*, 1985, **58**, 663.
39. Johari G. P., Hallbrucker, A. and E. Mayer, *Nature*, 1987, **330**, 552.
40. Bellissent-Funel, M.-C., Bosio, L., Hallbrucker A., Mayer, E. and Sridi-Dorbez, R.,
J. Chem. Phys., 1992, **97**, 1282.
41. Hallbrucker, A. and Mayer, E., *J. Chem. Phys.*, 1987, **91**, 503.
42. Hallbrucker, A., Mayer, E. and Johari G. P., *J. Chem. Phys.*, 1989, **93**, 4986.
43. Mishima, O. and Stanley H. E., *Nature*, 1998, **396**, 329.
44. Debenedetti, P. G. and Stanley H. E., *Phys. Today*, 2003, **56** (6), 40.
45. Debenedetti, P. G., *J. Phys.: Condens. Matter*, 2003, **15**, R1669.
46. Johari G. P., *J. Phys. Chem. B*, 1998, **102**, 4711.
47. Jenniskens, P., Banham, S. F., Blake, D. F., and McCoustra , *J. Chem. Phys.*,
1997,**107**, 1232.
48. Smith, R. S., Huang, C. Wong, E. K. L. and Kay, B. D., *Surf. Sci.*, 1996, **367**, L13.
49. Smith, R. S., Huang, C. and Kay, B. D., *J. Phys. Chem. B*, 1997, **101**, 6123.
50. Smith, R. S., and Kay, B. D., *Nature*, 1999, **398**, 788.
51. Smith, R. S., Dohnalek, Z., Kimmel, G. A., Stevenson K. P. and Kay, B. D., *Chem.*
Phys., 2000, **258**, 291.
52. Fisher, M. and Devlin J. P., *J. Chem. Phys.*, 1995, **99**, 11584.
53. Velikov, V., Borick, S. and Angell, C. A., *Science*, 2001, **294**, 2335.
54. Kivelson, D. Tarjus, G., *J. Phys. Chem. B.*, 2001, **105**, 6620.
55. Johari G. P., *J. Phys. Chem. B*, 2005, **122**, 144508.
56. Angell, C. A., *J. Chem. Phys.*, 1993, **97**, 6339.
57. Angell, C. A., *Chem. Rev.*, 2002, **102**, 2627.

58. Starr, F. W., Angell, C. A., Nave, L. E., Sastry, S., Scala, A., Sciortino, F. and Stanley, H. E., *Biophysical Chemistry*, 2003, **105**, 573.
59. Minoguchi, A., Richert, R. and Angell, C. A., *Phys. Rev. Lett.*, 2004, **93**, 215703-1.
60. Donth, E., *The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials*, 2001, Springer-Verlag, Berlin, Heidelberg, New York, pp. 1-10.
61. Anderson, P.W., Halperin, B. I., and Varma, C. M., *Philos. Mag.* 1972, **25**, 1.
62. Phillips, W. A., *J. Low Temp. Phys.* 1972, **7**, 351.
63. Hayes, J. M., Jankowiak, R., Small, G. J. in *Topics in Current Physics, Persistent Spectral Hole Burning: Science and Applications*, Moerner, W. E. (Ed.), 1988, Springer-Verlag, New York, pp. 153.
64. Jankowiak, R., Rechert, R., Bäessler, H. *J. Phys. Chem.*, 1985, **89**, 4569.
65. Jankowiak, R., Small, G. J. and Athreya, K. B. *J. Phys. Chem.* 1986, **90**, 3898.
66. Jankowiak, R., Small, G. J. and Ries, B. *Chem. Phys.*, 1987, **118**, 223.
67. Jankowiak, R., Hayes, J. M. and Small, G. J. *Phys Rev. B*, 1988, **38**, 2084.
68. Schmidt-Rohr, K. and Spiess, H. W., *Phys. Rev. Lett.*, 1991, **66**, 3070.
69. Heuer, A., Wilhelm, M., Zimmerman, H. and Spiess, H. W., *Phys. Rev. Lett.*, 1995, **75**, 2851.
70. Keubler, S. C., Heuer, A. and Spiess, H. W., *Phys. Rev. E*, 1997, **56**, 741.
71. Hinze, G., Diegemann, G. and Sillescu, H., *Europhys. Lett.*, 1998, **44**, 565.
72. Reinberg, S. A., Qiu, X. H., Wilhelm, M., Spiess, H. W. and Ediger, M. D., *J. Chem. Phys.*, 2001, **114**, 7299.
73. Cicerone, M. T. and Ediger, M. D. *J. Phys. Chem.*, 1993, **97**, 10489.
74. Cicerone, M. T. and Ediger, M. D. *J. Phys. Chem.*, 1996, **104**, 7210.

75. Wang, C.-Y., Ediger, M. D. *J. Phys. Chem. B*, 1999, **103**, 4177.
76. Wang, C.-Y., Ediger, M. D. *J. Chem. Phys.*, 2000, **112**, 6933.
77. Schiener, B., Chamberlin, R. V., Diezemann and Bohmer, R., *J. Chem. Phys.*, 1997, **107**, 7746.
78. Wendt, H. and Richert, R., *Phys Rev. E*, 2000, **61**, 1722.
79. Basche, Th., Moerner, W. E., Orrit, M., Wild, U., (Eds): *Single Molecule Optical Detection, Imaging and Spectroscopy*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996.
80. Basche, Th., Orrit, M., Rigler, R., (Eds): *Single Molecule Spectroscopy - Nobel Conference Lectures*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996.
81. Ha, T., Laurence, T. A., Chemla, D. S., Weiss, S., *J. Phys. Chem. B*, 1999, **103**, 6839.
82. Bartko, A. P. and Dickson, R. M., *J. Phys. Chem. B*, 1999, **103**, 11237.
83. Deschenes, L. A. and Vanden Bout, D. A., *J. Phys. Chem. B*, 2001, **105**, 11978.
84. Speedy, R. J., *J. Phys. Chem.*, 1992, **96**, 2322.
85. Kharlamov, B. M., Personov, R. I., Bykovskaya, L. A., *Opt. Spectrosc.*, 1976, **39**, 137.
86. Hayes, J. M. and Small, G. J., *Chem. Phys. Lett.*, 1978, **54**, 435.
Hayes, J. M. and Small, G. J., *Chem. Phys.*, 1978, **27**, 151.
87. Klafter, J. and Silbey, R., *J. Chem. Phys.*, 1981, **75**, 3973.
88. Shu, L. and Small, G. J., *Chem. Phys.*, 1990, **141**, 447.
89. Takahashi, Ju.-I., Tsuchiya, Ju. and Kawasaki, K., *Chem. Phys. Lett.*, 1994, **222**, 352.

CHAPTER 2

OPTICAL SPECTROSCOPY OF IMPURITIES IN SOLIDS

2.1. Electronic Spectra of Single Impurities in Solids

When an atom interacts with light, electrons in the ground state are promoted to empty or partially filled atomic orbitals (excited state). The excited atom, then, can dissipate excess energy and return to ground electronic state. A simple description of these phenomena is described by Einstein's model of absorption, spontaneous emission and stimulated emission [1]. However, when an electronic transition occurs in a molecule (several atoms) the nuclei are subjected to a change in Coulombic force as a result of the redistribution of electronic charge that accompanies the transition. Consequently, the nuclei respond by breaking into more vigorous vibration and the absorption spectrum shows a structure characteristic of the vibrational energy levels of the molecule. Simultaneous electronic and vibrational transitions are known as *vibronic transition*. The analysis of vibronic transition is based on the Frank-Condon principle that describes an electronic transition occurring within stationary nuclear framework. In other words, since the mass of an electron is so different from that of nuclei and that an electronic transition occurs so rapidly that the nuclear coordinates remain unchanged during the actual transition, but then readjust once the electrons have adopted their final distribution.

Fig. 2.1 illustrates the implications of the principle. This figure shows electronic transitions of a molecule in two electronic states that are represented by two molecular potential curves. Note that the potential curve in the excited state, S_1 , is typically displaced to

Figure 2.1. Schematic of potential energy curves for two electronic states of a guest molecule in a low temperature solid matrix used to describe Frank-Condon principle. The molecule makes a “vertical” transition from the ground vibrational state of the ground electronic states, S_0 , to the excited electronic state, S_1 , with a vibrational wavefunction that most resembles to initial vibrational wavefunction. E_{el} and E_v correspond the pure electronic and vertical transition energies, respectively. ψ_v and $\psi_{v'}$ are the phonon wave functions for phonon mode i in the ground and excited vibrational states, respectively, and q_i is the lattice normal coordinate.

the right relative to the potential curve in ground state, S_0 , due to the equilibrium bond length increases as a result of the molecular orbitals being introduced more anti-bonding character by excitation of electrons. The quantum mechanical description of the process is that the transition occurs from the ground vibrational state of S_0 to the vibrational state that it most resembles in S_1 and such transition is called “vertical”. The justification for this description is based on the evaluation of the transition dipole moment between the two vibronic states within Born-Oppenheimer approximation [2]. As a result, the probability of vibronic transition is found to be proportional to the product of the probability of the (pure) electronic transition and the square of the overlap integral (O) between the two vibrational states in their respective electronic states, which is also called the Frank-Condon (FC) factor (i.e. $FC = (O)^2 = \left| \int \psi_{v_e}^* \psi_{v_g} dq_N \right|^2$). ψ_v and $\psi_{v'}$ are the nuclear wave functions for the ground and excited vibrational states, respectively, and q_N is the nuclear coordinate. They are depicted as wavy lines crossing the corresponding vibrational levels in Fig 2.1. It should be noted that while Frank-Condon principle was originally introduced for molecular vibronic transitions with multiple vibrational levels; it is also valid for an impurity molecule being in interaction with delocalized phonon modes (and/or with local vibrational modes) [3]. In this case, ψ_v and $\psi_{v'}$ are the phonon wave functions for phonon mode i in the ground and excited vibrational states, respectively; and q_N is replaced by the lattice normal coordinate q_i .

Fig. 2.2 depicts the molecular electronic transitions of an individual chromophore in the three lowest energy levels when it interacts with light (see [4] for detail discussions). In this figure, S_0 is the ground state, S_1 is the first excited singlet state, and T_1 is the lowest triplet state. For absorption spectroscopy, the electronic transitions from the ground state, S_0 to the

Figure 2.2. Schematic representation of the three lowest electronic energy levels of a molecule: the ground state, S_0 , the first excited singlet state, S_1 , and the lowest triplet state, T_1 , (bold lines). Vibrational sublevels are also shown in each state (thin horizontal lines). The phonon free (0-0) transition takes place after excitation with photon of $h\nu$, while the left most arrow shows a vibronic excitation following a fast vibrational relaxation (small dotted arrow). The fluorescence emission (with rate k_{21}) is shown as dashed lines, which originate from S_1 and terminate on various vibrational levels of S_0 . k_{ISC} is the intersystem crossing rate from S_1 to T_1 . k_T is the triplet decay rate, which gives rise to phosphorescence emission.

first excited singlet state ($S_0 \rightarrow S_1$) gives rise to an absorption spectrum that consists of an origin (or (0-0) transition) band corresponding to the purely electronic transition and vibronic bands corresponding to the excitation of molecular vibronic modes. Due to the long lifetime of the T_1 -state of organic chromophores ($10^{-6} - 10^{-1}$ s) compared to S_1 lifetime (typically of several nanoseconds), the absorption band intensity of the $S_0 \rightarrow T_1$ transition is usually too low to be observed.

The transitions from purely electronic level $S_1 \rightarrow S_0$ and its vibrational sublevels give rise to an emission (fluorescence) spectrum, which consist of an origin band and vibronic bands at lower energies. Due to fast vibrational relaxation in the S_1 state (in the order of ps), the emission from vibronic sublevels of S_1 – the so-called “hot luminescence” – is very weak and is usually not observed in the emission spectrum. Non-radiative transition $S_1 \rightarrow T_1$ (intersystem crossing, ISC) is possible. After ISC takes place, vibrational relaxation to ground vibrational level of T_1 occurs. The triplet state can emit a photon by the $T_1 \rightarrow S_0$ transition. This process is called “phosphorescence” with the lifetime of 10^{-4} to 10^4 s. Note that when ISC from the singlet states into the triplet states occurs, it represents a common bottleneck because both absorption of photons and photon emission cease for a time approximately equal to the triplet lifetime. Therefore, ISC can lead to premature saturation of the emission rate from the chromophore (see section 2.6 for discussion).

At sufficiently low temperature in a solid matrix (for organic glasses, typically below 70 K), the absorption spectrum of a single chromophore consists of a sharp zero-phonon line (ZPL) and a phonon side band (PSB) on the higher energy side of the ZPL [5, 6]. The ZPL transition associated with the origin absorption band reflects a pure electronic transition, i.e., is phononless, and analogous to a gas-phase electronic transition that involves no change in

rotational quantum number. The PSB is the result of inelastic interactions of the chromophore with the phonon bath upon electronic transition (see section 2.2). The ZPL shape is a Lorentzian with a homogeneous linewidth, Γ_{hom} , (full width at half maximum, FWHM). The line shape function for a ZPL at frequency ω can be written as (for a detailed description, see Refs. 5 and 6):

$$l(\Omega - \omega) = \frac{1}{\pi} \frac{\Gamma_{\text{hom}}}{(\Omega - \omega)^2 + (\Gamma_{\text{hom}})^2} \quad (2.1)$$

where Ω is the observation frequency. The homogeneous linewidth Γ_{hom} is determined by the total dephasing time, τ_2 , of the optical transition of the chromophore and given by:

$$\Gamma_{\text{hom}} (\text{cm}^{-1}) = \frac{1}{\pi c \tau_2}, \quad (2.2)$$

where c is the speed of light and τ_2 is defined as:

$$\frac{1}{\tau_2} = \frac{1}{2\tau_1} + \frac{1}{\tau_2^*}. \quad (2.3)$$

In Eq. 2.3, τ_1 is the excited state lifetime of the chromophore and τ_2^* is the pure dephasing time. The pure dephasing time arises from the elastic interactions of the chromophore with bath phonons that result in the modulation of the single site transition frequency. Note that this interaction does not lead to electronic relaxation of the excited state, but rather to a decay of the phase coherence of the superposition state initially created by the photon [7].

Γ_{hom} is time and temperature dependent. The broadening of Γ_{hom} strongly depends on the host matrix structure, but it is functionally proportional to $T^{1.3} \log(t)$, where t is the observation time and T is the temperature [8]. The time dependence of Γ_{hom} arises from spectral diffusion which is the result of diffusional random walk process by the chromophore

transition frequencies due to configurational changes of host matrix with time. The temperature dependence of Γ_{hom} arises from the strongly temperature dependent term τ_2^* [5]. However, at liquid helium temperatures, the contribution of τ_2^* to Γ_{hom} can usually be neglected since the number of the thermally populated low frequency phonons (and/or other low energy excitations) is small; and the ZPL width is determined by the lifetime τ_l (for hyperquenched glassy methanol, ethanol and water at 4.7 K, $\tau_l \approx 5$ ns and $\Gamma_{\text{hom}} \approx 0.001 \text{ cm}^{-1}$ at [9]). At higher temperatures, the number of thermally populated low frequency phonons increases and results in increased electron-phonon scattering. Consequently, this leads to phase relaxation of the excited electronic state wavefunction, which shortens the lifetime in that particular quantum state and broadens the homogeneous linewidth. Therefore, the pure dephasing time τ_2^* dominates and determines the ZPL linewidth [5]. Typically, Γ_{hom} varies with temperature as $\sim T^{1.3}$, however its phenomenological origin is still a matter of debate [10].

2.2. Electron-Phonon Coupling

The coupling of electronic excitation with phonons can be explained using the potential energy curves of the ground state and excited state of a guest molecule in a low temperature solid matrix (see Fig. 2.3). In this figure, S_0 and S_1 denote potential energies of the electronic ground and excited states, respectively, whereas $\hbar\omega_i^g$ and $\hbar\omega_i^e$ are corresponding interaction energies of the guest molecule with the local phonon i at lattice normal coordinate q_i . The interaction of phonon quanta can be described using a harmonic oscillator model and may be written in the form [11]:

Figure 2.3. Schematic of potential energy curves and corresponding absorption spectra of the electronic transition from the ground state, S_0 , to the excited state, S_1 , of a guest molecule in a low temperature solid matrix. $\hbar\omega_i^g$ and $\hbar\omega_i^e$ are the corresponding vibrational energy quanta of local phonon mode i in a lattice normal coordinate q_i . Panels **a** and **b** represent the cases of weak and strong electron-phonon coupling, which correspond to the small and large changes of equilibrium position Δq_i , respectively.

$$V = \sum_i A_i q_i + \sum_{ij} B_{ij} q_i q_j. \quad (2.4)$$

In Eq. 2.4, the first term describes the linear electron-phonon coupling where A_i are the linear coupling coefficients while the second term describes the quadratic electron-phonon coupling where B_{ij} are the quadratic coupling coefficients. Detailed discussions of linear and quadratic coupling can be found in Refs. 12 - 15. In brief, the linear electron-phonon coupling describes the energy change in the excited state due to shifts in the equilibrium positions of the normal oscillator during the optical transition. In other words, the linear electron-phonon coupling gives rise to the PSB structure associated with the ZPL. Depending on the mixed solid system, the PSB structure can be due to delocalized phonons of the host or pseudo-localized phonons intimately associated with the probe molecule [16, 17]. The quadratic electron-phonon coupling describes the energy change in the excited state due to the change in the normal oscillator frequencies during an excitation. For $i = j$, it gives rise to homogeneous broadening of the ZPL, while for $i \neq j$, it describes the energy change due to the mixing of lattice normal coordinates (Dushinsky effect [18]).

The strength of electron-phonon coupling can be understood in term of geometry changes and/or changes of electronic charge distribution upon electronic excitation. The small change of equilibrium position between ground and excited electronic states, Δq_i , favors the transitions that are less likely to involve the change of vibrational quantum – resulting in weak electron-phonon coupling, i.e. high intensity of ZPL and relatively low intensity of PSB (Fig. 2.3a). The large change of the equilibrium position between excited and ground state increases the probability of vibronic transitions, which leads to the strong

electron-phonon coupling and results in relatively high intensity of PSB and low intensity of ZPL (Fig. 2.3b). Note that $\omega_i^s = \omega_i^e$ in the linear electron-phonon coupling approximation.

The relative intensity of the ZPL can be characterized using Debye-Waller factor (DWF), α (also known as FC factor) [6, 14, 17]:

$$\alpha = \frac{I_{\text{ZPL}}}{I_{\text{ZPL}} + I_{\text{PSB}}}, \quad (2.5)$$

where I_{ZPL} and I_{PSB} are the relative integrated intensities of ZPL and the PSB, respectively.

In the harmonic oscillator model at $T \sim 0$ for N phonon modes, the DWF factor is given by

$$\alpha = \exp(-S), \quad (2.6)$$

where S is the dimensionless Stokes shift (also known as the Huang-Rhys factor) and given by [6]

$$S(T = 0) = \frac{M_i \omega_i}{2\hbar} \sum_i (\Delta q_i)^2. \quad (2.7)$$

In Eq. 2.7, M and ω_i are the reduced mass and frequency of the phonon mode i , respectively, and Δq_i is the change of the equilibrium position corresponding to the lattice normal coordinate q_i . From Eq. 2.7, we see that $S \propto (\Delta q_i)^2$. Thus, S can be used to characterize the strength of the electron-phonon coupling. In general, electron phonon coupling is weak when $S < 1$. For $S > 1$, the electron-phonon coupling is strong [14, 17].

The DWF is temperature dependent. It decreases rapidly and, usually, monotonically as temperature increases, i. e. increasing temperature results in rapidly decreasing ZPL intensity. The temperature dependent DWF is given by [19]:

$$\alpha(T) = \exp \left[- \sum_i^N S(2\bar{n}_i + 1) \right], \quad (2.8)$$

where thermal occupation number, $\bar{n}_i = [\exp(\hbar\omega_i/kT) - 1]^{-1}$, is the average number of phonons of mode i at temperature T . $\alpha(T)$ reaches its maximum value at very low temperatures ($T \leq 10$ K for most organic glasses).

2.3. Single Site Absorption Spectrum.

In the low temperature limit ($T \rightarrow 0$), the general expression for the single site absorption spectrum observed at frequency Ω is given by [20, 21]:

$$L(\Omega - \omega) = \sum_{R=0}^{\infty} \frac{e^{-S} S^R}{R!} l_R(\Omega - \omega - R\omega_m), \quad (2.9)$$

where ω is the frequency of the ZPL, S is the Huang-Rhys factor, R are integers and enumerate phonon transition, and $l_R(\Omega - \omega - R\omega_m)$ is the normalized line shape function of the R phonon transition peaking at $\omega + R\omega_m$ with the mean phonon frequency, ω_m . Thus, $R = 0$ is the zero-phonon transition and $l_0(\Omega - \omega)$ is the Lorentzian line shape function of the ZPL, which is given by Eq 2.1. For $R \geq 1$, i.e. $R = 1, 2, 3, \dots$, which correspond to one-, two-, three- ... phonon profiles, $l_R(\Omega - \omega - R\omega_m)$ is given by the convolution of the one-phonon profile with itself R times. The pre-factors of $l_R(\Omega - \omega - R\omega_m)$, are Poisson weight factors for every R . They determine the intensity distribution of the PSB and turn out to be Frank-Condon factors for R phonon transitions.

In the case of weak electron-phonon coupling ($S < 1$), terms with $R > 1$ are small or indistinguishable from $R = 1$, i. e. the PSB is structureless, and Eq. 2.9 can be rewritten as:

$$L(\Omega - \omega) = e^{-S} l_0(\Omega - \omega) + (1 - e^{-S}) l_1(\Omega - \omega - \omega_m). \quad (2.10)$$

At higher temperature, the phonon creation and annihilation processes take place. Therefore, one must take into account the thermally populated phonon levels, i. e. the temperature dependent DWF (or FC factor) must be used. The single site absorption spectrum for weak electron-phonon coupling can be written as [22]:

$$L(\Omega - \omega, T) = e^{-S(2\bar{n}+1)} l_0(\Omega - \omega, T) + (1 - e^{-S(2\bar{n}+1)}) l_1(\Omega - \omega - \omega_m, T). \quad (2.11)$$

In Eq. 2.11, $l_0(\Omega - \omega, T)$ is the modification of Eq. 2.1, in which the temperature dependence of Γ_{homo} (Eq. 2.3) is taken into account (see section 2.5.4) and $\bar{n}$ is thermal occupation number as is defined above. $l_1(\Omega - \omega - \omega_m, T)$ is treated phenomenologically as a band which is a Gaussian on the lower energy side (close to the ZPL) and a Lorentzian on the higher energy side.

2.4. Inhomogeneous Broadening and Optical Bands of Impurities in Solids

Up to this point, the broadening mechanisms for Γ_{hom} of an individual impurity in a low temperature solid matrix have been discussed (see above). However, for a bulk sample, with many impurities in a solid matrix, the absorption bands are also broadened not just through homogeneous broadening but also inhomogeneous broadening. A detailed review of inhomogeneous broadening can be found in Ref. 23.

Let us first consider the interaction of chemically identical chromophores with the host environment for a perfect crystal lattice in the low temperature limit (see Fig. 2.4.a). Usually, all chromophores embedded in such lattice orient in a few ways; or ideally in only one way. Therefore, the chromophores interact with exactly the same immediate environment

Figure 2.3. Line broadening of embedded impurity molecules in perfect (a) and imperfect (b) lattices. Panel a represents impurity molecules being embedded into a perfect lattice. Homogeneous lines overlap and result in an absorption spectrum with a linewidth as broad as each individual ZPL. Panel b represents impurity molecules embedded into an imperfect lattice; consequently, each impurity molecule absorbs at different frequency, which leads to additional inhomogeneous broadening. The width of inhomogeneously broadened absorption band (dashed line) is typically $\sim 100 - 400\text{cm}^{-1}$, i.e. $\Gamma_{\text{inh}} \gg \Gamma_{\text{hom}}$.

of the host. As a result, all individual transitions have the same frequency, and in the absorption spectrum only homogeneous broadening is observed. Such a situation is shown in Fig. 2.4.a and it can be observed, for example, in Shpol'skii matrices (organic molecules embedded in microcrystalline alkane hosts) [24]. However, if the chromophores are in an imperfect crystal lattice or amorphous solid matrices as shown in Fig. 2.4.b, they interact with a large number of different environments due to structural disorder of the host. As a result, these chromophores absorb at different energies, which gives rise to inhomogeneous broadening. Inhomogeneous broadening does not affect the single site absorption spectra, but increases the bandwidth of the resulting absorption profile, thus it reflects the structural disorder of the host. In general, inhomogeneous broadening is referred to the statistical distribution of the single site absorption spectra (neglecting the PSBs and assuming very weak electron-phonon coupling), which is most often a Gaussian profile [25] (dashed line in Fig. 2.4b) with full width at half maximum of Γ_{inh} . Therefore, the absorption spectrum for the whole ensemble chromophores is a convolution of single site absorption spectrum (including the ZPL and PSB) and the distribution function of these sites. The result of the convolution gives the absorption spectrum a width of $\sim \Gamma_{inh} + S\omega_m$, [21, 26] where ω_m is the mean phonon frequency and S is the Huang-Rhys factor defined above.

According to the description of the inhomogeneous broadening mechanism above, absorption spectra of impurity centers in low temperature glassy and amorphous matrices usually suffer from large amounts of inhomogeneous broadening. In typical organic glasses, $\Gamma_{inh} \approx 100 - 400 \text{ cm}^{-1}$, which is about a factor of 10^5 broader than Γ_{hom} ($\approx 0.001 \text{ cm}^{-1}$), and $\omega_m \approx 20 - 40 \text{ cm}^{-1}$. Fig. 2.5 depicts a schematic of such an absorption spectrum. The broad

Figure 2.5. Schematic of an absorption spectrum consisting of one origin band $(0,0)$ with the band width of $\Gamma_{inh} + S\omega_m$ and a vibronic band $(0,1_\alpha)$. Γ_{inh} is the inhomogeneous width and ω_m is the mean phonon frequency. ν is vibrational frequency.

absorption spectrum consists of an origin band (0,0) with the width of $\sim \Gamma_{\text{inh}} + S\omega_m$, and a vibronic band (0,1 $_{\alpha}$) corresponding to the excitation of molecular vibronic mode α .

Consequently, inhomogeneous broadening obscures detailed information about ZPLs. For that reason, methods of selective excitation at low temperature such as fluorescence line narrowing (FLN) [27], spectral hole burning [5, 8, 28-30], photon echoes (PE)[15, 31-33], and single molecule spectroscopy (SMS) [34, 35] have been utilized to overcome the effects of inhomogeneous spectral broadening. Spectral hole burning and SMS especially provide extremely high spectral resolution and are powerful tools for probing structural disorder and the molecular dynamics of amorphous and glassy solids. This is especially true for SMS, which works at the ultimate limit of site-selective spectroscopy, i.e. spectrally and spatially selecting out an individual impurity in an ensemble.

2.5. Spectral Hole Burning

The phenomenon of hole burning in the electronic absorption band of chemically stable molecules in a frozen glassy solution was first reported by Personov and co-workers [36] for perylene and 9-aminoacridine in ethanol at 4.2 K. At about the same time, Gorokhovskii *et. al.* [37] reported similar observations for phthalocyanine in a Shpolskii matrix. Since then, spectral hole burning has been used as a site selective spectroscopy of impurities in crystalline and amorphous solids to reveal hidden information such as: Γ_{hom} of the ZPL, the electron-phonon coupling parameters, and even exciton-level structure in proteins. Moreover, it has been used as a powerful tool for probing the structural disorder and configurational tunneling dynamics of amorphous and glassy solids at low temperature. Detailed reviews of spectral hole burning can be found in Ref. 5, 8, 28-30.

Fig. 2.6 depicts hole burning in a typical guest-host system. If a narrow band laser with a frequency ω_B is used to irradiate the origin band of the inhomogeneously broadened absorption spectrum, then chromophores whose purely electronic transition (zero phonon transition) frequency in resonance with ω_B can change their absorption frequency with some finite probability (the frequency change mechanism is described in detail in section 2.5.1). Hole burning events spectrally eliminate a narrow subset of molecules from the absorption spectrum. Consequently, a sharp zero phonon hole (ZPH) at frequency ω_B is left in the post-burn absorption spectrum. Since the ZPL is accompanied by a PSB, the ZPH is accompanied by a phonon sideband hole (PSBH) on the higher energy side of ZPH. The burn laser also interacts with PSBs that accompany the ZPLs whose frequencies lie to lower energy of ω_B . These phononic excitations rapidly relax to the zero vibrational level. After such relaxation, the excited chromophores change their absorption frequencies and the signal loss at their origin absorption frequencies brings the emergence of a pseudo-PSBH in the spectrum at lower frequency than ω_B . In addition to phononic excitations, vibronic excitations are also possible. These vibronic excitations rapidly relax to the zero vibrational level in their electronically excited states. After hole burning takes place, these sites lose absorption at frequency of $\omega_A = \omega_B - \nu$, where ν is the vibrational frequency (with the condition that the intensity of inhomogeneous band at ω_A is greater than zero). As a result, the ZPH at ω_B is accompanied by a vibronic satellite hole at ω_A . In the same manner for the formation of PSBH on higher energy side of the ZPH, a hole burnt at ω_B is accompanied by a higher energy vibronic satellite hole at $\omega_C = \omega_B + \nu$. Note that the depth of vibronic satellite hole at ω_C is related to ZPH depth at ω_B via respective Frank-Condon factor. Similarly to the

Figure 2.6. Bands observable at hole burning frequency, ω_B . Top: the dashed and the solid lines represent the pre-burn and the post-burn absorption spectra, respectively. Hole burning spectrum is shown in the bottom panel (the difference between the pre-burn and post-burn absorption spectra). See text for details.

formation of the pseudo-PSBH of the ZPH, vibronic pseudo-PSBHs are formed at the lower energy side of vibronic holes (at ω_A and ω_C).

In widely used persistent hole burning systems such as porphines in polymers or organic glasses, the absorption of hole burned chromophores is known as an anti-hole or a photoproduct, and it forms within or close to the original inhomogeneous absorption band. Interference of the photoproduct with spectral hole quite often complicates theoretical treatment of the complete spectral hole shape. For NPHB systems, the photoproduct absorption is usually at higher energies from hole burned sites. For PHB, when chromophores are completely “destroyed”, the photoproduct of these chromophores may absorb light very far from origin position and only pure hole (without anti-hole) can be observed in the spectrum.

The ZPH shape, L_{hole} , in the absence of all other broadening factors, is $L_{\text{hole}} = L_{\text{ZPL}} \otimes L_B \otimes L_{\text{ZPL}} \otimes L_D$, where L_{ZPL} , L_B and L_D are the line shapes of ZPL, burn laser and detecting laser, respectively. In an ideal case, if the hole is burnt and detected with a very narrow band laser, $\Gamma_B = \Gamma_D \ll \Gamma_{\text{hom}}$, L_B and L_D become delta functions and the ZPH linewidth is $\Gamma_H = 2\Gamma_{\text{hom}}$. Such is the case for the studies performed in this dissertation, where $\Gamma_B = \Gamma_D \approx 1.0$ MHz and $\Gamma_{\text{hom}} = 25.0$ MHz. In the case of the laser linewidth being comparable to Γ_{hom} , due to the convolution, the resulting linewidth of is $\Gamma_H = 2\Gamma_{\text{hom}} + \Gamma_B + \Gamma_D$. However, for many real hole burning systems, the observed Γ_H is larger than the expected values due to a various effects such as fluence broadening, dephasing, and spectral diffusion taking place at the time from hole formation to hole detection.

From a temporal viewpoint, spectral hole burning can be classified as transient and persistent. Transient spectral hole burning (or population bottleneck hole burning) is created through the triplet state (see Fig. 2.1), which is used as a reservoir to store molecules in resonance with ω_B . The duration of triplet state lifetime, τ_T , serves as the depletion time of the ground state, S_0 [38, 39]. The absorption signal loss at ω_B can be measured by using a weak laser beam to monitor the population induced from the singlet excited state by a strong saturating burning beam [38], or by using a single beam to monitor the lifetime of the transient hole [39].

Two important mechanisms can cause persistent spectral hole burning - photochemical hole burning (PHB) and non-photochemical hole burning (NPHB). PHB describes hole burning that involves a photoreaction of the chromophore in its excited state, such as tautomerization, bond breaking, and isomerization [32, 40-43]. On the other hand, NPHB involves rearrangements of the guest-host matrix in which the absorbing chromophore is photochemically stable. In addition, in order to observe a persistent spectral hole, the post-burn ground state configuration of the chromophore-glass system must be different from, and highly kinetically inaccessible to, the pre-burn configuration. If the pre-burn state is accessible then the burnt hole is gradually filled. This process is called spontaneous hole filling (SHF). SHF is known as a thermally activated dark process. Most commonly, NPHB is observed in amorphous systems (glasses, polymers and protein hosts) because of their inherent configurational host-guest interactions. PHB and NPHB are known to be reversible processes, i.e. the hole generated can be filled by the hole burning process when ω_B is in resonance with the photoproduct of the initial hole. This hole filling mechanism is known as light induced hole filling (LIHF) [9]. Spectral holes can be also filled by a thermally

activated barrier hopping process, i.e., experimentally making the pre-burn configuration highly accessible. This can be done by thermal cycling, in which for finite time the temperature of the matrix is increased and decreased to the previous (burning) temperature. Typically at about 100 K, spectral holes are filled completely. Detailed reviews of hole filling processes can be obtained in Ref. 9.

Along with the hole filling processes described above, diffusional broadening of spectral holes (spectral diffusion, SD) also occurs (see Refs. 29, 30 for detailed reviews). It is a result of a diffusional random walk of chromophore transition frequencies due to configurational changes in the post-burn host matrix. SD occurs over a very wide timescales on ms to months [29, 30]. Since holes are always detected at a time later than burning, spectral diffusion always contributes to the spectral hole width.

However, it should be noted that not all guest-host systems can be used to produce spectral holes. In order to observe spectral holes, three following requirements must be satisfied: 1) a mechanism by which excitation of a chromophore can alter the energy of the excitation; 2) the presence of inhomogeneous broadening; and 3) a method of probing the original absorption during the persistence time of energy alteration.

2.5.1. NPHB Mechanism

In 1978, Hayes and Small formalized the very first mechanism of NPHB based on a *static* distribution of TLS to explain the frequency change mechanism for persistent spectral hole burning [44]. A scheme of transitions of TLSs coupled to an impurity (extrinsic two-level system, TLS_{ext}) is shown in Fig. 2.7. The superscripts α and β label the ground and

Figure 2.6. Schematic of the persistent NPHB mechanism. The diagram shows an extrinsic two level system (TLS_{ext}) of a guest molecule in the ground state (α) and excited state (β). Δ_α and Δ_β are asymmetry parameters in the ground and excited state, respectively. q represents the intermolecular coordinate, ω_B is the burn frequency.

excited electronic states of the probe. It is considered that excitation of the zero-phonon transition of a chromophore at frequency ω_B occurs in the left well, and is followed by a tunneling process in the excited state. The hole burning process of the chromophore completes with the relaxation to the ground state as depicted on the right well. The left to right relaxation that takes place in the excited electronic state leads to a blue-shifted antihole. Note that, this is not a general case (see below for further discussion).

Later, based on optical dephasing studies [45], it was suggested that for hole burning two types of TLS – extrinsic (TLS_{ext}) and intrinsic (TLS_{int}) – are important. TLS_{ext} are associated with the chromophore and its inner shell of solvent molecules that in NPHB, they are responsible for the initiation of the hole formation. TLS_{int} of the host are connected with the excess free volume of glasses and were proposed to cause the optical dephasing. Thus, selective optical excitation of the chromophores triggers the rearrangement of the host environment, which initiates the phonon-assisted tunneling processes that lead to hole formation. Therefore, the phonon-assisted tunneling in $\text{TLS}_{\text{ext}}^\beta$ is the rate-determining step for hole formation. The $\text{TLS}_{\text{ext}}^\beta$ energy diagram in Fig. 2.7 depicts the situation where phonon-assisted tunneling in the excited state involves phonon emission and the anti-hole site absorbs to higher energy of ω_B . There are seven other energy level schemes. Four of the eight lead to blue-shifted anti-hole sites, whereas the other four lead to red-shifted sites. Also, four of the schemes involve phonon absorption; the other four involve phonon emission.

The original hole burning mechanism of Hayes and Small [44] was based on the assumption of a *static* distribution of TLS_{ext} . Later, a number of experimental findings led to the conclusion that this assumption is invalid. These experimental observations were, first,

an anti-hole of a pronounced pseudo-PSBH lying predominantly to higher energy of the burn frequency ω_B , and second, the ability of ~ 100 % of the ZPL to be burned (when the contribution from phononic transitions to the absorption was taken into account). For the former, the observation of the blue-shifted anti-hole was explained by reasoning that hole burning caused a dynamical reconfiguration of the host that led to a diffusion of excess free volume, as first proposed by Cohen and Grest [47], and increased the free volume around the chromophore that would result in a weaker intermolecular interactions of the chromophore with inner shell solvent molecules in anti-hole configurations than in pre-burn configurations. These weaker intermolecular interactions resulted in the blue-shifting of the anti-hole. The second observation, i.e. ~ 100 % of the ZPL could be burned, contradicted with the prediction that ZPH depth is limited to 50 % since 50% of phonon-assisted tunneling in the excited state involving phonon absorption would not be expected to hole burn in the $T \rightarrow 0$ K limit. That is, one would expect that only 50% of the ZPL could be burned.

Because of these observations, Shu and Small [46] proposed that NPHB is the result of a hierarchy of tunneling events triggered by optical excitation that begin with the faster relaxing TLS_{int} in the outer shell and terminate in the inner shell. This outside-in chain of events would result in diffusion of excess free volume to the inner shell, opening the way for the rate determining step of NPHB that involves the $\text{TLS}_{\text{ext}}^\beta$. In this regard, it is widely accepted now that the TLS_{int} are inherently connected with the excess free volume of glasses. In the Shu-Small mechanism, one can view the events occurring in TLS_{ext} shown in Fig. 2.7 as being the result of prior relaxation events; the system at some instant of time is poised to undergo downward or iso-energetic tunneling in the excited state that is operative in the $T \rightarrow$

0 K limit. An important prediction of their model is that NPHB should cease upon formation of the crystalline phase from the glass because the former should be devoid of excess free volume.

However, a more recent analysis of the burn fluence dependence of the entire hole spectrum, which includes the ZPH, PSBH, and anti-hole, indicates that the Shu-Small mechanism for NPHB is inadequate for higher burn fluences. The Shu-Small mechanism considers one single hole burning act per chromophore/host system and it does not take the photoproduct into account. At high burn fluences, it has been proposed in Ref. 48 that a sequence of hole burning acts can occur in which first, a site is moved from its original absorption frequency to a new frequency by hole burning and second, it is brought back to the original absorption frequency by LIHF. Another improvement for the two-level Shu-Small model was the introduction of a "second channel" for hole burning, which is required to understand the evolution of the hole spectrum with increasing fluence. Both processes can be understood with the help of extrinsic multiple level system (MLS_{ext}) shown in Fig. 2.8, in which burning of configuration I with rate constant k_1 leads to anti-hole configuration (II), whose ZPL is red-shifted relative to ω_B . Following relaxation to the ground state, configuration II can absorb ω_B photons via its phonon sideband and revert to configuration I with rate constant k_2 (an example of LIHF). Configuration I can then be re-excited and converted to configuration II. This process could be repeated many times. However, configuration II can be converted to configuration III (with rate constant k_3) that is blue-shifted relative to ω_B . Thus, LIHF is not possible for configuration III. For this reason, we refer to configuration III as a "terminal" state, one that cannot absorb at ω_B . With $k_3 \ll k_2$

Figure 2.7. Extrinsic multi-level system model for NPHB. Indices β and α indicate chromophore in its excited and ground state. ω_B is the burn frequency of the laser and k_1 , k_2 , and k_3 are the tunneling rates. I, II, III, ..., and N denote chromophore-host configurations where I corresponds to the pre-burn configuration and II, III, ..., and N correspond to post-burn configurations.

and the II $\rightarrow$ III conversion being essentially irreversible, one can understand how multiple excitations eventually lead to an anti-hole that, for all intent and purposes, is entirely blue-shifted relative to ω_B .

Note that Shu-Small model does not require that NPHB *always* results in a blue-shifted anti-hole. This is not generally the case. Red-shifted anti-holes are observed in NPHB systems such as aluminum phthalocyanine tetrasulfonate (APT) in hyperquenched glassy ethanol and methanol [49]. The observation that anti-holes are *predominantly* blue-shifted is the result of dynamical interplay of the pseudo-PSBH, anti-hole band, and terminal states. Further modifications of NPHB are also discussed in Chapters 4 and 5.

2.5.2. Dispersive Hole Growth Kinetics

Given the immense structural disorder of amorphous solids, it is reasonable to expect that NPHB kinetics is highly dispersive. The concept of dispersive hole growth kinetics (HGK) was first introduced by Jankowiak *et. al.* [50]. The NPHB rate, R , is determined by tunneling in the excited state of the TLS_{ext} , in which it is assumed that two eigenstates of the TLS_{ext} are coupled via modulation of the TLS potential caused by the elastic wave in the medium (a phonon). At low temperature, the downward tunneling processes that emit a phonon should be prevalent. In a guest-host system with the Debye density of states and weak electron-phonon coupling, the downward phonon-assisted tunneling rate for a single $\text{TLS}_{\text{ext}}^\beta$ can be calculated by using Fermi Golden Rule (e.g. see Refs 7 and 51) and it is given as:

$$R \approx \left(\frac{3f^2W^2E}{16\pi\rho c^5\hbar^5} \right) \left(\langle \bar{n}_E \rangle_T + 1 \right). \quad (2.12)$$

In Eq. 2.12, ρ is the local sample density around the probe (i.e. it reflects free volume), c is the average sound velocity, f is related to the TLS_{ext} deformation potential difference. The thermal occupation number $\langle \bar{n}_E \rangle_T$, the tunnel splitting E and the tunneling frequency, W are defined above.

Because the tunneling frequency $W = \omega_0 \exp(-\lambda)$ depends exponentially on the tunneling parameter, λ , Eq.2.12 can be rewritten as $R = \Omega_0 \exp(-2\lambda)$, where Ω_0 is the pre-factor in the Fermi Golden rule expression for the TLS relaxation rate for NPHB. λ depends on several parameters that are subjected to statistical fluctuations, and λ is assumed to be the major source for distribution of relaxation rates. Most importantly, the λ -distribution assumed to be a Gaussian function centered at λ_0 [51] :

$$f(\lambda) = \frac{1}{\sigma_\lambda \sqrt{2\pi}} \exp \left[-\frac{(\lambda - \lambda_0)^2}{2\sigma_\lambda^2} \right] \quad (2.13)$$

is the major source of hole growth dispersion. In Eq. 2.13, σ_λ is the standard deviation of the λ -distribution. By linking this distribution with the phonon-assisted tunneling relaxation rate R , Jankowiak and co-workers [51-54] introduced and developed a model to describe dispersive hole growth kinetics (HGK) in the form of the fractional hole depth of the ZPH as:

$$D(\omega_B, t) = \int d\lambda f(\lambda) e^{-P\sigma_{LT}^p \phi(\lambda)t}. \quad (2.14)$$

In Eq. 2.14, P is the photon flux in number of photons ($\text{cm}^{-2} \text{s}^{-1}$), σ_{LT}^p is the peak absorption cross section (cm^2) at low temperature, and the NPHB quantum yield, $\phi(\lambda)$, is given by

$$\phi(\lambda) = \frac{\Omega_0 \exp(-2\lambda)}{\Omega_0 \exp(-2\lambda) + \tau_{fl}^{-1}} = \frac{R}{R + \tau_{fl}^{-1}}, \quad (2.15)$$

where τ_{fl} is the fluorescence lifetime.

However, the original model neglected, for simplicity, the contribution of intrinsic dispersion from photo-selection due to the polarization of the burn laser (the α -distribution) as well as the distribution stemming from off-resonant ZPL absorption (the ω -distribution). The distribution of the intrinsic dispersion from photo-selection reflects the random orientation of the transition dipole moment relative to the polarization of the laser. The α -distribution was first introduced by Koehler *et. al.* in 1985 [55]. These authors considered the effect of intrinsic dispersion and line width of persistent photochemical hole on the HGK [55]. Later, by incorporating both the α - and ω -distribution functions with the Gaussian λ -distribution function into a HGK model, Elschner and Bassler concluded that the contribution from the α - and ω -distribution to the HGK was weak [56]. This was confirmed by Turukhin and Gorokhovskiy [57] who concluded that the λ -distribution was the most important one, in agreement with the original HGK models [51-53]. However, none of these works provided details necessary for an accurate assessment of the relative importance of the λ -, α -, and ω -distributions to the dispersive HGK. The importance of the λ -distribution to the dispersive kinetics relative to those of the α - and ω -distributions has been recently asserted by Reinot and Small [58] who incorporated all three distributions in the HGK model, in which $D(\Omega, t)$ is given as:

$$D(\Omega, t) = 1.5 \int d\omega L(\Omega - \omega) G(\omega) \int d\lambda f(\lambda) \int d\alpha \sin \alpha \cos^2 \alpha e^{-P\sigma\phi(\lambda)L(\omega_B - \omega)\cos^2 \alpha t} . \quad (2.16)$$

In Eq. 2.16, $D(\Omega, t)$ describes the absorbance bleaching as function of frequency, Ω , and hole burning time, t . The first integral is the ω -distribution, where $L(\Omega - \omega)$ is the single site absorption spectrum (see Eq.2.3) and $G(\omega)$ the site distribution function. The second integral is the λ -distribution, and the third integral describes the α -distribution. The physical

meaning of exponential term in Eq. 2.16 is similar to that given by Eq. 2.14, except that in Eq. 2.16, σ corresponds to the integrated absorption cross section. Note that while Eq. 2.16 provides the shape of the full absorption hole spectrum, it does not contain terms describing hole-burning induced photoproduct. Thus, for all practical purposes, Eq. 2.16 is applicable for hole burn spectra in which the contribution from the PSBH and photoproduct negligibly small. A new model that takes the contribution from includes the photoproduct absorption into account is given in Chapter 4. Nevertheless, as mention above, Eq. 2.16 describes well the experimental HGK over 4 decades of burn fluence, as demonstrated in Ref. 58.

2.5.3. Temperature Dependence of ZPH

The theoretical limit for the hole width (Γ_H) is $2\Gamma_{\text{hom}}$, where Γ_{hom} is the ZPL width given by Eq. 2.2 and that is mostly contributed to by optical dephasing at non-zero temperatures. Experimentally, however, fluence always contributes to ZPH broadening, which is best understood as excessive off-resonance absorption via ZPL fringes. Therefore, to determine Γ_{hom} or theoretical limit of Γ_H , it is necessary to introduce a concept of zero-fluence hole width, Γ_0 , which is the hole width extrapolated to zero fluence from a set of experimental holes under finite fluence and temperature broadening, [35]. For many molecular systems at $T < 10$ K, Γ_H is found to follow $T^{1.3}$ temperature dependence [10]. However, stronger temperature dependence is observed at higher temperatures ($T \geq 10$), where dephasing is also caused by coupling with pseudo-localized phonons [59, 60]. Thus, the T -dependence of electronic dephasing is well described by the theory of Jackson and Silbey [59]. In their model, the temperature dependence of the ZPH is given as:

$$\frac{1}{2}\Gamma_H = \Gamma_0 + aT^\alpha + \sum_i b_i \bar{n}(\omega_i), \quad (2.17)$$

where Γ_H is the measured hole width and Γ_0 is the radiative lifetime limited width of the ZPL. $\bar{n} = [\exp(\hbar\omega/kT) - 1]^{-1}$ defines the phonon thermal occupation number. In Eq. 2.17, the second term (i.e. aT^α) describes dephasing due to diagonal modulation associated with the electron-TLS interaction [59]. For many probe molecules studied in organic glasses at low temperatures ($T \leq 10$ K) the exponent α varies from 1.1 to 1.3 [10]. The third term is associated with dephasing due to the exchange coupling with pseudo-localized phonon modes i ($i = 1, 2, \dots, m$) with frequency ω_i . The exchange coupling is obtained in the slow modulation limit, i. e. in which the difference in frequency, δ , of the pseudo-localized mode for the ground and excited electronic states of the probe is larger than the (circular) relaxation frequency, τ^{-1} [59]. The maximum temperature at which the ZPH can be observed is determined by its Franck-Condon factor, $\exp[-S(2\bar{n}(\omega_m) + 1)]$. Therefore, for studies of the ZPH at temperatures well above 15 K one requires a guest-host system with $S < 1$ (weak linear electron-phonon coupling) and a high value of ω_m . Chapter 6 provides an excellent example of such a system, i.e. aluminum phthalocyanine tetrasulphonate in hyperquenched glassy water, for which $S = 0.3$ and $\omega_m = 36 \text{ cm}^{-1}$.

2.6. Introduction to Single-Molecule Spectroscopy in Solids

The rapid development of methods for single molecule detection in the last two decades has testified that detection of single molecule has many unique features, which offer a variety of applications. In particular, single molecule spectroscopy (SMS) in solid has been

a tool to extract information about the behavior of individual molecules in complex condensed phase environments such as crystals, polymers, or glasses [61, 62]. Also, SMS has been used to detect the probability of a molecule residing in the triplet state, the magnetic resonance of one spin [63, 64], correlation properties of emitted photons [65, 66]. Currently, single protein molecules [67-69], single light harvesting systems [70], and fluorescence resonance energy transfer in single biomolecules have been observed. [71].

In general, SMS in solids can be accomplished in experimental conditions that the laser beam excites only one molecule in the probed volume at a time. Selection of single molecules can be performed by using a sample with very low concentration, or by tuning the excitation frequency into the low energy wing of the inhomogeneously broadened absorption bands lines where number of molecules in resonance with laser excitation is very low. In addition, all experimental aspects must be optimized to maximize "parasitic" background signals in order to obtain sufficient signal-to-noise ratio. Fluorescent microscopy techniques such as confocal microscopy, epi-fluorescence microscopy, scanning near field optical microscopy and total internal reflection illumination as well as various new photonics technologies have all advanced the progress of fluorescence SMS [72]. In particular, confocal microscopy is very useful to reduce the detection volumes to the sub-micrometer scale, thus reducing background signal significantly [72]. High quality optical filters (e.g. low-fluorescence glass filters (Schott), interference filters (Chroma, Omega) or holographic notch attenuation filters (Kaiser) can be used to efficiently reduce Rayleigh and Raman scattering [72]. In addition, highly sensitive avalanche photodiodes (APD) with very high quantum efficiency (≥ 0.75) and highly sensitive charge transfer coupled device cameras (CCD) can be now used to detect and image a single fluorophore [72].

One of the most challenging task for successful detection of SMS is to gain the signal-to-noise ratio (SNR). For single molecule detection (using fluorescence excitation) in a solid, the SNR can be approximated by the following equation [72, 73]:

$$\text{SNR} = \frac{D\phi_F \left(\frac{\sigma^P}{A} \right) \left(\frac{P_0}{h\nu} \right) \tau}{\sqrt{\frac{(D\phi_F \sigma^P P_0 \tau)}{Ah\nu} + C_b P_0 \tau + N_d \tau}} \quad (2.18)$$

where D is the overall efficiency for the detection of emitted photons (see [74, 75]); ϕ_F , fluorescence quantum yield; σ^P , peak absorption cross-section; P_0 , laser power; A , the focal spot area; $h\nu$, photon pump energy; τ , detector counting interval, N_d , dark count rate; and C_b , background count rate per Watt of excitation power. The numerator in Eq. 2.18 accounts for the peak detected fluorescence counts from one molecule in an interval of time τ , the three terms in the denominator represent shot noise contributions from the emitted fluorescence, background, and dark signal, respectively. According to Eq. 2.18, the best SNR can be attained by optimizing experimental conditions for the smallest possible focal volume containing the probe molecule, minimizing the focal area A , and thereby reduce the background signal. In addition, chosen probed molecules should ideally have a large peak absorption cross-section, high photostability and high fluorescence quantum yield, weak bottleneck into dark states (triplet states). Finally, detection operation should perform below saturation of the molecular absorption.

Large peak absorption cross-section, σ^P , is one of the most important factors for achieving SMS detection. Since the absorption probability of a single molecule from an incident photon of a pumping laser beam is σ^P/A , maximizing σ^P is beneficial for both strong

absorption of the incident laser beam and minimized background signals from unabsorbed photons. To estimate the value of σ^P , one can use Beer's law. At room temperature (RT), the peak absorption cross-section is given by

$$\sigma_{RT}^P = 2.303\varepsilon / N_A \quad (2.19)$$

in units cm^2 , where ε is the molecular extinction coefficient ($\text{L mol}^{-1} \text{cm}^{-1}$) and N_A is Avogadro's constant. The low temperature peak absorption cross-section, σ_{LT}^P is calculated using [58]:

$$\sigma_{LT}^P = \sigma_{RT}^P (\Gamma_{RT} / \Gamma_{\text{hom}}), \quad (2.20)$$

where Γ_{RT} and Γ_{hom} are the width of the room temperature absorption spectrum and the ZPL width at the low temperature used in the experiment, respectively.

An alternative formula for estimating the peak absorption cross-section in the low temperature limit is given by [73]:

$$\sigma_{LT}^P = 2c\tau_2 \left(\frac{S}{N_{\text{tot}}} \right)_{\text{ZPL}}, \quad (2.21)$$

where, c is the speed of light, τ_2 is the total dephasing times, S is the integrated absorption, and N_{tot} is the number density of absorbers producing S (units cm^{-2}). According to Eqs. 2.20 and 2.21, σ^P is inversely proportional to the ZPL linewidth, Γ_{hom} , and directly proportional to τ_2). Thus, narrow ZPL width provides a large peak absorption cross-section.

Although higher laser power produces higher signal, optical saturation must be avoided since after saturation further increase in laser power generates more background than signal. For organic molecules, saturation of the optical transitions become evident when the laser power $P_{\text{laser}} \approx 1 \text{ W cm}^{-2}$. Since at saturation the absorption rate has become comparable

to the fluorescence decay (the maximum rate that a single molecule can emit photons), further increase in laser power at saturation causes the molecule cannot decay back to ground state fast enough and thus, reducing the absorption ability of the molecule. The dependence of emission rate $R(I)$ of the molecule on the saturation intensity, I_s is expressed by the following expression [72, 73]:

$$R(I) = R_{\infty} \frac{I/I_s}{(1 + I/I_s)}, \quad (2.21)$$

where I is the pumping laser intensity, and R_{∞} is the maximum emission rate and is given by:

$$R_{\infty} = \frac{(k_{21} + k_{ISC})\phi_F}{2 + (k_{ISC}/k_T)}, \quad (2.22)$$

here, k_{21} is the rate of direct decay from S_1 to S_0 (see Fig 2.2), k_{ISC} is the rate of intersystem crossing, and k_T is the total decay rate from triplet back to S_0 .

On the other hand the dependence of absorption ability of the molecule on I_s is given by [72, 73]:

$$\sigma^P = \frac{\sigma_0^P}{(1 + I/I_s)}. \quad (2.23)$$

where σ_0^P is the low power peak absorption cross-section. The characteristic saturation intensity depends on the energy level structure of the molecule. For optical transitions of a molecule in an energy level structure approximating a two level system, the saturation intensity is given by [72]:

$$I_s = \frac{h\nu}{2\sigma^P\tau_F}, \quad (2.24)$$

where τ_F is fluorescence lifetime. However, for organic molecules ISC from singlet states into triplet states can represent a bottleneck and causes cessation of both absorption of photons and photon emission for a relatively long time. This effect results in premature saturation of the emission rate from the molecule and reduction of the absorption cross-section σ^P compared to the two level system case. Therefore, the premature saturation of the optical transition is dependent on whether the absorbing centers have strong bottlenecks in the pumping cycle (Fig 2.2). The saturation intensity for a molecule with a triplet bottleneck can be estimated using the following expression [72, 73]:

$$I_s = \frac{h\nu k_{21}}{2\sigma^P} \left[\frac{1 + (k_{ISC} / k_{21})}{1 + (k_{ISC} / 2k_T)} \right] \quad (2.25)$$

In Eq. 2.25, the factor outside the brackets is the two-level saturation intensity if there were no triplet bottleneck which represents an upper limit for the saturation intensity. According to this equation, to minimize the triplet bottleneck, the chosen molecules should be those which give small values of k_{ISC} and large values of k_T . Choosing organic rigid, planar aromatic molecules would satisfy these requirements.

In addition, the photostability of the impurity molecule and weak hole burning becomes essential to maintain the single-molecule signal at resonance with the probing laser frequency.

2.7. SMS in Studying the Glass Transition and Rotational Dynamics

In contrast to anisotropic systems, like crystals, where a correlation between the orientation of guest molecules and the geometry of host matrices is usually observed, in isotropic hosts (such as glassy solids), the transition dipole moments of guest molecules

exhibit random orientations. Based on the dipolar nature of fluorescent molecules, (i. e. the probability of excitation depends on $|\mu E|^2$, where μ is the molecular transition dipole vector and E is the excitation electric field vector [74]), the orientation of single molecules in the plane of the sample can be determined by spectrally resolving the polarization of the molecule [75, 76]. For the dipolar nature, several polarization-resolved techniques have been developed to extract orientational information of randomly orientated guest molecule in structurally disordered solids. The novel idea of these techniques is to detect the anti-correlated fluorescence signals with polarization in two orthogonal directions. Given that the absorption and emission dipoles of highly fluorescent molecules are parallel, the emission signal is maximum for the polarization of the probe laser beam aligned parallel to the dipole of the molecule, or minimum for the polarization of the probing laser beam aligned perpendicular to the dipole of the molecule. One possible method is to pump a single molecule with circularly polarized light and resolve the fluorescence by polarization. Another method is to pump a single molecule with orthogonal polarization lights. Both techniques result in anti-correlated orthogonal signals. The fluorescence polarization (a.k.a. the contrast signal or the different signal), A at time t is usually expressed as [75, 76]:

$$A = \frac{I_S(t) - I_P(t)}{I_S(t) + I_P(t)}, \quad (2.26)$$

where I_S and I_P are the orthogonal signals with respect to the detected polarizations.

However, when the molecule starts to rotate slowly with respect to the integration time, the two anti-correlated orthogonal signals of the molecule resulting from the two orthogonal polarizations begin to alternate their intensities. If the molecule is rotating rapidly, the signals will be unpolarized and the A value approaches zero.

A quantitative measure of the rotational dynamics of single molecules is to take the autocorrelation, $\Phi(t)$, of the fluorescence polarization $A(t)$, at time t . The $\Phi(t)$ is given as: [76]

$$\Phi(t) = \frac{\sum_{t'=0}^T A(t')A(t'+t)}{\sum_{t'=0}^T A(t')A(t')}, \quad (2.27)$$

where T is the total number of data points in a finite time series. By linking $\Phi(t)$ shown in Eq. (2.27) with the Kholrausch-Williams-Watts (KWW) "stretched exponential" function, $\Phi(t) = \exp[-t/\tau]^\beta$, one can obtain the decay constants τ and β (where τ is the relaxation time and β is a parameter). The obtained values of τ and β , then, are used to calculate the weighted average, single-molecule rotation correlation time, τ_c , using [77]:

$$\tau_c = \int_0^\infty \Phi(t) dt = \frac{\tau}{\beta} \Gamma(1/\beta), \quad (2.28)$$

With the value of τ_c obtained from (2.28), the ensemble average correlation time, $\langle \tau_c \rangle$, can be determined using $N^{-1} \sum_{j=0}^{N-1} (\tau_c)_i$, where N is the number of molecules studied [77].

For fragile glass former liquids, there is a distinct and abrupt decrease in viscosity as temperature increased above T_g , and the material exhibits liquid behavior when temperatures are above T_g . Therefore, in polarization-resolved SMS one would expect to observe that the two polarization-resolved signals of the probed molecule should alternate their intensities as the temperature is just above T_g (i.e. slow rotating regime). Further increase in temperature results in, at first, "randomly noisy" signals (i.e., fast rotating regime) and eventually the loss of signal difference. For strong glass former liquids, the rotational onset is expected at

higher temperature due to slower decrease in viscosity. Thus, quantitative measurements of the two orthogonal signals should allow studying the glass transition of fragile liquids. That is, detection of rotational onset of a probed molecule, using polarization-resolved SMS, should report when the matrix enters the supercooled liquid state (see Appendix). In addition polarization-resolved SMS can provide information about the rotational properties of probed molecules in various nanoenvironments. Hence, heterogeneous dynamics of probed molecules in supercooled liquids can be explored via autocorrelation of the fluorescence polarization.

References

1. Struve, W. S., *Fundamentals of Molecular Spectroscopy*, John Wiley and Sons, New York, Chichester, Brisbane, Toronto, Singapore, 1989, p. 275-277.
2. Struve, W. S., *Fundamentals of Molecular Spectroscopy*, John Wiley and Sons, New York, Chichester, Brisbane, Toronto, Singapore, 1989, p. 136-137.
3. Keil, T., *Phys. Rev.*, 1965, **140**, A601.
4. Skoog, D. A., Holler, F. J. and Neiman, T. A., *Principles of Instrumental Analysis*, 5th Edition., Hartcourt Brace College Publishers, Philadelphia, Fort Worth, Chicago, San Francisco, Austin, Montreal, Toronto, London, Sydney, Tokyo, 1998, p. 356-365.
5. Sild, O., Haller, K., (eds): *Zero-Phonon Lines and Spectral Hole Burning in Spectroscopy and Photochemistry*, Springer-Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo, 1988.
6. Rebane, K. K., *Impurity Spectra of Solids*, Plenum Press, New York, 1970.

7. Hayes, J. M., Jankowiak, R., Small, G. J. in *Topics in Current Physics, Persistent Spectral Hole Burning: Science and Applications*, Moerner, W. E. (Ed.), 1988, Springer-Verlag, New York, p. 153.
8. Völker, S., in *Relaxation Processes in Molecular Excited States*, Fünfschilling, J. (Ed.), Kluwer, Dordrecht, 1989, p. 113.
9. Jankowiak, R., Hayes, J. M., Small, G. J. *Chem. Rev.*, 1993, **93**, 1471.
10. Jankowiak, R. and Small, G. J., in *Disorder Effects on Relaxation Processes*, Blumen, A. and Richert, R. (Eds), Springer-Verlag, Heidelberg, Berlin, 1994, Chapter 15, p. 425-448
11. Sapozhnikov, M. N., *Phys. Stat. Sol. (b)*, 1976, **75**, 11.
12. Di Bartolo, B., *Optical Interactions in Solids*, Wiley, New York, 1968.
13. Pryce, M. L. H., in *Phonons in Perfect Lattices and Lattices with Point Defects*, Stevenson, R. W. H. (Ed.), Oliver and Boyd, London, 1965, p. 403.
14. Osadko, I. S., in *Advances in Polymer Science*, Dusek, K. (Ed), Springer-Verlag, Berlin, Heidelberg, 1988, p. 123-186.
15. Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*, New York: Oxford University Press, 1995, Chapter 9 - 11, p. 261 – 344.
16. Dawber, P. G. and Elliott, R. J., *Proc. Roy. Soc.(London)* 1963, **A273**, 222; Maradudin, A. A., Montroll, E. W., and Weiss, G. H., *Solid St. Phys.*, Academic, London, 1963, Suppl. 3; Stevenson R. W. H. (Ed.), *Phonons in Perfect Lattices and in Lattices with Point Imperfections*, Oliver and Boyd London, 1966; Bak, T. A. (Ed), *Phonons and Phonon Interactions*, Benjamin, W. A. Inc., New York, 1965; Wallis,

- R. F. (Ed), *Lattice Dynamics*, Pergamon Press, Inc., New York, 1965; Small, G. J., *Chem. Phys.* 1970, **52**, 656.
17. Personov, R. I., in *Spectroscopy and Excitation dynamics of Condensed Molecular Systems*, Agranovich, V. M. and Hochstrasser, R. M. (Eds), North-Holland, Amsterdam, 1983, p. 555 – 619.
 18. Dushinsky, F., *Acta Physiochem.*, 1937, **7**, 551.
 19. van der Zaag, P. J., Galaup, J. P. and Völker, S., *Chem. Phys. Lett.*, 1990, **166**, 263.
 20. Hayes, J. M. and Small, G. J. *J. Phys. Chem.*, 1986, **90**, 4928.
 21. Hayes, J. M., Gillie, J. K., Tang, D., Small, G. J. *Biochim. Biophys. Acta*, 1988, **932**, 287.
 22. Hayes, J. M., Lyle, P. A. and Small, G. J., *J. Phys Chem.*, 1994, **98**, 7337.
 23. Stoneham, A. M., *Rev Mod. Phys.*, 1969, **41**, 82.
 24. Gooijer, C., Ariese, F. and Hofstraat, J. W. (Eds): *Shpol'skii Spectroscopy and Other Site Selection Methods: Applications in Environmental Analysis, Bioanalytical Chemistry, and Chemical Physics*, A John Wiley & Son, Inc., New York, Chichester, Weinheim, Brisbane, Singapore, Toronto, 2000.
 25. Jankowiak, R., Rockwitz, K. D. and Bassler, H., *J. Phys. Chem.*, 1983, **87**, 552.
Elschner, A. and Bassler, *Chem. Phys.*, 1987, **112**, 285.
 26. Jankowiak, R., Hayes, J. M., Small, G. J. *Chem. Rev.*, 1993, **93**, 1471.
 27. Jankowiak, R., in *Shpol'skii Spectroscopy and Other Site Selection Methods: Applications in Environmental Analysis, Bioanalytical Chemistry, and Chemical Physics*, Gooijer, C., Ariese, F. and Hofstraat, J. W. (Eds) A John Wiley & Son, Inc.,

- New York, Chichester, Weinheim, Brisbane, Singapore, Toronto, 2000, Chapter 8, p. 235.
28. Moerner, W. E. (Ed.): *Topics in Current Physics, Persistent Spectral Hole Burning: Science and Applications*, 1988, Springer-Verlag, New York.
 29. Maier, H., Kharlamov, B. and Haarer, D., in *Tunneling Systems in Amorphous and Crystalline Solids*, Esquinazi (Ed.), Springer, Berlin, Heidelberg, New York, Barcelona, Budapest, Hong Kong, London, Milan, Paris, Singapore, Tokyo, 1998, p. 317.
 30. Creemers, T. M. H., Volker, S., in *Shpol'skii Spectroscopy and Other Site Selection Methods: Applications in Environmental Analysis, Bioanalytical Chemistry, and Chemical Physics*, Gooijer, C., Ariese, F. and Hofstraat, J. W. (Eds) A John Wiley & Son, Inc., New York, Chichester, Weinheim, Brisbane, Singapore, Toronto, 2000, Chapter 9, p. 273
 31. Hesselink, W. H. and Wiersma, D. A., in *Spectroscopy and Excitation dynamics of Condensed Molecular Systems*, Agranovich, V. M. and Hochstrasser, R. M. (Eds), North-Holland, Amsterdam, 1983, p. 249–263.
 32. Narasimhan, L. R., Littau, K. A., Pack, D. W., Bai, Y. S., Elschner, A. and Fayer, M. D., *Chem. Rev.*, 1990, **90**, 439.
 33. Koedijk, J. M. A., Wannemacher, R., Silbey, R. J. and Volker, S., *J. Phys. Chem.*, 1996, **100**, 19945.
 34. Basche, Th., Moerner, W. E., Orrit, M., Wild, U., (Eds): *Single Molecule Optical Detection, Imaging and Spectroscopy*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996.

35. Basche, Th., Orrit, M., Rigler, R., (Eds): *Single Molecule Spectroscopy - Nobel Conference Lectures*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996.
36. Kharlamov, B. M., Personov, R. I., Bykovskaya, L. A., *Opt. Commun.*, 1974, **12**, 191.
37. Gorokhovskii, A. A., Kaarli, R. K., Rebane, L. A. *JETP Lett.*, 1974, **20**, 216. Szabo, A., *Phys. Rev Lett.*, 1970, **25**, 924.
38. Szabo, A., *Phys. Rev Lett.*, 1970, **25**, 924.
39. Erickson, L. E. *Phys. Rev. B.*, 1975, **11**, 4512.
40. Volker, S., MacFarlane, R. M., Genack, A. Z., Trommsdorff, H. P., and van der Waals, J. H., *J. Chem. Phys.*, 1977, **67**, 1759.
41. Dick, B. *Chem. Phys.*, 1989, **136**, 429.
42. van den Berg, R., Visser, A. and Völker, S., *Chem. Phys. Lett.*, 1988, **144**, 105.
43. Lee, I.-J., Small, G. J. and Hayes, J. M., *Phys. Chem.*, 1990, **94**, 3376.
44. Hayes, J. M., Small, G. J. *Chem. Phys.*, 1978, **27**, 151.
45. Hayes, J. M., Stout, R. P., Small, G. J. *J. Phys. Chem.*, 1981, **74**, 4266.
46. Shu, L., Small, G. J. *Chem. Phys.*, 1990, **141**, 447.
47. Cohen, M. H. and Grest, G. S., *Phys. Rev. Lett.*, 1980, **45**, 1271.
48. Reinot, T., Zazubovich, W., Hayes, J. M. and Small, G. J. *J. Phys. Chem. B.*, 2001, **105**, 5083.
49. Reinot, T., Hayes, J. M. and Small, G. J. *J. Chem. Phys.*, 1997, **106**, 457.
50. Phillips, W. A. (Ed), *Amorphous solids - Low Temperature Properties*, Springer, Berlin, 1981.
51. Jankowiak, R., Richert, R., Bäessler, H. *J. Phys. Chem.*, **1985**, **89**, 4569.
52. Jankowiak, R. and Small, G. J. *Phys. Rev. B*, **1988**, **37**, 8407.

53. Jankowiak, R., Hayes, J. M. and Small, G. J. *Phys. Rev. B*, 1988, **38**, 2084.
54. Kenney, M. J.; Jankowiak, R. and Small, G. J. *Chem Phys.*, 1990, **146**, 47.
55. Koehler, W.; Breinl, W. and Friedrich, J., *J. Phys. Chem.*, 1985, **89**, 2473.
56. Elschner, A. and Bässler, H., *Chem. Phys.* 1988, **123**, 305.
57. Turukhin, A. V. and Gorokhovskiy, A. A., *Chem. Phys. Lett.*, 2000, **317**, 109.
58. Reinot, T. and Small, G. J., *J. Chem. Phys.*, 2000, **113**, 10207.
59. Jackson, B. and Silbey, R., *Chem. Phys. Lett.*, 1983, **99**, 331.
60. Jankowiak, R., Bassler, H. and Silbey, Chem Phys Lett, 1986, **125**, 139.
61. Basche, Th., Moerner, W. E., Orrit, M., Wild, U., (Eds): *Single Molecule Optical Detection, Imaging and Spectroscopy*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996.
62. Basche, Th., Orrit, M., Rigler, R., (Eds): *Single Molecule Spectroscopy - Nobel Conference Lectures*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996.
63. Kohler, J., Disselhorst, J. A. J. M., Donckers, M. C. J. M., Grouenen, E., Schmidt, J. and Moerner, W. E., *Nature*, 1993, **363**, 242.
64. Wrachtrup, J., von Borczyskowski, C., Bernard, J., Orrit, M. and Brown, R., *Nature*, 1993, **363**, 244.
65. Bernard, J., Fluery, Talon, H., and Orrit, M., *J. Chem. Phys.*, 1993, **98**, 850.
66. Zumbusch, A., Fluery, L., Brown, R., Bernard, J. and Orrit, M., *Phys. Rev. Lett.*, 1993, **70**, 3584.
67. Funatsu, T., Harada, Y., Tokumaga, M., Saito, K. and Yanagida T., *Nature*, 1995, **374**, 555.
68. Noji, H., Yasuda, R., Yoshida, M. and Kinosita, K., *Nature*, 1997, **386**, 299.

69. Dickson, R. M., Cubitt, A. B., Tsien R. and Moerner W. E., *Nature*, 1997, **388**, 355.
70. van Oijen, A. B., Ketelaars, M., Kohler, J. Aartsma, T. J. and Schmidt, J., *Science*, 1999, **285**, 400.
71. Weiss, S., *Science*, 1999, **283**, 244.
72. Moerner, W. E. and Fromm, D. P., *Review Scientific Instruments*, 2003, 74, 3597.
73. Moerner, W. E., in *Single Molecule Optical Detection, Imaging and Spectroscopy*, Basche, Th., Moerner, W. E., Orrit, M., Wild, U., (Eds), VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996, p. 1-29
74. Basche, Th., Ambrose, W. P. and Moerner, W. E., *J. Opt. Soc Am.*, 1992, **B9**, 829.
75. Ha, T., Laurence, T. A., Chemla, D. S., Weiss, S., *J. Phys. Chem. B*, 1999, **103**, 6839.
76. Deschenes, L. A. and Vanden Bout, D. A., *Science*, 2001, 292, 255.
77. Deschenes, L. A. and Vanden Bout, D. A., *J. Phys. Chem. B*, 2001, **105**, 11978.

CHAPTER 3

**NON-PHOTOCHEMICAL VERSUS PHOTOCHEMICAL HOLE BURNING
IN HYPERQUENCHED GLASSY WATER AND CUBIC ICE**

A paper published in and reprinted with permission from
Journal of Luminescence, 2002, **98**,183-188

T. Reinot¹, N. C. Dang², and G. J. Small³

Department of Chemistry, Iowa State University, Ames, IA 50011-3111, USA

Abstract

The Shu-Small mechanism [*J. Opt. Soc. Am. B*9, (1992) 724] for non-photochemical hole burning (NPHB) of electronic transitions of chromophores in amorphous hosts at low temperatures is based on a hierarchy of configurational tunneling events that begin in the outer shell and terminate in the inner shell that surrounds the chromophore. Connectivity between the intrinsic and extrinsic two level systems that stem from structural disorder and the excess

¹ Staff Scientist

² Graduate Student

³ Major Professor

free volume of glasses are key features of this mechanism. This mechanism has recently been modified to take into account multilevel extrinsic systems [*J. Chem. Phys.*, 2001, 114, 9105]. An important prediction of the Shu-Small mechanism is that NPHB should cease upon formation of a crystalline phase produced, for example, by warming of a vitrified glass. In this paper data are presented that are consistent with that prediction. The systems studied are aluminum phthalocyanine tetrasulphonate (APT) and free base phthalocyanine tetrasulphonate (PcT) in hyperquenched glassy films of water (HGW) and cubic ice (I_c). The hole burning mechanisms for APT and PcT are non-photochemical and photochemical, respectively. Surprisingly, the hole growth kinetics for PcT are as highly dispersive as are the kinetics for APT. This means that the kinetics for photoinduced proton tautomerization in PcT are strongly influenced by its nanoenvironment of water molecules, some of which are involved in H-bonding to the -NH groups of PcT.

Keywords: Hole burning, Hole burning mechanism, Hyperquenched water, Cubic ice

1. Introduction

Persistent non-photochemical hole burning (NPHB) is a striking example of configurational tunneling in amorphous solids at low temperatures. The effect is the burning of narrow spectral holes into an inhomogeneously broadened electronic absorption band of an imbedded chromophore that is triggered by excitation of the chromophore (for reviews see [1 - 3]). Unlike photochemical hole burning (PHB) [4], where the isochromat of chromophore sites selected by a narrow-line laser undergoes photochemistry, NPHB does not involve intramolecular photochemistry. In simplest terms it is a consequence of the post-burn configuration of the chromophore-glass system being different and highly kinetically

inaccessible to the pre-burn configuration. This explains why NPHB is generally restricted to amorphous hosts. NPHB, as it later became to be called, was first observed by Personov and co-workers [5].

It remained for Hayes and Small [6] to make the connection between NPHB and the aforementioned phonon-assisted tunneling between asymmetric bistable configurations (two-level systems, TLS). In their model, extrinsic TLS associated with the chromophore and its inner shell of solvent molecules are responsible for NPHB ($\text{TLS}_{\text{ext}}^{\text{e}}$ and $\text{TLS}_{\text{ext}}^{\text{g}}$, where g and e denote the ground and excited state of the chromophore). The tunneling was proposed to occur between the two wells of the $\text{TLS}_{\text{ext}}^{\text{e}}$. A static distribution of $\text{TLS}_{\text{ext}}^{\text{e}}$ was assumed with different values of the tunnel parameter (λ). Somewhat later, it was reported that the temperature dependence ($T < 15$ K) of the homogeneous width of zero-phonon lines (ZPL) in amorphous molecular hosts is anomalous relative to that in crystalline hosts [7, 8]. In amorphous hosts the dependence is close to linear. Several groups studying pure dephasing of the ZPL of RE^{3+} ions in inorganic glasses arrived at the same conclusion [9, 10]. This led to a number of theories that attributed the anomalous dephasing to modulation of the ZPL frequency due to tunneling of the intrinsic TLS (TLS_{int}) of the glass host (for review see [2]).

A number of observations made in the 80's led Shu and Small to conclude that NPHB cannot be understood in terms of a static distribution of TLS_{ext} . [11, 12] They proposed that NPHB is the result of a hierarchy of tunneling events triggered by optical excitation that begin with the faster relaxing TLS_{int} in the outer shell and terminate in the inner shell. This outside-in chain of events would result in diffusion of excess free volume to the inner shell, opening the way for the rate determining step of NPHB that involves the $\text{TLS}_{\text{ext}}^{\text{e}}$. In this

regard it is widely accepted that the TLS_{int} are a consequence of the excess free volume of glasses as first proposed by Cohen and Grest [13]. An important prediction of their model is that NPHB should cease upon formation of the crystalline phase from the glass since, by definition, the former should be devoid of excess free volume. Such was observed for aluminum phthalocyanine tetrasulphonate in hyperquenched glassy water upon formation of cubic ice at 150 K [14]. It was shown later that the NPHB quantum yield of APT in hyperquenched glassy ethanol also undergoes a dramatic decrease upon formation of the crystalline phase. [15] These observations provided convincing evidence that *excess free volume plays a key role in NPHB* and that it appears to be correlated with the density of TLS_{int} .

In this paper we report the first example of persistent spectral hole burning in ice, specifically free base phthalocyanine tetrasulphonate (PcT) in cubic ice (I_c) that is produced by warming low density HGW to 175 K. The structure of I_c is similar to that of hexagonal ice I_h [16]. I_h is produced by warming I_c to 225 K.

The observation of efficient PHB of PcT and very inefficient NPHB of APT in I_c provides additional support for the Shu-Small mechanism of NPHB. Unexpectedly, the hole growth kinetics of PcT in HGW are highly dispersive and similar to those of APT. (Preliminary results for PcT in I_c indicate that its kinetics are similar to PcT in HGW). This means that the kinetics of proton tautomerization of PcT are sensitive to its nanoenvironment of water molecules. Possible reasons for this are considered.

2. Experimental

The experimental setup is described in detail in [3]. Briefly, a ring dye laser was used for hole burning and reading of the burned holes. Laser power was stabilized using an electro-optical stabilizer, the laser beam was expanded to approximately match the sample size and was further attenuated using a set of neutral density filters. The laser power density could be varied from several nW/cm² up to several hundred mW/cm². The long-term line width of the laser was estimated to be less than 10 MHz, an order of magnitude narrower than the sharpest observed hole. Experiment control and data collection were done using a dedicated PC and locally developed software. The sample was prepared as a 10⁻⁴ M solution of APT or PcT in ion exchanged (nanopure) water. The liquid was delivered by a reciprocating plunger pump through the PEEK tubing and thermospray unit onto the copper plate cold finger of a liquid He cryostat. The thermospray consists of resistively heated stainless steel capillary and a 0.1 mm diameter sapphire nozzle. The temperature of the capillary and flow speed was chosen to produce about micrometer size droplets of liquid which, upon impinging on the conduction cooled polished copper plate, cooled at a rate of ~10⁷ K/s. Film thicknesses were ~20 μ m. A film made at the lowest obtainable temperature, $T = 4.7$ K, is called *fresh*. An *annealed* film was prepared by warming a fresh film to 145 K for 30 minutes. I_c was prepared by warming film up to 175 K for 30 minutes.

3. Results and Discussion

Fig.1 shows the 4.7 K fluorescence excitation spectra in the Q-region of APT and PcT in fresh HGW. The lowest energy band and the high energy shoulder in the APT spectrum

Figure 1. The fluorescence excitation spectra (4.7 K) of APT in fresh hyperquenched water (left) and PcT in fresh hyperquenched water (right). The doublet structure is due to the Q_x - and Q_y - bands with the former the lower energy band. Also shown are zero-phonon holes burned with a fluence of 60 nJ/cm². From top to bottom the holes are for fresh HGW, annealed HGW and cubic ice. See text for discussion why a zero-phonon hole in APT in cubic ice was not detected.

correspond, respectively, to the Q_x - and Q_y -states that are split by 220 cm^{-1} [17]. The splitting for PcT is much larger, 720 cm^{-1} , and the widths of its Q_x - and Q_y - bands are considerably broader than those of APT, Table 1. Efficient hole burning of APT and PcT restricted to the Q_x -state due to the 1 ps lifetime of the Q_y -state that is determined by $Q_y \rightarrow Q_x$ internal conversion. [15] The three zero-phonon holes (ZPH) on the right and two on the left of Fig. 1 are for PcT and APT, respectively. The burn wavelengths used are indicated by the two solid arrows. The burn intensity and burn time were 6.1 nW/cm^2 and 10 s. From top to bottom the ZPHs of PcT are for fresh HGW, annealed HGW and I_c . (The burn fluence used did not produce a detectable hole for APT in I_c .) In the same order the ZPH widths for APT in fresh and annealed HGW are 230 and 100 MHz, respectively. The fractional hole depths for PcT and APT are ~ 0.1 and ~ 0.05 . Thus, the hole burning efficiencies for the two chromophores in the two glasses are similar, as indicated by the hole spectra in Fig. 2. The relatively broad hole to the right of the ZPH in Fig. 2 is the pseudo-phonon sideband hole (PSBH). Note that the peak frequency (ω_m) of 34 cm^{-1} for the phonon profile of PcT is nearly the same as the 36 cm^{-1} value for APT. The 36 cm^{-1} phonon sideband has been assigned to a pseudo-localized mode associated with APT [18]. Replacement of Al^{3+} by two protons has little effect on that mode. The spectra shown in Fig. 2 and others obtained with different fluences led to values of 0.3 and 0.32 for the Huang-Rhys factor in APT and PcT in HGW. They are included in Table 1 along with the ω_m values. One further point is that the higher intensity of the PSBH of PcT suggests that its hole burning efficiency is probably higher than that of APT. This is borne out by the hole growth kinetics data, see below.

Returning to Fig. 1, the absence of a ZPH for APT in I_c (burn fluence of 60 nJ/cm^2) is consistent with previous results, which showed that the NPHB efficiency of APT undergoes a

Table 1. Hole burning parameters for APT and PcT in fresh and annealed HGW.

	APT in fresh HGW	PcT in fresh HGW
Q_x band FWHM (cm^{-1})	355	440
Fluorescence lifetime, τ_h (ns)	6.5	(6.5 used)
Tunnel frequency, Ω_0 (s^{-1})	7.6×10^{12}	7.6×10^{12}
RT absorption crosssection, σ_{RT} (cm^2)	7.6×10^{-16}	2.7×10^{-16}
LT absorption crosssection, σ_{LT} (cm^2)	2.0×10^{-10}	1.06×10^{-10}
Zero fluence holewidth at 4.7 K, γ (FWHM, MHz)	230	210
Tunnel parameter λ_0	8.5	7.8
Standard deviation of λ , σ_λ	1.0	1.02
Average quantum yield of hole burning, $\langle \phi \rangle$	0.015	0.06
Huang-Rhys factor, S	.30	.32
Peak phonon frequency, ω_m (cm^{-1})	36	34

Figure 2. Hole burned spectra (4.7K) for APT and PcT in fresh hyperquenched water obtained with the indicated burn fluence. The two sharp features are zero-phonon holes. To their right are the relatively broad pseudo-phonon sideband holes peaked at $\omega_m = 36 \text{ cm}^{-1}$ (APT) and 34 cm^{-1} (PcT).

drastic reduction upon formation of I_c (see Introduction). In the present study it was found that a burn fluence of 0.06 mJ/cm^2 , 1000 times higher than the above burn fluence, was required to produce a detectable hole in I_c . Again, this provides strong support for the Shu-Small mechanism. We note that for both APT and PcT the fluorescence intensity remained essentially constant in going from HGW (5K) to I_c . This excludes the possibility that during warming of the films, aggregation of the chromophores occurred since dimer formation leads to strong fluorescence quenching [19].

That the hole burning efficiencies of PcT in the two glasses and I_c are comparable is consistent with a PHB mechanism involving proton tautomerization. Hole burning in I_c was anticipated. What was not anticipated is that the hole growth kinetics are as highly dispersive as those of APT, as we now show.

The experimental ZPH growth kinetics curves obtained at 4.7 K for PcT and APT in fresh HGW and PcT in I_c are shown at the left of Fig. 3 where fractional hole depth is plotted vs. burn time (t). Based on our earlier, very detailed studies of dispersive kinetics of APT in annealed HGW [20] and other chromophore glass systems [21], as well as results from other groups [22], we were able to tell, by inspection, that the kinetics curves are highly dispersive. To the right of the experimental curves are fits for PcT in fresh HGW and I_c (for the sake of clarity fits for the other curves are not shown) obtained using the standard equation for NPHB:

$$D(\Omega, t) = 1.5 \int d\omega L(\Omega - \omega) G(\omega) \int d\lambda f(\lambda) \int d\alpha \sin \alpha \cos^2 \alpha e^{-P\sigma\phi(\lambda)L(\omega_B - \omega)\cos^2(\alpha)t}, \quad (1)$$

which is the fractional hole depth at frequency Ω following a burn at ω_B for time t with spectral photon flux P (no. of photons $\text{cm}^{-2} \text{ s}^{-1}$). The frequency ω is that of the ZPL and

$G(\omega)$ is the Gaussian distribution of ZPL frequencies with a FWHM of Γ_{inh} . With $t = 0$, $D(\Omega, 0)$ is the normalized absorption spectrum prior to burning. In Eq. (1), σ is the integrated absorption cross-section with units of $\text{cm}^{-2} \text{s}^{-1}$. $f(\lambda)$ is the normalized Gaussian distribution function for the TLS_{ext} tunnel parameter centered at λ_0 with a standard deviation σ_λ . The NPHB quantum yield, $\phi(\lambda)$, is given by $\Omega_0 \exp(-2\lambda) [\Omega_0 \exp(-2\lambda) + \tau_{\text{fl}}^{-1}]^{-1}$, where τ_{fl} is the fluorescence lifetime. The numerator is the tunneling rate. $L(\omega_i - \omega)$ [$\omega_i = \Omega, \omega_{\text{p}}$] is the single site absorption profile consisting of the zero phonon line (ZPL) and phonon sideband structure. The angle α is the angle between the laser polarization and transition dipole vectors. It leads to “intrinsic” dispersive kinetics from randomly oriented transition dipoles such as in a homogeneous glass. In what follows we refer to the α distribution. The ω distribution stems from the off-resonant absorption of the ZPL. It also leads to intrinsic dispersive kinetics. Thus, in analyzing dispersive kinetics one must take into account the α , ω , and λ distributions. In Ref [20] it was shown that for all NPHB systems studied thus far, the λ distribution is of primary importance with the ω and α distributions becoming more important at the latter stage of the burn ($\sim$ last 10% that saturates the ZPH). The values of the parameters in Eq. 1 used to obtain the fits in Fig. 3 for PcT in fresh HGW are given in Table 1. All but the values of λ_0 and σ_λ (free parameters) and Ω_0 were determined experimentally. The parameter values for APT in fresh HGW are also listed. The values of the 4.7 K peak absorption cross-sections used when the ω distribution is neglected are also given in Table 1. The value of the rate pre-factor Ω_0 of 7.6×10^{12} was chosen to be equal to the value used in our earlier studies of NPHB systems. As reported in [20], uncertainties in

Ω_0 , σ , τ_{fl} , and P do not affect σ_λ and, therefore, the relative contributions of the α , ω , and λ distributions to the dispersive kinetics. They do affect the value of the average hole burning quantum yield, $\langle \phi \rangle$ (results not shown).

The proton tautomerization of PcT at liquid He temperatures is due to tunneling. The two tautomers in a disordered host are associated with the minima of a TLS. Thus, the use of Eq. (1) to simulate its PHB kinetics is justified. There are eight distribution combinations that can be considered, including one that neglects the α , ω , and λ distributions, the 0 distribution. The fits obtained with λ , $\alpha\omega$, $\lambda\alpha$, and $\lambda\omega\alpha$ are shown in Fig. 3 (with regard to the last distribution, only the ZPL of the single site absorption profile was taken into account since the electron-phonon coupling is weak). The fit for the $\alpha\omega$ distribution is poor, as are the fits for zero, α and ω distributions (not shown). The λ , $\lambda\alpha$, and $\lambda\omega\alpha$ distributions provide acceptable fits as does the $\lambda\omega$ distribution (not shown). Clearly, the λ distribution is of primary importance over the first four decades of burn time (fluence). This is consistent with the results for APT in annealed HGW, where six decades of burn fluence was used [20]. From that work and the results in Fig. 3, it is clear that the kinetics for PcT in fresh HGW obtained over six decades of burn fluence would show that $\lambda\omega\alpha$ distribution provides the best fit for the data. We hasten to add that the results presented in [20] establish that the λ_0 and σ_λ values determined by the λ distribution for the first ~80% of the burn are nearly identical to the values obtained by using the $\lambda\omega\alpha$ distribution to fit the kinetics over a burn fluence range that extends to saturating the ZPH. It is the value of σ_λ that determines the degree of dispersiveness of the hole growth kinetics. Concerning the simulations of the kinetics for APT in fresh HGW that led to the λ_0 and σ_λ values given in Table 1, it was also

Figure 3. Hole growth kinetics curves (4.7K) for PcT in fresh hyperquenched water and cubic ice and APT in fresh hyperquenched water (three noisy curves at the left). To the right are fits to the hole growth curve for PcT in fresh hyperquenched water obtained with the $\alpha\omega$, λ , $\lambda\alpha$, and $\lambda\omega\alpha$ distributions. See text for discussion.

found that only λ , $\lambda\alpha$, $\lambda\omega$, and $\lambda\omega\alpha$ distributions yielded satisfactory fits. Preliminary analysis of the data for PcT in I_c indicates that its higher burning efficiency relative to that of PcT in fresh HGW is mainly the result of the difference in induced absorption rates with the rate of the former being a factor of ~ 2 higher than that of the latter, see above.

To conclude, we address the interesting question of why the PHB kinetics of PcT in HGW and I_c are also highly dispersive. We calculated that the quantum yield for the first 5% of the burn is a factor of 10^3 higher than that of the last 5% of the burn. We propose that the dispersion is due to structural disorder that affects the H-bonding of water molecules to the H atoms of the two NH groups and the two N atoms which are not covalently linked to H atoms. Support for this comes from recent quantum calculations on the effect of water on H atom transfer in 7-azaindole [23]. H-bonding was found to have a profound effect on the barrier separating the two tautomers in both the ground and S_1 states of 7-azaindole. Calculations of the type reported in [23] are planned for PcT. In addition, deuteration experiments are planned that should test the above hypothesis. Also planned are experiments of free base phthalocyanine in non H-bonding host media. We anticipate that the PHB kinetics will be far less dispersive than in PcT in HGW and I_c .

Acknowledgement.

Support for this research was provided by the Solid State Chemistry and Polymers Program of the National Science Foundation under Grant No. DMR-9908714. We thank Professor Mark Gordon at Iowa State University for useful discussions on how H-bonding of water molecules might affect the proton tautomerization of PcT.

References

1. R. Jankowiak, J. M. Hayes, G. J. Small, Chem. Rev. 93 (1993) 1471.
2. J. M. Hayes, R. Jankowiak, G. J. Small, In *Persistent Spectral Hole Burning: Science and Applications*; Moerner, W. E., Ed.; Springer-Verlag: Berlin, 1988; Chapter 5.
3. T. Reinot, V. Zazubovitch, J. M. Hayes, G. J. Small, J. Phys. Chem. B 105 (2001) 5083.
4. A. A. Gorokhovskiy, R. Kaarli, L. A. Rebane, JETP Lett. 20 (1974) 216.
5. M. Kharlamov, R. I. Personov, L. A. Bykovskaya, Opt. Commun. 12 (1974) 191.
6. J. M. Hayes, G. J. Small, Chem. Phys. 27 (1978) 151.
7. J. M. Hayes, R. P. Stout, G. J. Small, J. Chem. Phys. 73 (1980) 4129.
8. J. M. Hayes, R. P. Stout, G. J. Small, J. Chem. Phys. 74 (1981) 4266.
9. P. M. Selzer, D. L. Huber, D. S. Hamilton, W. M. Yen, M. J. Weber, Phys. Rev. Lett. 36 (1976) 813.
10. P. Avouris, A. Campion, M. A. El-Sayed, J. Chem. Phys. 67 (1977) 3397.
11. L. Shu, G. J. Small, J. Opt. Soc. Am. B 9 (1992) 724.
12. L. Shu, G. J. Small, Chem. Phys. 141 (1990) 447.
13. M. H. Cohen, G. S. Grest, Phys. Rev. Lett. 45 (1980) 1271.
14. W.-H. Kim, T. Reinot, J. M. Hayes, G. J. Small, J. Phys. Chem. 99 (1995) 7300.
15. T. Reinot, J. M. Hayes, G. J. Small, J. Chem. Phys. 106 (1997) 457.
16. F. Franks, In: *Water, a comprehensive treatise*, Ed. F. Franks, Plenum Press: NY (1982) Vol.7 Ch. 4.
17. T. Reinot, J. M. Hayes, G. J. Small, M. C. Zerner, Chem. Phys. Lett. 299 (1999) 410.
18. T. Reinot, W.-H. Kim, J. M. Hayes, G. J. Small, J. Chem. Phys. 104 (1996) 793.

19. P. C. Martin, M. Gouterman, B.V. Pepich, G. E. Renzoni, D. C. Schindele *Inorg. Chem* 30 (1991) 3305.
20. T. Reinot, G. J. Small, *J. Chem. Phys.* 113 (2000) 10207.
21. M. J. Kenney, R. Jankowiak, G. J. Small, *Chem. Phys.* 146, (1990) 47.
22. A. Elschner, H. Bässler, *Chem. Phys.* 123, (1988) 305.
23. G. M. Chaban, M. S. Gordon, *J. Phys. Chem.* 103 (1999) 185.

CHAPTER 4

**A MODEL FOR PERSISTENT HOLE BURNED SPECTRA AND HOLE GROWTH
KINETICS THAT INCLUDES PHOTOPRODUCT ABSORPTION:
APPLICATION TO FREE BASE PHTHALOCYANINE IN HYPERQUENCHED
GLASSY ORTHO-DICHLOROBENZENE AT 5 K**

A paper published in and reprinted with permission from
Journal of Chemical Physics, 2003, **119**, 10404-10414

T. Reinot¹, N. C. Dang² and G. J. Small³

Department of Chemistry, Iowa State University, Ames, IA 50011

Abstract

Persistent nonphotochemical and photochemical hole burning of the $S_0 \rightarrow S_1$ origin absorption bands of chromophores in amorphous hosts such as glasses, polymers and proteins at low temperatures have been used to address a number of problems that range from structural disorder and configurational tunneling to excitation energy transfer and charge separation in photosynthetic complexes. Often the hole burned spectra are interfered by

¹ Staff Scientist

² Graduate Student

³ Major Professor

photoproduct (anti-hole) absorption. To date there has been no systematic approach to modeling hole burned spectra and the dispersive kinetics of zero-phonon hole growth that accounts for the anti-hole. A “master” equation that does so is presented. A key ingredient of the equation is a time-dependent, 2-dimensional site excitation frequency distribution function (SDF) of the zero-phonon lines. Prior to hole burning ($t = 0$) the SDF is that of the educt sites. For $t > 0$ the SDF describes both educt and photoproduct sites and allows for burning of the latter that revert to the educt sites from which they originate (light-induced hole filling). Our model includes linear electron-phonon coupling and the three distributions that lead to dispersive hole growth kinetics, the most important of which is the distribution for the parameter λ associated with tunneling between the bistable configurations of the chromophore-host system that are interconverted by hole burning. The master equation is successfully applied to free base phthalocyanine (Pc) in hyperquenched glassy ortho-dichlorobenzene (DCB) at 5 K. The mechanism of hole burning is photochemical and involves tautomerization of the two protons at the center of the macrocycle (Pc) that occurs in the $S_1(Q_x)$ and/or $T_1(Q_x)$ state of Pc. A single set of parameter values (some of which are determined directly from the hole burned spectra) provides a satisfactory description of the dependence of the hole burned spectra and hole growth kinetics on the location of the burn frequency within the inhomogeneously broadened Q_x absorption band. The hole growth kinetics are found to be quite highly dispersive, although to a lesser degree than the kinetics for free base phthalocyanine tetrasulphonate in hyperquenched glassy water (T. Reinot et al., *J. Luminescence* **98**, 183, 2002). The dispersion is attributed to structural heterogeneity of solvent molecules in the inner shell that leads to a distribution of chromophore-host interactions that affect the height of the barrier separating the two tautomers. The new

master equation should also prove useful with no additional assumptions or modifications for interpretation of nonphotochemical hole burned spectra.

1. Introduction

It is well-known that porphine molecules in crystalline and amorphous hosts undergo efficient photochemical hole burning at liquid helium temperatures, as reviewed in Ref. 1. The mechanism is proton tautomerization that occurs in the $S_1(Q_x)$ state, or possibly the $T_1(Q_x)$ state², and involves the two inner protons of the macrocycle. The process involves tunneling of these protons that is equivalent to their rotation by 90° . The matrix environment renders the two tautomers energetically inequivalent. The two tautomers can be interconverted with light and distinguished by polarized hole burning experiments.³ Hole burning with probe molecules such as mesoporphyrin has been effectively used to study conformations and structural fluctuations in proteins at low temperatures.⁴ The tunneling can be modeled using an asymmetric double well potential (two-level system, TLS) with the reaction coordinate primarily associated with intramolecular rotation of the protons. Electronic reorganization accompanies tautomerization. A tunneling TLS model has also been used to explain persistent nonphotochemical hole burning (NPHB) of chromophores in amorphous hosts such as glasses, polymers and even proteins, as reviewed in Ref. 5 and 6. In this case, however, the reaction coordinate is intermolecular and associated with the chromophore and its inner shell of host molecules. This type of TLS is referred to as extrinsic, TLS_{ext} . For H-bonding matrices, deuteration experiments have shown that the coordinate involves H-bonding rearrangement in the inner shell.⁷⁻⁹ The intrinsic TLS (TLS_{int}) of the glassy host, that exist in the outer shell and are associated with the excess free

volume of glasses¹⁰, also play an important role in NPHB.¹¹ Tunneling of the TLS_{int} triggered by excitation of the chromophore results in diffusion of excess free volume to the inner shell, opening the way for the rate determining step of NPHB that involves the TLS_{ext} . Because of structural heterogeneity, there is a distribution of TLS_{ext} with varying barrier height, asymmetry parameter, etc. As a result, the growth kinetics of the zero-phonon hole (ZPH) are highly dispersive as first observed over ten years ago.¹² The most detailed experimental and theoretical studies of dispersive kinetics are for Al-phthalocyanine tetrasulphonate (APT) in hyperquenched glasses of water (HGW) and ethanol (HGE) at 5 K.¹³

We recently reported on photochemical hole burning of free base phthalocyanine tetrasulphonate (PcT) in HGW, the objective being to further test the mechanism of Shu and Small¹⁴ for NPHB. A key component of their mechanism is the importance of excess free volume of amorphous hosts for NPHB. (Efficient NPHB is generally observed only for glassy hosts.) The prediction was that upon formation of the crystalline phase from the glass the NPHB efficiency should undergo a pronounced decrease, an expectation met for APT in water, methanol and ethanol.¹⁵ For water the decrease was over 3 orders of magnitude (the transition from the glass to cubic ice occurs at ~ 155 K). Still, the question arose as to whether in warming the glass to 155 K aggregation of APT molecules occurred that significantly shortened the lifetime of its Q_x state. Such shortening could explain the cessation of hole burning upon formation of cubic ice. This possibility led to the experiments with PcT in HGW reported in¹⁶, for which the hole burning mechanism is photochemical (proton tautomerization). Formation of cubic ice had only a minor effect on the hole burning efficiency (high) of PcT, a result that argued strongly against aggregation of APT molecules

in water being responsible for the cessation of NPHB upon formation of cubic ice. Other factors arguing against aggregation are: the conservation of fluorescence signal upon cubic ice formation since dimers and higher aggregates of APT are non-fluorescent; and the lack of dimer related bands in the spectrum (centered at ~ 704 nm). There was a second reason for the PcT/HGW experiments; namely, if the hole growth kinetics (HGK) were single exponential (non-dispersive) the ZPH profile should be flat topped after saturation of the ZPH.¹⁷ By saturation is meant the maximum depth of the ZPH. Such a profile was not observed.¹⁷ It was then found that¹⁶ the HGK of PcT in HGW are as dispersive as those of APT in HGW, a quite surprising result since proton tautomerization is typically viewed as an intramolecular process. The standard deviation (σ_λ) of the tunnel parameter (λ) distribution function for both systems is close to 1.0. The dispersive kinetics of PcT in HGW was attributed to structural disorder of the inner shell of water molecules that affects H-bonding of certain water molecules to the NH groups in the center of the macrocycle and leads, therefore, to a distribution of barrier heights that separate the two tautomers.

In this paper photochemical hole burning results are presented for free base phthalocyanine (Pc) in ortho-dichlorobenzene (DCB) at 5 K. The initial objective was to determine if the weaker interactions between Pc and DCB (relative to PcT and water) result in significantly less dispersion in the kinetics. This turned out not to be possible using the conventional master equation for hole burned spectra that does not account for photoproduct (anti-hole) absorption. For Pc in DCB the position of the anti-hole relative to the burn frequency ω_B (coincident with the ZPH) exhibits a strong dependence on the position of ω_B within the inhomogeneously broadened $S_0 \rightarrow Q_x$ absorption band. Furthermore, the peak frequency of phonons that couple to the electronic transition is very low, only 10 cm^{-1} . The

coupling results in phonon side band hole structure that overlaps the ZPH; i.e. the 10 cm^{-1} mode appears to be overdamped. For analysis of the results it proved necessary to develop a new master equation for hole burned spectra that accounts for the ω_B -dependence of the anti-hole as well as hole burning of anti-hole sites that leads to filling of the educt sites from which they originate. The latter is often referred to as light-induced hole filling (LIHF).^{18,19} A key ingredient of this equation is a time-dependent, 2-dimensional site excitation frequency distribution function (SDF) that describes how the initial (prior to burning) 1-dimensional SDF of educt sites evolves to a 2-D SDF that describes the zero-phonon lines (ZPL) of both educt and anti-hole sites. Electron-phonon coupling and a distribution of λ -values are included in the model. Simulations of the hole spectra required three approximations, all of which were guided by experiment. A single set of values for the parameters, some of which were determined directly from the hole spectra, was found to provide satisfactory fits to hole spectra and HGK curves of the ZPH obtained with burn frequencies that range from the high to low energy sides of the Q_x absorption band. The kinetics are less dispersive ($\sigma_\lambda \sim 0.5$) than those of APT and PcT in HGW. The new master equation should prove useful in future studies of photochemical and nonphotochemical hole burning systems. For NPHB no modifications of the theory, as applied herein to PHB, are necessary.

2. Experimental

Free base phthalocyanine (Pc) and 1,2-dichlorobenzene (DCB) were purchased from Porphyrin Products and Aldrich, respectively, and used as received. Pc is practically insoluble in most solvents but is soluble in DCB.²⁰ Solutions with concentrations up to

10^{-4} M were obtained without noticeable aggregation using ultrasonication followed by extensive shaking and filtering. The room temperature absorption spectra were recorded before and after filtering, which allowed for reliable determination of the integrated absorption cross-section (σ) of the Q_x absorption band that enters into the equation for hole burned spectra.

The apparatus used to prepare hyperquenched glassy films of DCB containing Pc is described in detail in Refs. 6 and 21. Briefly, hyperquenched films were produced by thermospray deposition of the sample onto a polished copper substrate attached to the cold finger of a Janis ST-100 continuous flow helium cryostat. The lowest temperature obtained was 4.7 K. Unless otherwise stated, spectral holes were burned and read at that temperature. The body of the cryostat was mounted in a vacuum chamber with a base pressure of $\approx 2 \times 10^{-7}$ Torr. The thermal spray is inserted into the vacuum chamber through a vacuum fitting. Inlet and outlet temperatures of 132 °C and 325 °C for the thermospray resulted in ≈ 2 μ m diameter DCB droplets. Liquid was delivered by a reciprocating plunger pump. Film thicknesses of ≈ 10 μ m were used.

The optical setup of the experiment has been extensively described in Ref. 6. The only improvement in the laser-based apparatus is the development of in-house software that provides 32-bit data collection, more facile detection of the hole growth kinetics and improved automation and control of the experiment. Briefly, the laser system used for hole burning and reading was an actively stabilized Coherent 699-29 ring dye laser (Exciton LD-688 dye; long term linewidth < 10 MHz) pumped by a 6W Ar-ion laser (Coherent, Innova-90). The intensity of the laser beam was stabilized electro-optically (Cambridge Research and Instrumentation, LS100). The beam was then expanded in a beam expander and

attenuated using a set of neutral density filters. The fluorescence from the sample passed through a long wavelength pass filter (Omega Optical, AELP-730) and was detected with a photomultiplier tube (Hamamatsu, R2949) followed by a photon counter (Stanford Research SR400).

ZPH profiles were recorded in the fluorescence excitation mode using 20 MHz resolution. A resolution of 0.4 cm^{-1} was used for recording the entire hole spectrum, which encompasses the ZPH, the phonon sideband hole structure and the anti-hole (photoproduct absorption). The burn fluences used are given in the text and figure captions. Care was taken to ensure that the laser intensities used to read spectra were sufficiently low to preclude hole burning, typically $\sim 20 \text{ nW/cm}^2$. Hole growth kinetics curves were obtained by monitoring the decrease in fluorescence intensity as a function of burn time.

Model calculations were done on a 2 GHz personal computer using locally developed software written in Microsoft Visual C++.

3. Model For Simulation Of Hole Spectra And Dispersive Hole Growth Kinetics

With the neglect of photoproduct (anti-hole) absorption the absorption spectrum after a burn at ω_B with photon flux P (no. of photons $\text{cm}^{-2}\text{s}^{-1}$) and burn time t is given by ¹⁷.

$$A(\Omega, t) = 1.5 \int d\omega L(\Omega - \omega) G(\omega) \int d\lambda f(\lambda) \int d\alpha \sin \alpha \cos^2 \alpha e^{-P\sigma\phi(\lambda)L(\omega - \omega_B)\cos^2 \alpha t}, \quad (1)$$

where ω is the frequency of the zero-phonon line (ZPL) and $G(\omega)$ is the Gaussian distribution of ZPL frequencies, the so-called site-distribution function (SDF). $L(\Omega - \omega)$ is the single site absorption spectrum that consists of the ZPL and phonon sideband (PSB). $f(\lambda)$ is the normalized Gaussian distribution function for tunnel parameter λ centered at λ_0 with

standard deviation σ_λ . α is the angle between the polarization of the burn laser and the transition dipole of the chromophore and σ is the integrated absorption cross-section of the chromophore in units of $\text{cm}^2 \text{s}^{-1}$. $\phi(\lambda)$ is the hole burning quantum yield given by $\Omega_0 \exp(-2\lambda)/(\Omega_0 \exp(-2\lambda) + \tau_{fl}^{-1})$, where τ_{fl} is the fluorescence lifetime of the chromophore. The numerator is the tunneling rate. A quantum mechanical expression for Ω_0 is given in Ref. 8. We note that uncertainties in the values of Ω_0 , P and σ do not affect σ_λ and, therefore, the relative contributions of the λ -, α - and ω -distributions to the dispersive kinetics of zero-phonon hole (ZPH) growth.¹³ The ω -distribution accounts for the fact that ZPLs whose Lorentzian profiles overlap the laser profile can be exactly on-resonance with ω_B or off-resonance. This is accounted for in the argument of the exponential in Eq. (1). The normalized pre-burn absorption spectrum is obtained from Eq. (1) by setting $t = 0$. The hole burned spectrum is defined as $A(\Omega, t) - A(\Omega, 0)$. In the measurement of (HGK) of the ZPH at ω_B , $1 - A(\omega_B, t)/A(\omega_B, 0)$ is the fractional hole depth at time t . Eq. (1) is valid when the laser linewidth is much narrower than the width of the ZPL, which is the case in our experiments. For weak electron-phonon coupling (Huang-Rhys factor $S < 1$) the single site absorption spectrum is given by

$$L(\Omega - \omega) = L_{ZPL}(\Omega - \omega)e^{-S} + L_{PSB}(\Omega - \omega + \omega_m)(1 - e^{-S}), \quad (2)$$

where L_{ZPL} is the Lorentzian line shape of the ZPL (FWHM = γ) centered at ω and L_{PSB} is the shape of the phonon sideband. The coupling for Pc in DCB is weak. Chromophores in glassy hosts most often exhibit a single-peaked one-phonon profile centered at ω_m (as is the case for Pc in DCB) that can be well-described by a Gaussian on its low energy side and a

Lorentzian on its high energy side.²² An expression for $L(\Omega-\omega)$ valid for strong electron-phonon coupling is given in Ref. 23.

To account for photoproduct absorption (the anti-hole) and light-induced hole filling (LIHF) due to excitation of photoproduct sites, Eq. (1) requires modification. The first step is to replace $G(\omega)$ with a time-dependent “2-dimensional” (2-D) SDF, $G(\omega_i, \omega_j, t)$. Prior to hole burning ($t = 0$) G is diagonal ($\omega_j = \omega_i$) and $G(\omega_j, \omega_j, t = 0)$ is $G(\omega)$ in Eq. (1), $\omega_j \rightarrow \omega$. ω_j is the frequency at which a ZPL absorbs. The index i is a tag which indicates that the photoproduct absorbing at ω_j originates from **educt** sites at the diagonal position (i,i) of G . $G(\omega_i, \omega_j) \Delta\omega_j$ is the probability that photoproducts originating from educt sites that absorb at ω_i , absorb in the interval $\Delta\omega_j$ about ω_j . It should be kept in mind that each ZPL has a PSB associated with it. Hole burning results in Refs. 24 and 25 indicate that the electron-phonon coupling is at best weakly dependent on the position of the ZPL within the SDF and so we neglect such a dependence. Photomemory is used, which means that in the act of LIHF any given photoproduct site reverts to the educt site from which it originates. The results in Ref. 26 indicate that this is a good assumption for both NPHB and PHB. Another assumption is that the hole burning and LIHF tunneling rates of a given site are equal. Unequal rates could be easily incorporated into our model.

At time t the absorption intensity at frequency Ω is given by

$$A(\Omega, t) = \int d\omega_j L(\Omega - \omega_j) g(\omega_j, t), \quad (3)$$

with

$$g(\omega_j, t) = \sum_i G(\omega_i, \omega_j, t). \quad (4)$$

With reference to Eq. (1) $g(\omega_j, t)$ is analogous to $G(\omega)$ and represents a new SDF that accounts for hole burning and LIHF after a burn for time t .

The second step in modifying Eq. (1) is to introduce time-dependent tunneling distribution functions for the educt and photoproduct, $f_e(\omega_i, \lambda, t)$ and $f_p(\omega_i, \lambda, t)$. Educt sites defined by $G(\omega_i, \omega_i, t)$ are associated with $f_e(\omega_i, \lambda, t)$ while photoproduct sites defined by $G(\omega_i, \omega_j \neq \omega_i, t)$ are associated with $f_p(\omega_i, \lambda, t)$. Since we assume that the hole burning rate and LIHF rate for each and every site are equal it follows that

$$f_p(\omega_i, \lambda, t) = f_0(\lambda) - f_e(\omega_i, \lambda, t) \text{ for all } i, \quad (5)$$

where $f_0(\lambda)$ is the time-independent Gaussian distribution function $f(\lambda)$ in Eq. (1). Thus, f_e and f_p are complementary. At $t = 0$, $f_e(\omega_i, \lambda, 0) = f_0(\lambda)$ since there are no photoproduct sites. Noting that the tunneling rate for educt sites is proportional to $\exp(-2\lambda)$, *vide supra*, this means, for example, that educt sites with small λ values burn first so that at early times f_p is dominated by small λ values. Conversely, because f_e and f_p are complementary the contribution from small λ values to f_e decreases. In general both f_e and f_p are not Gaussian and are not normalized. We introduce the normalization constants

$$N_e(\omega_i, t) = \left[\int d\lambda f_e(\omega_i, \lambda, t) \right]^{-1} \quad (6)$$

and

$$N_p(\omega_i, t) = \left[\int d\lambda f_p(\omega_i, \lambda, t) \right]^{-1}. \quad (7)$$

The third modification is to replace the photon flux P in Eq. (1) by $P \cdot p(\omega_i, \omega_j, t)$, where

$$p(\omega_i, \omega_j, t) = \frac{G(\omega_i, \omega_j, t)}{g(\omega_j, t)}, \quad (8)$$

which accounts for the fact that the burn photons at $\omega_B = \omega_j$ are shared between the educt and photoproduct sites according to their absorption intensities at ω_j . Note that summation of the numerator over i results in $p = 1$.

We now describe an iterative procedure for solving the problem at hand which involves dividing the total burn time t into M intervals, $\Delta t = t_n - t_{n-1}$ and $n = 1, \dots, M$. For the educt at time t_n the SDF is

$$G(\omega_i, \omega_i, t_n) = G(\omega_i, \omega_i, t_{n-1}) - I_e(\omega_i, \omega_i, t_{n-1}, \Delta t) + \int d\omega_j I_p(\omega_i, \omega_j, t_{n-1}, \Delta t), \quad (9)$$

while for the photoproduct ($\omega_j \neq \omega_i$),

$$G(\omega_i, \omega_j, t_n) = G(\omega_i, \omega_j, t_{n-1}) - I_p(\omega_i, \omega_j, t_{n-1}, \Delta t) + I_e(\omega_i, \omega_i, t_{n-1}, \Delta t) \cdot \Pi(\omega_i, \omega_j). \quad (10)$$

The subtrahend in Eq. (9) represents the number of educt sites that absorb at ω_i and undergo hole burning in the time interval $\Delta t = t_n - t_{n-1}$ to produce photoproduct sites that absorb at $\omega_j \neq \omega_i$. The last addend represents repopulation of educt sites (ω_i) due to LIHF of photoproduct sites (ω_j). The subtrahend in Eq. (10) defines the number of product sites that absorb at ω_j and by LIHF return to their parent sites that absorb at ω_i , i.e. they replenish the (i, i) element of G . The final addend describes creation of photoproduct sites that absorb at $\omega_j \neq \omega_i$ and originate from educt sites that absorb at ω_i . The function $\Pi(\omega_i, \omega_j)$ is the

normalized photoproduct shape function for photoproduct sites (j) that originate from educt sites that absorb at ω_i . I_e and I_p in Eqs. (9) and (10) are given by

$$I_e(\omega_i, \omega_i, t_{n-1}, \Delta t) = G(\omega_i, \omega_i, t_{n-1}) \cdot [1 - N_e(\omega_i, t_{n-1}) \int d\lambda f_e(\omega_i, \lambda, t_{n-1}) F(X(\omega_i, \omega_i, t_{n-1}, \Delta t))] \quad (11)$$

$$I_p(\omega_i, \omega_j, t_{n-1}, \Delta t) = G(\omega_i, \omega_j, t_{n-1}) \cdot [1 - N_p(\omega_i, t_{n-1}) \int d\lambda f_p(\omega_i, \lambda, t_{n-1}) F(X(\omega_i, \omega_j, t_{n-1}, \Delta t))] \quad (12)$$

where

$$X(\omega_i, \omega_j, t_{n-1}, \Delta t) = P \cdot p(\omega_i, \omega_j, t_{n-1}) \cdot \sigma \cdot \phi(\lambda) \cdot L(\omega_j - \omega_B) \cdot \Delta t \equiv x \quad (13)$$

and

$$F(x) = 1.5 \int d\alpha \sin \alpha \cdot \cos^2 \alpha \cdot e^{-x \cos^2 \alpha} = \frac{1.5}{x} \left[\frac{\sqrt{\pi}}{2} \cdot \frac{\text{erf}(\sqrt{x})}{\sqrt{x}} - \exp(-x) \right]. \quad (14)$$

Since $x > 0$, $F(x)$ ranges in value between 0 and 1.

Similar to Eq. (9) for $G(\omega_i, \omega_i, t_n)$ there is also a 'feed' and 'drain' term for the educt tunneling distribution function:

$$f_e(\omega_i, \lambda, t_n) = f_e(\omega_i, \lambda, t_{n-1}) F(X(\omega_i, \omega_i, t_{n-1}, \Delta t)) + f_p(\omega_i, \lambda, t_{n-1}) \cdot \frac{\int' d\omega_j I_p(\omega_i, \omega_j, t_{n-1}, \Delta t)}{\int' d\omega_j G(\omega_i, \omega_j, t_{n-1})}, \quad (15)$$

where the first addend is the drain term and $F(x)$ is given by Eq. (14). The second addend is the feed term in which the ratio of the two integrals is the fraction of photoproduct sites that return to their parent educt sites that absorb at ω_i . The prime on the integrals, which are evaluated numerically, indicates that $j \neq i$. We note that at the time $f_e(\omega_i, \lambda, t_n)$ is calculated

all terms on the R.H.S. have been determined. The denominator in Eq. (15) is the difference between the number of educt sites at $t = 0$ and t_{n-1} . The numerator is the third term in Eq. (9) representing photoproduct sites returning to their parent sites that absorb at ω_i .

The absorption spectrum at time t_n is given by

$$A(\Omega, t_n) = \int d\omega_j L(\Omega - \omega_j) \sum_i [G(\omega_i, \omega_i, t_n) + G(\omega_i, \omega_{j \neq i}, t_n)] = \int d\omega_j L(\Omega - \omega_j) g(\omega_j, t), \quad (16)$$

with $g(\omega_j, t)$ defined by Eq. (4). This equation is equivalent to the 1-D master equation (1) with $t = 0$. So, our methodology for taking into account photoproduct absorption and LIHF involves solving that equation repeatedly at times between zero and the burn termination time. With Eqs. (9) – (12), Eq. (16) becomes

$$\begin{aligned} A(\Omega, t_n) = & \int d\omega_j L(\Omega - \omega_j) \\ & \times \sum_i [G(\omega_i, \omega_i, t_{n-1}) N_e(\omega_i, t_{n-1}) \int d\lambda f_e(\omega_i, \lambda, t_{n-1}) F(X(\omega_i, \omega_i, t_{n-1}, \Delta t)) \\ & + \int d\omega_j G(\omega_i, \omega_j, t_{n-1}) N_p(\omega_i, t_{n-1}) \int d\lambda f_p(\omega_i, \lambda, t_{n-1}) F(X(\omega_i, \omega_j, t_{n-1}, \Delta t)) \\ & + G(\omega_i, \omega_j, t_{n-1}) N_p(\omega_i, t_{n-1}) \int d\lambda f_p(\omega_i, \lambda, t_{n-1}) F(X(\omega_i, \omega_j, t_{n-1}, \Delta t)) \\ & + G(\omega_i, \omega_i, t_{n-1}) N_e(\omega_i, t_{n-1}) \int d\lambda f_e(\omega_i, \lambda, t_{n-1}) F(X(\omega_i, \omega_i, t_{n-1}, \Delta t)) \cdot \Pi(\omega_i, \omega_j)]. \end{aligned} \quad (17)$$

Calculation of hole burned spectra requires the photoproduct shape function $\Pi(\omega_i, \omega_j)$ in Eq. (10) and (17), which cannot be predicted. One must rely, therefore, on the experimental spectra to obtain a first approximation to the shape function. The procedure used is given in the following section as is the procedure used to determine the initial ($t = 0$) SDF ($G(\omega)$ in Eq. (1)) and the dependence of the center frequency of the photoproduct profile on ω_B .

To reduce computing time care was taken to optimize each step in the simulation procedure based on Eq. (17). Most important was to introduce nonlinear increments for both frequency axes of the 2-D SDF $G(\omega_i, \omega_j, t)$. A basic increment of 100 GHz was used to cover the entire hole burned spectrum. In the vicinity of a sharp ZPH and the onset of phonon sideband hole structure the frequency increment was decreased in a nonlinear manner. As a result the dimension of G , ($N \times N$), could be reduced from $N \sim 10^6$ (obtained from the width of the entire hole burned spectrum relative to that of the narrow ZPL) to $N \sim 2000$. Concerning the $d\omega_j$ integration in Eq. (17), the frequency axis was linearized and the fast Fourier transform technique (FFT) used. The angular integral $F(x)$, Eq. (14), was calculated analytically for $0 \leq x \leq 10$ and fitted with a 5th order polynomial; for $x > 10$, $F(x)$ was approximated by $(9\pi/16x)^{1/2}$. The average error in this procedure was on the order of 10^{-5} . The tunneling integral ($d\lambda$) was calculated as a simple sum. The range of the tunnel parameter $\lambda > 0$, $\lambda_0 \pm 5\sigma_\lambda$, was divided into 100 segments; selecting more segments led to no significant change in the value of the tunneling integral. The time increments, $\Delta t = t_n - t_{n-1}$, in Eqs. (9) and (10) were selected equidistant on a logarithmic scale with 2, 5, or 10 time segments per decade. The total number of segments used to calculate each of the five hole growth kinetics curves in Fig. 4 over ~ 4 decades of burn time was ~ 40 . The calculated spectra in Figs. 3 and 5 were obtained with 10 time increments (over 2 decades) per ZPH. The calculation of the hole burned spectrum in Fig. 5 with 28 ZPH and a 7500×7500 G matrix took ~ 12 hr with a 2 GHz Pentium 4 PC with 1.0 GB DDR333 memory.

4. Results and Discussion

The 5.0 K fluorescence excitation spectrum of Pc in hyperquenched DCB is shown in Fig. 1. The intense bands at 695.0 nm and 661.6 nm are due to the $S_0 \rightarrow Q_x$ and $S_0 \rightarrow Q_y$ transitions of Pc. The large Q_x - Q_y splitting of 720 cm^{-1} is advantageous for hole burning studies of the Q_x band since the absorption to the Q_y -state does not interfere with the Q_x band. For interpretation of the hole burning results, obtained with ω_B values that range from the high to low energy sides of the Q_x band, it is important, however, to know the contribution of vibronic transitions of the Q_x state that contribute to the Q_x band, especially on its high energy side. The low energy shoulder of the Q_y band at $\sim 672 \text{ nm}$ (see arrow) is due to such vibronic transitions as shown by vibronic satellite hole burning spectroscopy,²⁷ Fig. 2. The spectra (5.0 K) in Fig. 2 were obtained with a burn wavelength (λ_B) of 672.0 nm located in the low energy shoulder and a burn fluence of 11 mJ/cm^2 . The pre-burn and post-burn excitation spectra are shown in the upper panel. The hole burned spectrum, which is the difference between the two excitation spectra, is shown in the lower panel. In addition to the ZPH at λ_B , five satellite ZPHs appear at lower energies. They are displaced from the ZPH at λ_B by 466, 566, 680, 720 and 796 cm^{-1} that are vibrational energies of the Q_x state. Satellite hole spectra obtained with longer λ_B values revealed activity of lower energy modes, the lowest energy mode observed being at 230 cm^{-1} . The vibronic transitions contribute mainly to the high energy side of the Q_x band. It was determined that the hole burning efficiencies of the vibronic transitions are over two orders of magnitude lower than those of the ZPL of the pure electronic transition (and accompanying phonon sideband) that dominate the low energy side and main part of the Q_x band (results not shown). The main reasons for the lower efficiencies of vibronic transitions are: 1) the Franck-Condon factors for the vibrational

Figure 1. Fluorescence excitation spectrum of Pc in hyperquenched DCB at 5 K showing the Q_x and Q_y bands. The shoulder located by the arrow is due to vibronic transitions of the $S_0 \rightarrow Q_x$ transition. The dashed curve is the non-burnable (NB) background, which in combination with the calculated Q_x band provides a good fit (not shown) to the entire absorption spectrum. The SDF is the site excitation frequency distribution function of the Q_x state.

Figure 2. Pre-burn and post-burn fluorescence excitation spectra (upper panel) of Pc/DCB at 5 K. The latter was obtained with $\lambda_B = 672.0$ nm, and burn intensity/time of 0.11 mW/cm^2 and 100 s. Lower panel: the difference (hole burned) spectrum. The numbers labeling the satellite ZPHs are vibrational energies of the Q_x state in cm^{-1} . The inset shows a shallow (9%) ZPH burned at 703.0 nm with a width of 6.0 GHz.

modes are small (we estimate $\lesssim 0.1$). Thus, the integrated absorption cross-sections (σ) for vibronic transitions are about a factor of 10 smaller than σ of the pure electronic transition; and 2) the induced absorption rates of vibronic ZPLs are reduced further because of vibrational relaxation that typically occurs in a couple of picoseconds, short compared to the ~ 100 ps dephasing time of the pure electronic transition. The latter dephasing time (T_2) was obtained from the widths of shallow ZPHs burned into the low energy side of the Q_x band. One such ZPH obtained with $\lambda_B = 703.0$ nm is shown in the inset of Fig. 2. The full-width at half-maximum (FWHM) of the ZPH (fractional hole depth of 0.09) is 6.0 GHz (0.25 cm^{-1}), which is twice the width of the ZPL, γ . T_2 is given by $(\pi\gamma c)^{-1}$, where the unit of γ is cm^{-1} and c is the speed of light. Calculations with Eq. (1) indicated that the contribution from fluence broadening to the hole widths is less than 10%. The widths of ZPH burned at 686.0, 689.0 and 695.0 nm were the same, well within experimental uncertainty, ± 10 %. (Unless otherwise noted the widths of spectral features given in what follows are FWHM values.) It was determined experimentally that for the burn fluences used to obtain the main results of this paper (Figs. 3–5), hole burning of vibronic bands does not occur. Thus, the vibronic bands that contribute to absorption in the Q_x band region do not undergo hole burning. As a result, these bands provide a non-burnable background. Similarly, the Q_y band is non-burnable. ZPH burned into the Q_y band exhibited a width (FWHM) of 6.5 cm^{-1} , which is much broader than the widths of ZPH burned into the Q_x band, *vide supra*. The 6.5 cm^{-1} width is the result of uncertainty broadening due to $Q_y \rightarrow Q_x$ internal conversion that occurs in 1.6 ps. [Since the width of the ZPH is twice the width of the ZPL (γ),¹ the lifetime of the Q_y state is given by $(2\pi\gamma c)^{-1}$, where c is the speed of light.] The 1.6 ps lifetime can be

compared with the 1.0 ps lifetime of the Q_y state of Al-phthalocyanine tetrasulphonate in hyperquenched glassy water at 5 K ($Q_x - Q_y$ splitting of $\sim 220 \text{ cm}^{-1}$).²⁸

The dashed curve in the inset of Fig. 1 defines the non-burnable background absorption. It is its low energy tail that extends into the region of the Q_x band that is most important for simulation of the results in Figs. 3-5. The procedure used to obtain the dashed curve was as follows. First, the initial ($t = 0$) SDF of the Q_x band ($G(\omega)$) in Eq. (1) was determined by requiring that its convolution with the single site absorption spectrum fit the low energy side of the Q_x band. This is reasonable since the electron-phonon coupling is weak. The width of the SDF was set equal to twice the half-width of the observed Q_x band on its low energy side. The single site absorption spectrum, which is defined by the ZPL width, the Huang-Rhys factor S and the shape of the phonon sideband, was determined from hole burned spectra obtained with various burn fluences and burn frequencies located at the low energy side of the Q_x band. The phonon sideband, with a maximum at $\omega_m = 10 \text{ cm}^{-1}$ (*vide infra*) was fitted with two half-Lorentzian profiles, one for its low energy side (half-width Γ_l) and one for its high energy side (half-width Γ_h). The values of the parameters that define the single site absorption spectrum and the SDF differed only slightly from the final values obtained by simulating the hole spectra in Fig. 3. The latter are given in Table I. The calculated SDF and Q_x absorption band are shown in the inset of Fig. 1. The maximum of the SDF is red-shifted by 9.5 cm^{-1} relative to the maximum of the Q_x band. The expected shift is $\sim S \omega_c$, where ω_c is the mass center of the phonon sideband, $\omega_c \sim \omega_m + (\Gamma_h - \Gamma_l)/2$, which for $S = 0.5$, $\Gamma_h = 22 \text{ cm}^{-1}$, $\Gamma_l = 5 \text{ cm}^{-1}$, and $\omega_m = 10 \text{ cm}^{-1}$ (Table I) equals 9.25 cm^{-1} .

The next step in determining the non-burnable background was to model the Q_y band and vibronic bands of the $S_0 \rightarrow Q_x$ transition with Gaussians so that in combination with the

Figure 3. Frame A: 5 K pre-burn excitation spectrum (black) and post-burn excitation spectra obtained with burn fluences of 1.1 mJ/cm² (blue) and 11 mJ/cm² (red) and $\lambda_B = 699.4$ nm, upper panel. The hole burned spectra are shown in the lower panel. The smooth black curve through the red spectrum is the calculated spectrum. Frame B (same color-coding); same as above but with $\lambda_B = 690.5$ nm, see text for details and explanation of the bracketed region of the red hole burned spectrum. The smooth black curve through the red spectrum is the calculated spectrum obtained with the same parameter values (Table 1) used to obtain the calculated spectrum in frame A.

Table I. Common parameter values used in simulation of hole spectra and growth kinetics and computational details.

Parameter ^a	Value
Zero-phonon line width (FWHM)	0.067 cm ⁻¹
Peak energy of PSB (ω_m) ^b	10 cm ⁻¹
Huang-Rhys factor (S)	0.5
Profile of PSB	$\Gamma_l = 5 \text{ cm}^{-1}$; $\Gamma_h = 22 \text{ cm}^{-1}$ ^c
Average center position of photoproduct (W_0) ^d	-53 cm ⁻¹
Initial photoproduct absorption limits (W_1 ; W_2) ^d	-215 cm ⁻¹ ; 110 cm ⁻¹
Width (Γ_x) of photoproduct profile (FWHM)	193 cm ⁻¹
Shift of photoproduct profile ($\pm \Delta W$)	67 cm ⁻¹
Width of Q_x SDF (FWHM)	212 cm ⁻¹
Maximum of the Q_x SDF ^d	-9.5 cm ⁻¹
Integrated absorption cross-section (σ)	$8.0 \times 10^{-3} \text{ cm}^2\text{s}^{-1}$
Fluorescence lifetime (τ_f)	6.5 ns
The tunneling prefactor (Ω_0) ^e	$7.6 \times 10^{12} \text{ s}^{-1}$
Fast Fourier transform resolution	0.2 GHz, 262144 points
Frequency axis base division	100 GHz
Frequency axis division within ± 5 GHz of ZPH	0.2 GHz
Frequency axis division within +50 and -150 GHz	1 GHz

^a ω_m , Γ_l , Γ_h , and S were determined directly from hole spectra of the type shown in Fig. 3. The first three were not adjustable parameters in simulating the results in Figs. 4 and 5; S was an adjustable parameter in fitting the results in Fig. 4 but note that the value of 0.5 given above is very similar to the values given in Table II. The absorption cross-section was measured using the room temperature absorption spectrum.

^b PSB = phonon side band

^c The PSB was fitted with a Lorentzian with a half-width $\Gamma_l = 5 \text{ cm}^{-1}$ on the low energy side and a Lorentzian with a half-width $\Gamma_h = 22 \text{ cm}^{-1}$ on the high energy side.

^d Measured relative to the center of the Q_x absorption band.

Figure 4. Frame I: Noisy curves 1–5 are ZPH growth kinetics at 5 K obtained in the order 1–5 with 630 ± 20 nW/cm² and a burn time of 1500 s. The corresponding λ_B -values are given in the text. The smooth curves through the experimental curves are calculated, see text for details. The resulting λ_0 , σ_λ , S and $\langle\phi\rangle$ [average hole burning quantum yield] are given in Table II. Curve 1' is the theoretical fit to experimental curve 1 obtained with $\sigma_\lambda = 0$. The inset shows the 5 experimental curves after base-line correction, see text for details. That the 5 curves are almost perfectly superimposed is consistent with the λ_0 , σ_λ and S values for the 5 burn wavelengths being very similar (see Table II). Frame II: curve A is the pre-burn fluorescence excitation spectrum and curve B is the post-burn fluorescence excitation spectrum obtained immediately after completion of the hole growth kinetic measurement (Frame I). The lower panel shows the hole burned spectrum and a theoretical fit, see text for details.

Table II. Parameter values obtained by simulating the hole growth kinetics curves in Fig. 4.

Hole	Wavelength (nm)	λ_0	σ_λ	S	$\langle\phi\rangle$
1	695.15	6.84	.52	.50	.09
2	699.85	6.78	.54	.52	.10
3	704.00	6.72	.54	.54	.11
4	689.00	6.86	.48	.45	.08
5	686.00	6.86	.48	.48	.08

Figure 5. Right: 5 K pre-burn fluorescence excitation spectrum and post-burn fluorescence excitation spectrum after burning 28 holes in the low to high energy direction with a burn intensity of 0.11 mW/cm^2 and burn time of 10 s for each hole. Left: the calculated pre-burn and post-burn fluorescence excitation spectra, see text for details.

calculated Q_x band a good fit to the observed absorption spectrum was obtained. Four Gaussians were used centered at 732, 538, 293, and 833 cm^{-1} with widths of 83, 103, 133 and 283 cm^{-1} , respectively. The first of these is due to the Q_y band. Setting its amplitude equal to 1, the amplitudes of the other Gaussians are 0.26, 0.06 and 0.18, respectively.

A. Modeling of the photoproduct absorption. As mentioned, it is not possible to predict the shape and position of the photoproduct profile. Pc in DCB is an interesting case in that the position of the photoproduct profile relative to λ_B depends on the location of λ_B within the Q_x band, as shown in Fig. 6. Curve a is the Q_x absorption band. Curves b and c are the fluorescence excitation spectra following 'heavy' burns at 700 and 691 nm (see arrows) with a burn fluence of 3 J/cm^2 . The hole burned spectra, b-a and c-a, are shown in the lower panel. The ZPH in the upper frame coincident with λ_B are barely observable because they are totally saturated and because the accompanying pseudo-phonon sideband hole (pseudo-PSBH) is also saturated. The objective of this experiment was to determine the energy range over which photoproduct sites absorb. Note that photoproduct absorption (anti-hole) resulting from red excitation is shifted to the blue of λ_B , and that it lies within the pre-burn absorption band. Blue excitation results in an anti-hole that is red-shifted to λ_B and, furthermore, extends considerably to lower energy of the pre-burn absorption band. The latter observation is interesting because it shows that Pc-DCB configurations produced by photoinduced proton tautomerization at 5 K do not exist in the liquid (recall that the DCB glass was produced by hyperquenching.)

We define W_1 and W_2 as the low and high energy limits of photoproduct absorption. From Fig. 6, $W_2 - W_1 \sim 330 \text{ cm}^{-1}$. The width of the Q_x band is 215 cm^{-1} . The photoproduct profile was approximated by a Gaussian with a width $\Gamma \sim 200 \text{ cm}^{-1}$. Γ was

Figure 6. Upper panel: pre-burn (a) and two post-burn fluorescence excitation spectra obtained with $\lambda_B = 691.0$ nm (c) and $\lambda_B = 700$ nm (b), 5 K. The burn fluence used was very high, 3 J/cm^2 (50 mW/cm^2 for 60 s). The ZPH are completely saturated as is the pseudo-PSBH. Lower panel: the b-a and c-a hole spectra. Note that the photoproduct (anti-hole) absorption obtained with $\lambda_B = 691.0$ nm extends significantly to the red of the pre-burn absorption spectrum; the average shift of the anti-hole is -330 cm^{-1} while for the b-a spectrum the shift is $+155 \text{ cm}^{-1}$.

taken to be independent of the frequency ω_i of educt sites (allowing Γ to vary with ω_i did not improve the fits to the hole spectra). However, from Fig. 6 it is evident that the center frequency of the photoproduct profile depends on ω_i . The center frequency is denoted by $W(\omega_i)$. A simple model defined by the following equations was used for $W(\omega_i)$:

$$\begin{aligned} W(\omega_i) &= W_1 + \Gamma/2 && \text{for } \omega_i > W_2 - \Gamma/2; \\ W(\omega_i) &= W_2 - \Gamma/2 && \text{for } \omega_i < W_1 + \Gamma/2; \text{ and} \\ W(\omega_i) &= W_2 + W_1 - \omega && \text{for } W_1 + \Gamma/2 < \omega_i < W_2 - \Gamma/2. \end{aligned} \quad (18)$$

W_1 and W_2 are measured relative to the maximum of the Q_x band. The time-independent photoproduct absorption profile is given by

$$\Pi(\omega_i, \omega_j) = \frac{1}{\sqrt{2\pi}\Sigma} \cdot e^{-\frac{(W(\omega_i) - \omega_j)^2}{2\Sigma^2}}; \quad \Sigma = \frac{\Gamma}{2\sqrt{2\ln 2}} \quad (19)$$

Initial simulations indicated that $W_0^d = (W_1 + W_2)/2$ is shifted to lower energy from the Q_x -band maximum by $\sim 50 \text{ cm}^{-1}$. The position of the photoproduct profile was allowed to vary by $\Delta W = \pm [(W_2 - W_1) - \Gamma]/2 \sim 65 \text{ cm}^{-1}$. In the simulations W_0 , ΔW and Γ were adjustable parameters. Their final values, which are given in Table I, differ slightly from the initial estimated values given above.

B. Simulation of hole burned spectra. Hole spectra (5.0 K) obtained with moderate burn fluences were used to determine the values of parameters that characterize the electron-phonon coupling and photoproduct absorption. Examples are shown in Fig. 3 for $\lambda_B = 699.5$

and 690.5 nm, burn fluences of 1.1 and 11 mJ/cm² and spectral resolution of 0.4 cm⁻¹. The fluorescence excitation spectra for $\lambda_B = 699.5$ nm were obtained first, in the order pre-burn (black), post-burn (1.1 mJ/cm², blue) and post-burn (11 mJ/cm², red) as shown in Fig. 3A. The difference between the last two and the pre-burn spectrum (the hole spectra) are shown in the lower panel; blue for 1.1 mJ/cm² and red for 11 mJ/cm². In accordance with the results in Fig. 6, the photoproduct profile is shifted to the blue of the ZPH at $\lambda_B = 699.5$ nm. Most of its intensity derives from the pseudo-PSBH with a maximum at $\omega_m = 10$ cm⁻¹. The smooth black curve is the theoretical fit to the red hole spectrum obtained using Eq. (17). The non-burnable background was taken into account in the simulation. The values of λ_0 and σ_λ used were based on an initial (approximate) analysis of the ZPH growth kinetics with λ_B located on the low energy side of the Q_x absorption band. These values differed by $\sim 10\%$ from the final values that are given later; λ_0 and σ_λ are relatively unimportant in the determination of the electron-phonon coupling and location and shape of the photoproduct profile.

The $\lambda_B = 690.5$ nm spectra in Fig. 3B (same color-coding as in frame A) were obtained with the same sample after annealing at 50 K and cooling to 5.0 K. The holes burned with $\lambda_B = 699.5$ nm were only partially erased. Annealing at higher temperatures was not possible due to fracturing of the hyperquenched film. The hole spectra in the bottom panel of frame B show that the photoproduct absorption is red-shifted relative to the ZPH, which is in accordance with the results in Fig. 6. The smooth black curve is the fit to the red spectrum obtained with the same parameter values used to obtain the fit in frame A. The region of photoproduct indicated by the bracket is due to some filling of the incompletely erased holes burned with $\lambda_B = 699.5$ nm (frame A). The hole located by the dashed arrow is

due to a vibronic satellite hole at 232 cm^{-1} relative to the ZPH at 690.5 nm , with 232 cm^{-1} the energy of the excited state vibration. The shape and location of the one-phonon profile (defined by ω_m , Γ_b , Γ_h ; *vide supra*) were obtained directly from the observed pseudo-PSBH of the blue hole burned spectrum in frame B. Values of ω_m , Γ_b , Γ_h ; as well as the values of parameters that define the photoproduct (W_0 , Γ , ΔW), the width of the SDF of the Q_x band (Γ_x) prior to burning, the Huang-Rhys factor (S) and the width of the ZPL (γ) are given in Table I. The last six of these were free parameters in the simulations although the regions of parameter space searched were guided by values estimated using the results in Figs. 1 and 2 and other results (not shown).

The fits to the hole spectra in Fig. 3 are viewed as quite satisfactory, especially since they were obtained with the same set of parameter values for burn wavelengths located at the high and low energy sides of the Q_x band. It may be concluded, therefore, that the simple model for the dependence of the position of the photoproduct absorption (anti-hole) on the frequency ω_i of the educt sites (Eqs. 18) is quite reasonable, as is the assumption that photoproduct profile is a Gaussian. One last point about Fig. 3 is that the simulated spectra are consistent with the total absorption after burning being conserved. Conservation is expected for 90° rotation of the central protons when the ZPH and pseudo-PSBH approach saturation⁴.

C. Hole growth kinetics (HGK) and additional hole spectra. HGK curves were measured at five λ_B -values with the same burn intensity ($630 \pm 20\text{ nW/cm}^2$) and burn time (1500 s). They are curves 1–5 in the left frame (I) of Fig. 4 that correspond to λ_B -values of 695.15, 699.85, 704.00, 689.00 and 686.00 nm, respectively. The labels 1–5 indicate the order in

which the holes were burned. The pre-burn excitation spectrum (A) is shown in frame II. Spectrum B was measured following termination of the HGK experiment with a scan intensity of 6 nW/cm^2 . The hole burned spectrum, B-A, is shown in the lower panel. The smooth curve is the calculated spectrum obtained using the parameter values in Table I and the λ_0 and σ_λ values in Table II. The good agreement between the observed and calculated spectra is gratifying, showing again that our model captures the essential elements of hole burning, photoproduct absorption and laser-induced hole filling. The fits to the five HGK curves are also satisfactory. They were obtained using the parameter values in Table I; λ_0 , σ_λ and S were adjustable parameters. Their values are given in Table II. The S -values are similar to our initial estimated value of 0.5. The discrepancy at the end of the burn for curves 1 and 2 is due to the interplay between photoproduct absorption, the pseudo-PSBH and the ZPH.

As is evident, the values of λ_0 , σ_λ and S for the five burn wavelengths are similar. This might seem surprising since the experimental HGK curves are so different. One might have guessed that S and/or λ_0 increase as λ_B is tuned from the red to blue side of the Q_x band. There are three main factors responsible for the good fits obtained with λ_0 , σ_λ and S values that differ by only a few percent. First, the non-burnable background (curve NB in Fig. 1), which extends into the Q_x band, becomes more important as the burn wavelength decreases. Thus, for example, the difference between the observed fractional hole depths at the end of the burn for curves 3 and 5 is reduced when the non-burnable background is taken into account. Second, curves 2–5 were burned after curve 1 which means that both educt and photoproduct sites absorbing at ω_B undergo hole burning. That is, for the former curves the time dependent SDF, $g(\omega_j, t)$ in Eq. (4), is different from the initial ($t = 0$) SDF relevant to

curve 1. The dependence of the SDF on time for curves 2–5 increases with increasing curve number. The third factor is the electron-phonon coupling, which results in the contribution of phonon transitions (relative to the ZPL transition) increasing as ω_B is tuned to higher energy in the Q_x band.²⁹ Equation (17) takes into account all three factors. Which of the three is most important depends on the system, ω_B and the burn fluence. For the results in Fig. 4, the first and third factors were most important since the burn fluences used were sufficiently low ($\sim 1 \text{ mJ/cm}^2$) to produce quite weak photoproduct absorption (see blue hole spectra in Fig. 3).

Further evidence for the distributions of ZPH quantum yields for the five burn wavelengths being similar is shown in the inset of Fig. 4. HGK curves 1, 2, 4 and 5 were normalized to curve 3 by subtracting a constant α from all points followed by multiplication by a constant β . Given the quite complete overlap between the five curves it is not surprising that the λ_0 , σ_λ and S values in Table II are similar as are the average quantum yields $\langle\phi\rangle$.

The σ_λ values of ~ 0.5 (Table II) established that the HGK of Pc in hyperquenched DCB at 5.0 K are dispersive. The smooth curve 1' in Fig. 4 is the fit to the observed kinetics curve 1 (displaced vertically for clarity) obtained with $\sigma_\lambda = 0$. Obviously, the fit 1' to the same experimental curve is poorer than the fit 1. This confirms that the kinetics are dispersive but less so than for free base phthalocyanine tetrasulphonate (PcT) in HGW at 5.0 K for which a value of 1.0 was determined.¹⁶ The dispersion in that system was attributed to structural disorder of the water molecules in the inner shell which affects the H-bonding of nearby water molecules to the two NH groups of PcT. As a result, there is a distribution of barrier heights separating the two tautomers in the Q_x state. It should be kept in mind that electronic reorganization accompanies tautomerization. In the case of Pc in

DCB, relatively weak Cl $\cdots$ H H-bonding³⁰ and π - π stacking interactions are expected to affect the barrier, but to a lesser extent than the H-bonding in PcT/HGW. Presumably, the weaker Pc-DCB interaction results in the narrower distribution of λ -values.

Finally, the results in Fig. 5 provide additional evidence for the model described in section III capturing the essential features of hole burned spectra with photoproduct absorption and light-induced hole filling taken into account. The two noisy curves are the experimental pre-burn and post-burn excitation spectra, the latter obtained after burning 28 holes with a burn intensity of 0.11 mW/cm² for 10 s. The burn direction was from low to high energy. The maximum of the hole burned spectrum is shifted to the red by ~ 9 cm⁻¹ relative to the maximum of the pre-burn spectrum. This shift is reproduced in the calculated spectra shown to the left of the experimental spectra. The calculated spectra were obtained with the parameter values in Table I and averaged values of $S = 0.5$, $\sigma_\lambda = 0.5$ and $\lambda_0 = 6.8$ (Table II). The explanation for the red-shift is provided by the results in Fig. 6, which show that burning on the high energy side of the Q_x band results in photoproduct absorption (anti-hole) that extends significantly to the red of the pre-burn absorption spectrum, while burning on low energy side produces a blue-shifted anti-hole that lies within the pre-burn spectrum. This is reflected by the value of $W_0 = -53$ cm⁻¹ in Table II. The calculated and observed hole spectra are in reasonable agreement. An exact comparison of ZPH depths is not possible since the experimental resolution of ~ 0.4 cm⁻¹ used was not sufficient to resolve the ZPH. Nevertheless, comparison of the ZPH on the low energy side suggests a trend, which is that the experimental ZPH depths are shallower than the calculated depths. This discrepancy can be removed by relaxing one of the assumptions of the model, which is that the hole burning rate and light-induced hole filling (LIHF) rate (hole burning rate of

photoproduct) for each and every site are equal. (Recall that photoproduct memory was assumed, which means that hole burning of photoproduct sites returns them to the educt sites from which they originated.) Allowing for the LIHF rate to be higher than that of hole burning would remove the discrepancy.

It is to be appreciated that the new master equation with its time dependent 2-dimensional site excitation energy distribution function can be applied to non-photochemical hole burned spectra with no modification.

Acknowledgements

Support for this research was provided by the Solid State Chemistry and Polymers Program of the National Science Foundation (Grant DMR-9908714).

References

1. S. Völker, *Relaxation Processes in Molecular Excited States*, Ed. J. Fünfschilling, Kluwer: Dordrecht, The Netherlands, 113 (1989).
2. I. Renge, H. Wolleb, H. Spahni, and U.P. Wild, *J. Phys. Chem. A* **101**, 6202 (1997).
3. I.-J. Lee, G.J. Small, and J.M. Hayes, *J. Phys. Chem.* **94**, 3376 (1990).
4. M. Köhler, J. Friedrich, and J. Fidy, *Biochim. Biophys. Acta* **1386**, 255 (1998).
5. R. Jankowiak, J.M. Hayes, and G.J. Small, *Chem. Rev.* **93**, 1471 (1993).
6. T. Reinot, V. Zazubovich, J.M. Hayes, and G.J. Small, *J. Phys. Chem.* **105** 5083 (2001).
7. M. Berg, C.A. Walsh, L.R. Narasimhan, K.A. Littau, and M.D. Fayer, *J. Chem. Phys.* **88**, 1564 (1988).

8. M.J. Kenney, R. Jankowiak, and G.J. Small, Chem. Phys. **146**, 47 (1990).
9. W.-H. Kim, T. Reinot, J.M. Hayes, and G.J. Small, J. Chem. Phys. **104**, 6415 (1996).
10. M.H. Cohen, and G.S. Grest, Phys. Rev. Lett. **45**, 1271 (1980).
11. L. Shu, and G.J. Small, Chem. Phys. **141**, 447 (1990).
12. R. Jankowiak, R. Richert, and H. Bässler, J. Phys. Chem. **89**, 4569 (1985).
13. T. Reinot, and G.J. Small, J. Chem. Phys. **113**, 10207 (2000).
14. L. Shu, and G.J. Small, J. Opt. Soc. Am. **B 9**, 724 (1992).
15. T. Reinot, J.M. Hayes, and G.J. Small, J. Chem. Phys. **106**, 457 (1996).
16. T. Reinot, N. C. Dang, and G.J. Small, J. Lumin. **98**, 183 (2002).
17. T. Reinot, and G.J. Small, J. Chem. Phys. **114**, 9105 (2001).
18. B.L. Fearey, T.P. Carter, and G.J. Small, Chem. Phys. **101**, 279 (1986).
19. J. Kikas, K. Haller, and R. Jaaniso, J. Mol. Struct. **174**, 77 (1988).
20. L. Edwards, and M. Gouterman, J. Mol. Spectr. **33**, 292 (1970).
21. W.-H. Kim, T. Reinot, J.M. Hayes, and G.J. Small, J. Phys. Chem. **99**, 7300 (1995).
22. J.M. Hayes, R. Jankowiak, and G.J. Small, *Topics in current physics. Persistent spectral holeburning: Science and applications* Ed. W.E. Moerner, Springer-Verlag, NY, Vol. **44**, 153 (1987).
23. I.-J. Lee, J.M. Hayes, and G.J. Small, J. Chem. Phys. **91**, 3463 (1989).
24. P.A. Lyle, S. Kolaczowski, and G.J. Small, Chem. Phys. Lett. **207**, 436 (1993).
25. J.M. Hayes, P.A. Lyle, and G.J. Small, J. Phys. Chem. **98**, 7337 (1994).
26. T. Reinot, J.M. Hayes, and G.J. Small, J. Chem. Phys. **110**, 4820 (1999).
27. J. Friedrich, H. Scheer, B. Zickendraht-Wendelstadt, and D. Haarer, J. Lumin. **24-25**, 815 (1981).

28. T. Reinot, J.M. Hayes, G.J. Small, and M.C. Zerner, Chem. Phys. Lett. **299**, 410 (1999).
29. K.K. Rebane, and L.A. Rebane, *Topics in current physics. Persistent spectral holeburning: Science and applications* Ed. W.E. Moerner, Springer-Verlag, NY, Vol. **44**, 17 (1987).
30. A. Dkhissi, L. Houben, R. Ramaekers, L. Adamowicz, and G. Maes, J. Phys. Chem. A **103**, 11020 (1999).

CHAPTER 5

**DISPERSIVE HOLE GROWTH KINETICS AND FLUENCE BROADENING OF
THE ZERO-PHONON HOLE OF IMPURITIES IN AMORPHOUS HOSTS**

A paper published in and reprinted with permission from

Chemical Physics 2004, **297**,187-194

N. C. Dang¹, J. M. Hayes², T. Reinot² and G. J. Small³

Department of Chemistry, Iowa State University, Ames, IA 50011-3111, USA

Abstract

A detailed treatment of the relationship between the dispersive growth kinetics of the zero-phonon hole (ZPH) of an impurity molecule in an amorphous host and burn fluence broadening of the ZPH is presented. Focus is on nonphotochemical hole burning (NPHB). The equation used for simulations accounts for dispersion due a distribution of tunneling parameters (λ -distribution), the angle between the laser polarization and the transition dipole (α -distribution), and off-resonant absorption of the zero-phonon line (ω -distribution). Two

¹ Graduate Student

² Staff Scientist

³ Major Professor

cases are considered: burned laser linewidth narrow relative to the homogeneous width of the zero-phonon line; and the reverse situation. Results are presented for two model systems whose parameter values are similar to those of Aluminum-phthalocyanine tetrasulphonate (APT) in hyperquenched glassy water and in hyperquenched glassy ethanol. For comparison, results are presented for the case where the hole growth kinetics are non-dispersive (single-exponential). It is found that at the early stage of burning fluence broadening is considerably more severe for a dispersive system than for a non-dispersive system. A straightforward explanation for this is given. The results are compared with those of earlier works on dispersive hole growth kinetics and fluence broadening. The results reveal the types of experiment needed to understand the aforementioned relationship, a requirement for determination of the homogeneous width of the ZPH that reflects the dynamics of the system.

1. Introduction

Measurement of the homogeneous linewidth, Γ_H , of pure electronic transitions of impurity molecules in amorphous or glassy solids is a powerful approach to probe the low temperature dynamics of such materials. This is due to Γ_H having contributions not only from the excited state lifetime of the impurity, but also from optical dephasing which reflects interaction of the molecule with the low frequency modes of the solid host. In amorphous solids at low temperatures, these low frequency modes often consist of phonon-like restricted motions of the host molecules localized near the impurity centers and the so-called two-level systems (TLS) which correspond to nearly iso-energetic configurations of the host.

TLS are a universal feature present in glasses at low temperature. The TLS model was first proposed by Anderson et al. [1] and by Phillips [2] to account for anomalies in the low temperature properties of glasses. These workers independently proposed that some atoms or molecules composing the glass can occupy either of two nearly isoenergetic minima of the local structure potential energy surface. Each of the minima represents a different local structure of the glass. At low temperatures, transitions between the minima occur via phonon assisted tunneling. To account for the observed glass anomalies, the asymmetric double well potentials (the TLS) are characterized by a broad distribution of potential barriers (tunneling frequencies) and asymmetries. Because of these broad distributions, there is a wide (temperature dependent) range of tunneling rates between the TLS minima.

However, direct measurement of Γ_H in a bulk sample, with its information about low temperature dynamics is not possible because Γ_H is obscured by the large inhomogeneous broadening, Γ_I , characteristic of impurity emission and absorption in amorphous or glassy solids. Fortunately, there are now well-developed methods to extract Γ_H in the presence of a large Γ_I . Among these are photon echo [3-7] in the time domain, and hole burning [8-12] and fluorescence line narrowing [13-15] in the frequency domain. It is hole burning, and particularly non-photochemical hole burning (NPHB) that is of interest here.

NPHB at low temperatures is a manifestation of the tunneling between different glass/impurity configurations, as first proposed by Hayes and Small [16]. The result is the burning of a narrow hole (the zero-phonon hole, ZPH) into the absorption spectrum of the impurity that is triggered by electronic excitation of the impurity. In contrast to photochemical hole burning where the impurity undergoes excited state photochemistry, NPHB does not involve intramolecular photochemistry. Simply put, it is a consequence of

the post-excitation impurity/glass configuration being different from and kinetically inaccessible to the pre-burn configuration. Although the original Hayes-Small mechanism for NPHB [16] proposed that a static distribution of extrinsic TLS (TLS_{ext}), i.e. TLS introduced into the glass by the presence of the impurity, was sufficient to explain the hole burning, it was later demonstrated that NPHB involves a hierarchy of tunneling events triggered by electronic excitation [17]. In the Shu-Small model [18], NPHB begins with the intrinsic TLS (TLS_{int}) in the outer solvent shell and terminates with the TLS_{ext} inner solvent shell tunneling. This outside-in chain of events results in diffusion of free volume to the inner shell, opening the way for the rate determining step of NPHB that involves TLS_{ext} .

Because of the previously mentioned broad distribution of TLS barriers and asymmetries, there is a corresponding distribution of hole burning rates that lead to the hole growth kinetics being dispersive. These dispersive kinetics have long been known and various models have been proposed to fit the experimental ZPH growth data [19-23]. The approach used by Kenney et al. [19] was that the distribution of the TLS_{ext} tunneling parameter, λ , is the major cause of the dispersion which leads to a log normal distribution for the tunneling rate. Following Jankowiak et al. [20], they took the λ -distribution to be a Gaussian. From the analysis of experimental data, the mean (λ_0) and the standard deviation (σ_λ) of the distribution are determined. Neglected in this analysis are the intrinsic dispersion from photoselection due to the use of a polarized excitation source and due to off-resonant absorption. The distributions to which these effects give rise are referred to as α and ω , respectively, by Reinot and Small [21]. Here, α is the angle between the laser polarization and the chromophore's transition dipole. The ω -distribution accounts for the fact the zero-phonon line (ZPL) of a given site can be off-resonant with the burn laser frequency but still

absorb via the wings of the Lorentzian ZPL. In Ref. 19, Kenney et al. argued that the contribution from the α -distribution should be weak for the first half of the hole growth. The same conclusion was also reached by Elschner and Bässler [22] who also argued that the ω -distribution should be less important than that of λ . Turukhin and Gorokhovskiy [23] also concluded that the λ -distribution is more important than that of the α -distribution.

More recently, Reinot and Small [12] have included the contributions from all three distributions to analyze ZPH growth kinetic data obtained over six decades of burn fluence for the dye aluminum phthalocyanine tetrasulphonate (APT) in hyperquenched glassy water (HGW) at 5 K. They found that indeed the λ -distribution is of primary importance and well describes that data for the first $\sim 80\%$ (three decades of fluence) of the burn. The contributions from the α - and ω -distributions only become significant for the last part of the burn. Neither of these latter distributions, either alone or together, provides an adequate fit to the initial burn data. Importantly, the values of λ_0 and σ_λ obtained using all three distributions differ little from the values determined using the λ -distribution alone. The values for APT/HGW appear to be typical of those for many dye/amorphous host systems.

Not considered explicitly in any of the above models were the effects of fluence on the hole evolution. Further, the above models assume that the excitation source has a linewidth, Γ_{laser} , such that $\Gamma_{\text{laser}} \ll \Gamma_{\text{H}}$. Although this assumption is generally true for continuous wave excitation, pulsed excitation often uses a broader excitation source. Recently, Gorchelev et al. [24] presented a kinetic analysis which showed that a broad band source can eliminate the dispersion effects of the ω -distribution. Regarding fluence effects on hole growth, Talon et al. [25] have described its effects on both holewidth and hole

growth. Although the kinetic model used by Talon et al. is similar to that of [20, 22], Talon et al. did employ several simplifying assumptions. Most notably, they modeled the λ -distribution as a flat distribution between minimum and maximum values. In addition, electron-phonon coupling that leads to phonon sideband hole structure in the near vicinity of the ZPH was neglected.

In this paper, the equation describing hole growth kinetics used by Reinot and Small [12] is used to model hole growth and to calculate the broadening of the ZPH as a function of burn fluence. The results using this equation that accounts for all three sources of dispersion are compared to those of Talon et al. [25]. The equation is also modified to account for laser linewidth and calculations modeling a laser line width greater than Γ_H are presented. These are discussed in comparison to the results of Gorchelev et al. [24].

2. Calculation Methods

2.1. The NPHB equation:

As stated in Ref. 12, the normalized absorption, $A(\Omega, t)$ at frequency, Ω , following a burn at ω_B for a time t with the photon flux P (no. of photons $\text{cm}^{-2} \text{s}^{-1}$) and the integrated absorption cross-section, σ ($\text{cm}^2 \text{s}^{-1}$) is given by:

$$A(\Omega, t) = 1.5 \int d\omega L(\Omega - \omega) G(\omega) \int d\lambda f(\lambda) \int d\alpha \sin \alpha \cos^2 \alpha e^{-P\sigma f(\lambda)L(\omega - \omega_B)\cos^2(\alpha)t}. \quad (1)$$

In this equation, ω is the frequency of the ZPL, and $G(\omega)$ is its distribution. $G(\omega)$ is taken to be a Gaussian with a FWHM, Γ_I .

In Eq. (1), λ is the tunnel parameter for the TLS_{ext} and $f(\lambda)$ is its normalized Gaussian distribution function centered at λ_0 , with a standard deviation of σ_λ . The integration over λ

is done numerically within limits $\lambda_0 \pm 5\sigma_\lambda$ and with step size $d\lambda = 0.05 \sigma_\lambda$. Neither larger nor smaller step sizes significantly change the absorption spectrum. Within these limits, unphysical negative λ values are avoided. The NPHB quantum yield, $\phi(\lambda)$, is given by

$$\phi(\lambda) = \frac{\Omega_0 \exp(-2\lambda)}{\Omega_0 \exp(-2\lambda) + \tau_f^{-1}}, \quad (2)$$

where τ_f is the excited state lifetime of the chromophore. The numerator is the phonon-assisted tunneling rate. The quantum mechanical expression for Ω_0 is given in [18].

In Eq. (1) it is assumed that the excitation source is a linearly polarized laser, and α is the angle between the laser polarization and the transition dipole vectors. The angular integration can be solved analytically and the result is

$$F(x) = \frac{3}{2x} \left(\frac{\pi^{1/2} \text{erf}(x^{1/2})}{2x^{1/2}} - \exp(-x) \right) \quad (3)$$

where $x = P\sigma_{RT}\phi(\lambda)tL(\omega - \omega_B)$ is positive for all physically reasonable argument values. The value of $F(x)$ was pre-calculated for all x and fitted with a polynomial in the interval of $x \in [0, 10]$. For $x > 10$, $F(x)$ was accurately approximated by $(9\pi/16x)^{1/2}$.

$L(\omega_i - \omega)$ [21] is the normalized single site absorption spectrum (SSAS) that consists of the ZPL and phonon sideband (PSB). The SSAS enters into Eq. (1) in two places. First, in the convolution with the site distribution function (SDF), $G(\omega)$, and second, in the exponent, where it is in reflected form. The physical meaning of such reflection becomes clear when it is recalled that following excitation at ω_B of a site via its PSB, phononic relaxation to the zero-point vibrational level occurs on a picosecond time scale, which is several orders of magnitude faster than the inverse rate of hole burning. With, ω_m the mean

phonon frequency, a pseudo-PSB hole at $\omega_B - \omega_m$ results that is located to the red of the ZPH at ω_B by ω_m . In the low burn fluence limit the pseudo-PSB hole is the mirror image of the real-PSB hole that is located to the blue of the ZPH by ω_m and builds on the ZPH according to the Frank-Condon principle. The results of calculations to be presented are for two systems that have been studied experimentally, both of which exhibit weak electron-phonon coupling (the Huang Rhys factor $S < 1$). For weak electron-phonon coupling, $L(\Omega - \omega)$ in Eq. (1) can be rewritten as (low temperature limit):

$$L(\Omega - \omega) = L_{ZPL}(\Omega - \omega)e^{-S} + L_{PSB}(\Omega - \omega)(1 - e^{-S}), \quad (4)$$

with an analogous expression for $L(\omega - \omega_B)$. Here L_{ZPL} is the normalized Lorentzian line shape function of the ZPL with a FWHM of Γ_H , e^{-S} is its Franck-Condon factor, and L_{PSB} and the factor $(1 - e^{-S})$ are the one-phonon profile of the phonon side band (PSB) and its Franck-Condon factor. An expression for the SSAS valid for arbitrary electron-phonon coupling strength and temperature is given in [26]. Simulations of hole burned spectra for the case of strong electron-phonon coupling can be found in [27, 28].

2.2. Finite laser linewidth

From the interpretation of the equation above, it is seen that Eq. (1) assumes a narrow laser linewidth relative to Γ_H . To expand this limitation for the scope of this paper, the laser line shape has to be taken into account. Thus, Eq. (1) is rewritten as

$$A(\Omega, t) = 1.5 \int d\omega L(\Omega - \omega) G(\omega) \int d\lambda f(\lambda) \int d\alpha \sin \alpha \cos^2 \alpha e^{-P \sigma \phi(\lambda) L'(\omega - \omega_B) \cos^2(\alpha) t}, \quad (5)$$

where $L(\omega - \omega_B)$ in Eq. (1) has been replaced by

$$L'(\omega - \omega_B) = \int d\nu \Lambda(\nu - \omega_B) L(\omega - \nu), \quad (6)$$

which is the convolution of normalized laser line shape and the SSAS. $\Lambda(\nu)$ is the normalized laser line shape with a standard deviation of σ_g at ω_B and is given by:

$$\Lambda(\nu - \omega_B) = \frac{1}{\sigma_g \sqrt{2\pi}} e^{-\frac{(\nu - \omega_B)^2}{2\sigma_g^2}}. \quad (7)$$

From Eq. (6) it is easy to see that in case the laser line is infinitely narrow i.e. for $\lim_{\sigma_g \rightarrow 0} \Lambda(\nu - \omega_B) = \delta(\nu - \omega_B)$, Λ becomes a Dirac delta function and Eq. (5) reverts to Eq. (1).

Γ_{hole} and hole depths for both cases (narrow and broad laser line widths) are calculated using Eq. (1) and Eq. (5), respectively. Parameters for the calculations of each specific study are given in Tables 1 and 2, and explained in the text. Calculations were done using locally written software, which is optimized for speed in MS Visual C++ 6.0 and performed on a 2.0 GHz Pentium 4 computer running under MS Windows 2000. To measure Γ_{hole} and hole depths, single hole burned spectra at various times are calculated with an increment of 10.0 MHz for the step size. The evolution of Γ_{hole} and of hole depth are then plotted as a function of fluence.

3. Results and Discussion

In Tables 1 and 2 are listed the two parameter sets used for calculations. The burning frequency, ω_B is set at the center of the SDF, $G(\omega)$. The parameters in Table 1 are similar to those determined for annealed APT in HGW [23]. APT in HGW is the highest efficiency molecular hole burning system known [12, 21, 29, 30]. It is characterized by weak electron-phonon coupling, a high phonon frequency, and very narrow Γ_H . In contrast, APT in hyperquenched glassy ethanol (HGE), from which the parameters of Table 2 are chosen,

Table 1. The parameter set used to calculate the hole profiles. To be consistent with earlier work parameters were chosen to describe APT in HGW or APT in water saturated poly-HEMA. The laser linewidths and fluences used are given in the captions of figures and in the text.

Parameters	
FWHM of Site Distribution Function $G(\omega)$, Γ_I (cm^{-1})	355
FWHM of ZPL width, Γ_H (cm^{-1})	0.0018 (0.055 GHz)
Laser power, I (W)	10^{-6}
Phonon Side Band width ^a (cm^{-1})	26, 38
Fluorescence lifetime, τ_f (ns)	6.5
Integrated absorption cross-section, σ ($\text{cm}^2 \text{s}^{-1}$)	1.2×10^{-2}
Pre-factor of tunneling rate, Ω_0 (s^{-1})	7.6×10^{12}
Tunnel parameter λ_0	8.2
Huang-Rhys factor, S	0.2
Peak phonon frequency, ω_m (cm^{-1})	36

^a The PSB (phonon sideband) is modeled as a Gaussian on the low energy side and a Lorentzian on the high energy side with full-widths of 26 and 38 cm^{-1} , respectively.

Table 2. The parameter set used to calculate the hole profiles. These parameters were chosen closely to the parameters used describe APT in ethanol. The laser linewidths and fluences used are given in the captions of figures and in the text.

Parameters	
FWHM of Site Distribution Function $G(\omega)$, Γ_I (cm^{-1})	355
FWHM of ZPL width, Γ_H (cm^{-1})	0.033 (1.0 GHz)
Laser power, I (W)	10^{-6}
Phonon Side Band width ^a (cm^{-1})	15, 33
Fluorescence lifetime, τ_f (ns)	6.5
Integrated absorption cross-section, σ ($\text{cm}^2 \text{s}^{-1}$)	1.2×10^{-2}
Pre-factor of tunneling rate, Ω_0 (s^{-1})	7.6×10^{12}
Tunnel parameter λ_0	8.2
Huang-Rhys factor, S	1
Peak phonon frequency, ω_m (cm^{-1})	26

^a The PSB (phonon sideband) is modeled as a Gaussian on the low energy side and a Lorentzian on the high energy side with full-widths of 15 and 33 cm^{-1} , respectively.

has a stronger electron-phonon coupling, a lower phonon frequency and a larger value for Γ_H [31]. These parameter sets were chosen to provide realistic calculations relative to actual experimental data.

3.1. $\Gamma_{\text{laser}} \ll \Gamma_H$

Using the parameters of Table 1 and Eq. (1), the fluence dependence of the hole width, Γ_{hole} , was calculated for $\Gamma_{\text{laser}} = 0.002$ GHz, i.e., much smaller than $\Gamma_H = 0.055$ GHz. Two values of σ_λ were used: $\sigma_\lambda = 0.95$ and $\sigma_\lambda = 0.00095$. The first value corresponds to what has been determined for APT in HGW, [23] while the latter value results in there being essentially no dispersion due to the λ -distribution. The results are shown in Fig. 1. The curves A correspond to the dispersive case ($\sigma_\lambda = 0.95$) and the curves B to the non-dispersive case ($\sigma_\lambda = 0.00095$). Curves A₁ and B₁ describe the calculated hole growth, while A₂ and B₂ show the change in ZPH width with fluence. Curve B₁ for the non-dispersive hole growth deviates only slightly from exponential hole growth while curve A₁ is highly non-exponential (i.e., dispersive). The figure shows that the hole broadens more quickly for the dispersive case than in the absence of dispersion. Over the first 2½ orders of burn fluence, the broadening is close to linear for the non-dispersive case but is clearly non-linear over the same time course for the dispersive case. As shown in the inset to Fig. 1, over the fluence range from 0.001 to 0.5 $\mu\text{J}/\text{cm}^2$, the holewidth increases more rapidly for the dispersive system than for the non-dispersive. This range covers about the first half of the hole growth. Thereafter, the tunneling distribution becomes less important and the ratio of fluence broadening for the two systems becomes more nearly equal.

Also included in Fig. 1 are experimental data for APT in an annealed HGW film. At

Figure 1. Comparison of fractional hole depths (A_1 , B_1) and ZPH widths (A_2 , B_2) as a function of fluence for $\Gamma_H = 0.055\text{GHz}$, for parameter set 1 (Table 1). $\Gamma_{\text{laser}} = 0.002\text{ GHz}$. System A has $\sigma_\lambda = 0.95$ and system B has $\sigma_\lambda = 0.00095$. The solid circles are experimental hole broadening data for APT in an annealed HGW film. The insert is a comparison of the relative ZPH broadening Γ_A/Γ_B as a function of fluence in the two systems. At $t = 0$ and at $t = \infty$, ZPH widths in A and B are equal.

low fluence, the data closely follows the calculated curve (A_2). Above $1 \mu\text{J cm}^{-2}$, however, the calculations show more broadening than is observed experimentally. This difference is due to anti-hole formation - the effects of which are not included in Eq. (1). This discrepancy is fully discussed in Ref. 29. Experimental hole growth kinetics data is not shown in this paper since the parameters for the calculations used are those obtained from fitting such data. In Ref. 21 it is shown that Eq. (1) well describes the hole growth kinetics over 5 orders of magnitude of fluence.

A few further points should be made about the results shown in Fig. 1. First, the limiting fractional hole depth for both systems is 0.82, i.e., e^{-S} , as expected [21]. Second, although hole widths for holes less than 10% deep are frequently used as a good approximation for the zero-fluence hole width, this is a poor approximation for the dispersive system. For the data shown, the hole width at 10% depth is 0.13 GHz for the dispersive system and 0.12 GHz for the non-dispersive system, while the zero-fluence width is 0.11 GHz. Finally, the results of Fig. 1 allow calculation of the noise contribution to observed broadening. The relative noise may be defined as $x = [1 + (N/fI)]$ where f is the fractional hole depth, I , the signal intensity, and N , the noise intensity ($N = \sqrt{I}$). Approximating the signal as $10^4 \text{ photons s}^{-1}$ and the noise as $10^2 \text{ counts s}^{-1}$, the relative broadening due to noise at a hole depth of 10% is $x = 1.1$, which is the same as the broadening factor calculated in the non-dispersive case, but less than the broadening factor calculated in the dispersive case, 1.2. Thus, measured holewidths for the non-dispersive case are accurate to 10% for $f = 0.1$.

In Fig. 2, similar data calculated using the parameters of Table 2 is plotted. These parameters have a larger S , a smaller ω_m , and a larger Γ_H . As in Fig. 1, the curves A describe

the growth (A_1) and broadening (A_2) of the dispersive system ($\sigma_\lambda = 0.95$), while the curves B describe the growth (B_1) and broadening (B_2) of the non-dispersive system ($\sigma_\lambda = 0.00095$). Comparing Figs. 1 and 2, it is obvious that the hole growth proceeds more slowly for the parameters of Table 2, i.e. the HGE-like parameters. While for parameter set 1, 10% holes resulted for a fluences of $\sim 0.1 \mu\text{J cm}^{-2}$ and $0.05 \mu\text{J cm}^{-2}$, for parameter set 2, the fluences required are $\sim 7.8 \mu\text{J cm}^{-2}$ and $4.8 \mu\text{J cm}^{-2}$. (The difference in burn fluence values is mainly due to the difference in value of Γ_H , the induced absorption rate of the ZPL being inversely proportional to Γ_H .) The broadening of the holes at this depth for parameter set 2 is 1.5 and 1.1 (dispersive and non-dispersive systems, respectively) compared to the broadening of 1.2 and 1.1 for parameter set 1. Thus for the non-dispersive case the broadening remains about the same at 10% hole depth but is increased substantially in the dispersive system.

Note also that the hole growth curves (A_1 , B_1) in Fig. 2 do not approach the limiting hole depth up to the largest value of fluence shown. The expected saturated ZPH depth is $e^{-S} = 0.37$. The reason for exceeding this value is shown in the inset to the figure. This shows the hole profile for a fluence of $100 \mu\text{J cm}^{-2}$ for system A. Note that because of the lower phonon frequency, the ZPH and PSB hole are not resolved so that $\sim 11\%$ of the ZPH depth is actually due to overlap with the PSB hole. The dotted arrows to the left and the right of the sharp ZPH are the pseudo- and real-PSB holes, respectively. It is interesting to compare the results of Figs. 1 and 2 with the results obtained by Talon et al. [25] who simplified the calculation by substituting a Gaussian distribution of tunneling rates with a flat distribution between minimum (R_m) and maximum (R_M) rates. Their calculation for $R_M = 0.01$ is equivalent to the non-dispersive case studied here, while their $R_M = 1.0$ results are close to

Figure 2. Comparison of fractional hole depths (A_1 , B_1) and ZPH widths (A_2 , B_2) as a function of fluence for $\Gamma_H = 1.0$ GHz for parameter set 2 (Table 2). $\Gamma_{\text{laser}} = 0.002$ GHz. System A has $\sigma_\lambda = 0.95$ and system B has $\sigma_\lambda = 0.00095$. The insert is a calculated hole profile for a fluence of $100 \mu\text{J cm}^{-2}$ for system A ($h = 0.11d$). The dotted arrows to the left and the right of the sharp ZPH indicate the pseudo- and real-PSB holes, respectively.

the dispersive calculations herein. In Fig. 2 of [25], hole depth is shown as a function of burn fluence. Although the data in that figure are scaled differently from the data here, the curves for $R_M = 0.01$ and $R_M = 1.0$ are similar to curves A₁ and B₁ of Fig. 1, here. The results differ, however, in that the present results with a Gaussian distribution of tunneling parameters indicate faster burning at low fluence than in [25]. This difference is due to Talon et al. [25] neglecting the very fast rates that dominate the low fluence hole burning. Neglecting these fast, early time rates also influences the hole broadening results (Fig. 3 of Talon et al. [25]). For $R_M = 1.0$, they find that the width for a 10% hole is broadened by a factor of 1.1, while the present results indicate a broadening by a factor of 1.2 in the dispersive case. The difference is significant.

3.2. $\Gamma_{\text{laser}} > \Gamma_H$

In this section, Eq. (5) is used to calculate hole shapes as a function of fluence using a laser width, $\Gamma_{\text{laser}} = 2.0$ GHz. Using the APT/HGW-like parameters of Table 1, yields the results shown in Fig. 3 for the dispersive (A) and non-dispersive (B) cases. As in the narrow laser case (Fig. 1), the fluence broadening is larger for the dispersive system. Note, however, that the initial holewidth is now determined by the convolution of the laser and homogeneous widths. Because the initial hole is so broad, the broadening factors are smaller: for a 10% hole, the broadening factors are 1.15 and 1.05 in the dispersive and the non-dispersive case, respectively. As was done for the narrow laser linewidth, the ratio of broadening factors for the dispersive and non-dispersive cases is shown in the inset to Fig. 3. Here, although the dispersive system initially broadens more rapidly, by saturation the two widths are the same.

Finally, in Fig. 4, the growth and broadening are shown for the parameters of Table 2 and for $\Gamma_{\text{laser}} = 2.0$ GHz. Here, the laser width and the homogenous width are close in value

Figure 3. Comparison of fractional hole depths (A_1 , B_1) and ZPH widths (A_2 , B_2) as a function of fluence for $\Gamma_H = 0.055$ GHz, for parameter set 1 (Table 1). $\Gamma_{\text{laser}} = 2.0$ GHz. System A has $\sigma_\lambda = 0.95$ and system B has $\sigma_\lambda = 0.00095$. The insert is a comparison of the relative ZPH broadening Γ_A/Γ_B as a function of fluence in the two systems. At $t = 0$ and at $t = \infty$, ZPH widths in A and B are equal.

Figure 4. Comparison of fractional hole depths (A_1 , B_1) and ZPH widths (A_2 , B_2) as a function of fluence for $\Gamma_H = 1.0$ GHz for parameter set 2 (Table 2). $\Gamma_{\text{laser}} = 2.0$ GHz. System A has $\sigma_\lambda = 0.95$ and system B has $\sigma_\lambda = 0.00095$. The insert is a calculated hole profile for a fluence of $1000 \mu\text{J cm}^{-2}$ for system A ($h = 0.11d$). The dotted arrows to the left and the right of the sharp ZPH indicate the pseudo- and real-PSB holes, respectively.

($\Gamma_H = 1.0$ GHz) and the initial hole width is given by their convolution. Nevertheless, the broadening follows the same trend as seen for narrow band burning: the dispersive system broadens more quickly than does the non-dispersive system. As in Fig. 2, the hole depth does not saturate at e^{-S} which is again due to overlap of the ZPH and PSB holes as shown in the inset. Comparing Figs. 3 and 4, it is seen that burning for the system with larger Γ_H (Fig. 4) is slower than for the smaller Γ_H system (Fig. 3). Consequently, a larger fluence is required to burn a 10% deep hole.

Although the present paper is concerned more with dispersion due to the λ -distribution and the paper by Gorchelev et al. [24] is more concerned with the ω -distribution, the results here are relevant to that work. It needs to be noted that in [24], the authors derive an equation for hole growth for an unpolarized excitation source and neglect contributions to hole burning from phonon absorption. To be clear, what Gorchelev et al. call the dispersion due to the inhomogeneous distribution corresponds to dispersion due to the ω -distribution in this paper while what is termed a distribution of quantum efficiencies in Gorchelev et al. is what is referred to as the λ -distribution here. Gorchelev et al. claim that little is added to the dispersion due to the inhomogeneous distribution by also including a distribution of quantum efficiencies. Their Fig. 1 which supports this claim is in disagreement with the results presented here. In that figure, curve 3 describes hole growth with dispersion due to the ω -distribution only. It is approximately equivalent to curve B₁ of Fig. 2 in this paper although curve B₁ also includes dispersion due to the α -distribution. Gorchelev et al. also calculated hole growth including a distribution of quantum efficiencies, curve 4 of Fig. 1 in Ref. 24. This curve is similar to curve A₁ of Fig. 2 in this paper. Although Fig. 1 of Gorchelev et al.

and Fig. 2 of this paper interchange whether fluence or hole depth is plotted logarithmically, it is clear from both figures that inclusion of the λ -distribution results in faster burning over at least the first half of the burn. This is in agreement with the results of Reinot and Small [12, 21] who showed that the λ -distribution is dominant for the first $\sim 80\%$ of the burn and at odds with the conclusion of Gorchelev et al.

The results in this paper most relevant to those of Gorchelev et al. [24] are contained in Fig. 3, curve B₁. In that figure, the laser line width is ~ 30 times the ZPL width and the width of the λ -distribution is 0.00095, i.e., the λ -distribution contributes insignificantly to the dispersion. Over the first half of the burn (3+ decades of fluence), this curve is very close to single exponential, verifying that dispersion due to the ω -distribution is essentially eliminated. However, the final half of the burn is decidedly non-exponential. Dispersion here arises from both the α -distribution and burning through phonon absorption which contributes more prominently at high burn fluences. It is interesting that it is at high burn fluence where Gorchelev et al. see departure from single exponential hole growth that they attribute to a second channel for photochemistry.

4. Concluding Remarks

Although the phenomenon of fluence broadening of the zero-phonon hole (ZPH) of impurity molecules imbedded in host solids has been recognized for many years, scant attention had been given to the relationship between fluence broadening and dispersive hole growth kinetics. Dispersive hole growth kinetics is a signature of non-photochemical hole burning (NPHB) for a chromophore in an amorphous host, a consequence of structure disorder. However, even in the case of photochemical hole burning involving

'intramolecular' photochemistry of the chromophore, the hole growth kinetics can be dispersive when the host is amorphous, as has been shown for free-base porphines and phthalocyanines [30]. For such systems the hole burning mechanism involves photoinduced tautomerization of the two protons at the center of the macrocycle.

The 'master' equation used for the simulations includes, for the first time, the three distributions that contribute to the dispersive hole growth kinetics and fluence broadening. They are the λ -, α - and ω -distributions associated with the tunneling parameter λ , the angle between the laser polarization and transition dipole, and the off-resonant absorption of the zero-phonon line, respectively. In addition, linear electron-phonon coupling that leads to the phonon sideband that builds on the zero-phonon line is also taken into account. The results show that for a typical NPHB system (dispersive kinetics) fluence broadening at the early stage of hole burning is considerably more severe than for the equivalent non-dispersive system (narrow laser linewidth or broad laser linewidth limit). For example, in the narrow laser linewidth limit and for a fractional hole depth of 0.10, the contribution from fluence broadening to the ZPH width can be expected to be at least 30% while for a non-dispersive system the value is about 10%. Given a typical uncertainty in a holewidth measurement of $\pm 10\%$, a fractional hole depth considerably less than 0.1 is required to eliminate the contribution from fluence broadening for a dispersive system. The reason for fluence broadening being more important for a dispersive system than the equivalent non-dispersive system at the early stage of hole burning is that the dispersive hole growth kinetics are dominated by the λ -distribution that leads to a log normal distribution for the phonon-assisted tunneling rate associated with NPHB. For the non-dispersive system the λ -value, λ_0 , determines the rate constant for hole burning. For a dispersive system, λ_0 is the average

value of the tunnel parameter. Thus, at the early stage of hole burning there are sites whose hole burning rate constants are greater in value than that obtained with λ_0 . This explains why in Figs. 1-4 the hole depth increases more rapidly for the dispersive system at the early stage of hole burning. At the latter stage of hole burning, fluence broadening for a dispersive and non-dispersive system are comparable. This is because the λ -distribution becomes less important while the α - and ω -distributions become more important.

Finally, it should be noted that dispersive hole growth kinetics data should be consistent with fluence broadening data as dictated by Eq. (1). In experiments designed to test for consistency it will be important to monitor interference of the ZPH by phonon sideband hole structure. Systems exhibiting weak electron-phonon coupling ($S \lesssim 1$) would be most suitable for study.

Acknowledgement:

This research was supported by the Solid State Chemistry and Polymers Program of NSF under grant no. DMR-9908714.

References.

- [1] P. W. Anderson, B. I. Halperin and C. M. Varma, *Philos. Mag.* **25**, (1972) 1.
- [2] W. A. Phillips, *J. Low Temp. Phys.* **7**, (1972) 351.
- [3] N. A. Kurnit, I. D. Abella, and S. R. Hartmann, *Phys. Rev. Lett.* **13** (1964) 567.
- [4] T. J. Aartsma and D. A. Wiersma, *Phys. Rev. Lett.* **36** (1978) 1360.
- [5] R. L. Shoemaker, in "Laser and Coherence Spectroscopy" (ed. J. I. Steinfeld,

- Plenum Press, New York, 1978) p. 197.
- [6] J. B. W. Morsink, W. H. Hesselink, and D. A. Wiersma, *Chem. Phys.* **71**, (1982) 289.
- [7] W. H. Hesselink and D. A. Wiersma, in "Spectroscopy and Excitation Dynamics of Condensed Molecular Systems" (eds. V. M. Agranovich and R. M. Hochstrasser, North Holland, Amsterdam, 1983) p. 249 and references therein.
- [8] S. Völker, in "Molecular Excited States, Optical Relaxation Processes at Low Temperatures" (ed. J. Fünfschilling, Kluwer, Dordrecht, 1989) p. 113-242.
- [9] J. M. Hayes, R. Jankowiak, and G. J. Small, in "Persistent Spectral Hole Burning: Science and Applications" (ed. W. E. Moerner, Springer-Verlag, Berlin, 1988) p. 153-202.
- [10] D. Haarer, "Persistent Spectral Hole Burning: Science and Applications" (ed. W. E. Moerner, Springer-Verlag, Berlin, 1988) p. 79-125.
- [11] R. Jankowiak, J. M. Hayes, and G. J. Small, *Chem. Rev.* **93**, (1993) 1471.
- [12] T. Reintot, V. Zazubovich, J. M. Hayes, and G. J. Small, *J. Phys. Chem.* **105**, (2001) 5083.
- [13] A. Szabo, *Phys. Rev. Lett.* **25** (1970) 924; *ibid.* **27** (1972) 169.
- [14] L. A Riseberg, *Phys. Rev. A* **7** (1973) 671.
- [15] S. G. Johnson, I.-J. Lee, and G. J. Small, in "Chlorophylls" (ed. H. Scheer, CRC Press, Boca Raton, 1991) p. 739-768.
- [16] J. M. Hayes and G. J. Small, *Chem. Phys.* **27**, (1978) 151.
- [17] L. Shu and G. J. Small, *Chem. Phys.* **141**, (1990) 447.
- [18] L. Shu and G. J. Small, *J. Opt. Soc. Am. B*, **9**, (1992) 724.
- [19] M. J. Kenney, R. Jankowiak and G. J. Small, *Chem. Phys.* **146**, (1990) 47.

- [20] R. Jankowiak, R. Richert and H. Bässler, *J. Phys. Chem.* **89**, (1985) 4569.
- [21] T. Reinot and G. J. Small, *J. Chem. Phys.* **113**, (2000) 10207.
- [22] A. Elschner and H. Bässler, *Chem. Phys.* **123**, (1988) 305.
- [23] A. V. Turukhin and A. A. Gorokhovsky, *Chem. Phys. Lett.* **317**, (2000) 109.
- [24] A. A. Gorchelev, E. P. Snegirev, N. I. Ulitsky and B. Kharlamov, *Chem. Phys.* **285**, (2002) 289.
- [25] H. Talon, M. Orrit and J. Bernard, *Chem. Phys.* **140**, (1990) 177
- [26] P. A. Lyle, S. V. Kolaczowski and G. J. Small, *J. Phys. Chem.* **97**, (1993) 6926.
- [27] J. M. Hayes, S. Matsuzaki, M. Rätsep and G. J. Small, *J. Phys. Chem. B* **104**, (2000) 5625.
- [28] V. Zazubovich, S. Matsuzaki, T. W. Johnson, P. R. Chitnis and G. J. Small, *Chem. Phys.* **140**, (1990) 177
- [29] T. Reinot and G. J. Small, *J. Chem. Phys.* **114**, (2001) 9105.
- [30] T. Reinot, N. C. Dang and G. J. Small, *J. Lumin.* **98**, (2002) 183.
- [31] T. Reinot, J. M. Hayes and G. J. Small, *J. Chem. Phys.* **106**, (1997) 457.

CHAPTER 6

**PROBING CONFINED WATER WITH NONPHOTOCHEMICAL HOLE BURNING
SPECTROSCOPY:
ALUMINUM PHTHALOCYANINE TETRASULFONATE IN
POLY(2-HYDROXYETHYLMETHACRYLATE)**

A paper published in and reprinted with permission of
Journal of Physical Chemistry A, 2003, **107**, 10514-10520

N. C. Dang^a, J. M. Hayes^b, T. Reinot^b and G. J. Small^c

Department of Chemistry and Ames Laboratory-USDOE, Iowa State University, Ames, IA
50011-3111, USA

Abstract

Nonphotochemical hole burning is used to measure the linear electron-phonon coupling, the temperature dependence of the pure dephasing and the zero-phonon hole growth kinetics of aluminum phthalocyanine tetrasulfonate (APT) in glassy water confined in pores (~ 30 Å) of films of poly(2-hydroxyethylmethacrylate) (poly-HEMA). The hole

^a Graduate Student

^b Staff Scientist

^c Major Professor

burning properties of APT in the polymer are compared with those of APT in hyperquenched glassy films of water and ethanol. Below ~ 8 K in the polymer, the dephasing, which is dominated by coupling to the intrinsic two level systems (TLS_{int}) of the glass is found to be more similar to that of APT in unannealed hyperquenched glassy water (HGW) films than in annealed HGW films. This shows, for the first time, that confinement does not lead to a significant decrease in the TLS_{int} density. At higher temperatures, dephasing due to exchange coupling with a pseudo-localized mode at 42 cm^{-1} becomes dominant. This coupling is due to diagonal quadratic electron-phonon coupling that leads to a change in mode energy upon electronic excitation of APT. The 42 cm^{-1} vibration is assigned to the transverse acoustic mode of confined water. In HGW the energy of this mode is 50 cm^{-1} . The interaction of APT with surface bound water and the polymer surface also leads to reduction of the energy of the linearly coupled (Franck-Condon active) phonon mode from 38 cm^{-1} for HGW to 32 cm^{-1} . Hole growth kinetics measurements for APT in polymer saturated with D_2O are compared with those in polymer saturated with H_2O . In the heavy water the hole burning is 330 times slower. The equivalent factor for heavy HGW is 800. Thus, the mechanism of hole burning involves proton tunneling associated with the extrinsic two-level systems (TLS_{ext}) introduced by the dye. In contrast, dephasing data indicate that the coordinate of the TLS_{int} is spatially extended and involves only small amplitude motion of protons. Differences between the hole burning properties of APT in poly-HEMA and in HGW and hyperquenched ethanol are discussed in terms of the interactions of APT with bound (non-freezable) water and the hydroxyethyl groups of the polymer.

1. Introduction

Recently, much attention has focused on the dynamical properties of water in confined spaces. Water in confined spaces differs in both structural and dynamic properties from bulk water. Understanding these differences is important for a variety of diverse areas. For example, protein structure and function are both often dependent on imbedded water.¹⁻³ Water filled pores are often the channels through biological membranes.⁴ Water in vesicles formed from block copolymers is important in developing drug delivery systems and for modeling of cell functions. Because of this importance, studies of water in a myriad of confined spaces are now widespread.

Dielectric relaxation and solvation dynamics of water in confined spaces has been recently reviewed by Nandi et al.⁵ In that review, it is pointed out that water in cage-like hosts (e.g. cyclodextrans and calixirenes), microporous solids (e.g. zeolites), micelles, and semi-rigid materials (e.g. polymers and hydrogels) can serve as simpler surrogates for understanding the complex role of water in biological molecules (proteins and DNA). In all these varied media, the water can be divided into two types: free water with properties similar to those of unconfined, bulk water, and bound water that differs markedly from bulk water in its properties. Note that there is not always a sharp demarcation between these two types of water. In proteins and other biological macromolecules, the bound water is often referred to as biological water. Femtosecond solvation dynamics of biological water have been recently reviewed by Pal et al.⁶

Of interest here is the organic polymer, poly(2-hydroxyethyl methacrylate) (poly-HEMA). This is a water-absorbing polymer that can contain an equilibrium water content approaching 40%. The pore size of the polymer is ~ 30 Å. A spherical cavity of this

dimension would contain ~ 500 water molecules.⁷ Water in poly-HEMA is known to occupy two distinct environments. A portion of the water can crystallize at temperatures near the ice point of normal water and is referred to as freezable water. The freezable water can be identified as the unbound water described above. The remainder of the water, $\sim 44\%$ of the total, does not crystallize.⁸ This is called non-freezable water and corresponds to the bound water. It is thought to constitute the layer of water in contact with the polymer inner surfaces that interacts with the polymer via hydrogen bonding. Note that bound water occupying 44% of the total volume of a spherical cavity of 30 Å diameter is found in a layer of < 3 Å thickness. It is disruption of the normal water hydrogen bond network by polymer-water hydrogen bonds that prevents this water from freezing. Both water fractions can be vitrified but the T_g associated with each fraction is different. For the bound water, $T_g = 162$ K, while for the free water, $T_g = 132$ K.⁹ The latter value is similar to the T_g value for hyperquenched glassy water, HGW¹⁰, and is one indication that the free water has little interaction with the polymer and is akin to bulk water in its properties.

We report here the results of nonphotochemical hole-burning (NPHB) spectroscopic studies of Al-phthalocyanine tetrasulphonate (APT) in water-soaked poly-HEMA. The current mechanism for NPHB is reviewed in ¹¹. Suffice it to say that NPHB is a site excitation energy selective technique that eliminates the contribution from inhomogeneous broadening to the optical transitions of chromophores in amorphous hosts and that the mechanism of hole burning involves configurational tunneling of the chromophore/host system triggered by electronic excitation of the chromophore. Hole burning of APT in wet poly-HEMA was reported in ¹². In that work, however, measurements were restricted to a single temperature, 4.5 K. Nevertheless, the results established that NPHB of APT is

efficient, as had been found for APT in confined water in other porous materials^{13, 14}, and, furthermore, that the linear electron-phonon coupling of APT's $S_0 \rightarrow S_1$ (Q_z) transition in wet poly-HEMA differs significantly from that in hyperquenched glassy water (HGW). To further explore the effects of confined water on the spectral dynamics and hole burning properties of APT we present pure dephasing data for the range 4 to 80 K and zero-phonon hole growth kinetics data obtained at 4.5 K. Growth kinetics data are also presented for heavy water (D_2O). The results are compared with those of APT in HGW. Importantly, it is found that the basic mechanism of pure dephasing for poly-HEMA and HGW are the same, that the hole growth kinetics for poly-HEMA are about as dispersive (distributed) as those for annealed HGW, and that the linear electron-phonon coupling for the two host systems are similar. However, some significant differences are observed and discussed in terms of the interactions of APT with bound (unfreezable) water and the hydroxyethyl groups of the polymer.

2. Experimental

D_2O (Aldrich), poly-HEMA (Aldrich), and methanol (Fisher, 99.9%) were all used without further purification. Nanopure water ($R > 10 \text{ M}\Omega \text{ cm}^{-1}$) was locally purified. Poly-HEMA ($\sim 1 \text{ g}$) was dissolved in methanol (10 ml) by shaking. Several drops of this solution were dropped onto a glass coverslip and dried overnight in a covered container at 40°C . Transparent films of $\sim 0.5 \text{ mm}$ thickness, adherent to the glass substrate were obtained. Residual solvent was removed by vacuum drying at 40°C for several hours. Before use, these samples were soaked in nanopure water that was changed daily for two weeks.

To prepare the APT/poly-HEMA samples, the films described above were soaked in a 10^{-5} M APT in water solution for 24 h. Deuterated water samples were prepared similarly in a glove bag filled with dry nitrogen. The samples were mounted on a copper plate for cooling, with the polymer side facing the plate. Cooling was by immersion into liquid helium. The cooling rate is estimated to be 0.5 K s^{-1} . Temperature was measured with a DT-470 silicon diode (Lakeshore, Inc.) also mounted in contact with the copper plate.

The laser system used for hole burning and measuring fluorescence excitation spectra has been described in detail elsewhere.^{15, 16} In brief, the laser system is a Coherent 699-29 ring dye laser (DCM or LD 688 dye, linewidth $< 10 \text{ MHz}$) pumped by a Coherent Innova argon ion laser (6W, all lines). The laser intensity was regulated with an electro-optic beam stabilizer (Cambridge Research and Instrumentation, LS100). A beam expander and neutral density filters were used to adjust the power density at the sample. Fluorescence from the sample was filtered by a long pass filter (Omega Optical, AELP-730) and detected by a Hamamatsu R-2949 photomultiplier tube followed by a photon counter (Stanford Research, SR400). Fluorescence excitation spectra were recorded with a resolution of 20 MHz for the low temperature ($< 25 \text{ K}$) data and 0.4 cm^{-1} at higher temperatures. Care was taken to ensure that the laser intensities used to read spectra were low enough to prevent hole burning during reading. Hole growth kinetics were measured by monitoring the fluorescence intensity as a function of time.

3. Results

Fluorescence excitation spectra of APT in HGW at 5 K and in poly-HEMA at 4.5 K are compared in Figure. 1. The structure of the dye molecule is included as an inset in

Figure 1. A. Fluorescence excitation spectra of APT in HGW ($T = 5 \text{ K}$) and in water saturated poly-HEMA ($T = 4.5 \text{ K}$). The chemical structure for APT is shown, also. B. Hole spectra for APT in HGW and in water-saturated poly-HEMA. The spectra in B are on the same wavelength scale as in A.

the figure. Note that in either matrix, the APT absorption consists of two broad, unresolved bands. Previously, it has been shown that these two bands are the Q_x and Q_y transitions of the molecule.¹⁷ In ¹⁷, it was demonstrated that the Q -band transition of APT, which is expected to be degenerate based on molecular symmetry, is split by the binding of two water molecules to the aluminum atom. Note that the APT/poly-HEMA absorption is red-shifted 6.5 nm (210 cm^{-1}) relative to that of APT/HGW. Q_x transition energies for APT in several glasses are listed in Table 1.

The lower panel of Figure 1 shows two medium fluence holes burned into the APT Q_x -absorption. The upper hole spectrum is for APT in HGW, while the lower spectrum is for APT/poly-HEMA. The holes shown were burned at 675.0 nm for APT/HGW and at 685.0 nm for APT/poly-HEMA. In the figure, the zero-phonon hole (ZPH) in poly-HEMA appears slightly broader than in HGW. For both samples, the ZPH are fluence broadened to some extent. At 5 K, for annealed HGW, the ZPH width can be as narrow as 110 MHz, while for fresh APT/HGW, the width is 550 MHz. In poly-HEMA at 4.5 K, the ZPH width is 900 MHz. Note that the peak phonon frequencies, ω_m , associated with the pseudo-phonon sideband hole (pseudo-PSBH) differ for the two samples. The high value of ω_m (38 cm^{-1}) for APT/HGW is in large measure responsible for being able to resolve ZPH in HGW up to almost T_g . For APT/poly-HEMA, the lower value of ω_m (32 cm^{-1}) results in a smaller range over which the ZPH can be resolved from phonon sideband holes, restricting the ZPH width measurements. Nevertheless, 32 cm^{-1} is significantly larger than values of $\omega_m < 25\text{ cm}^{-1}$ common in many non-water-containing polymer/dye systems.¹⁸ One final point regarding the two hole spectra is that the anti-hole (positive absorption increase to the blue of the ZPH)

Table 1. Q_x transition energies, Q_x - Q_y splittings, and Peak Phonon Frequencies for APT in Various Glasses.^a

	Q_x (cm ⁻¹)	ΔQ_{xy} (cm ⁻¹)	ω_m (cm ⁻¹)
Dry poly-HEMA ^b	14,650	340	25
Wet poly-HEMA ^b	14,700	260	32
HGW	14,910 ^c	230 ^c	38 ^d
HGE	¹ 4,700 ^c	180 ^c	26 ^d
HGM	14,740 ^c	190 ^c	17 ^d

^a At room temperature, the Q_x transition energies are 14,831, 14,718, and 14,696 cm⁻¹ for water, ethanol, and methanol, respectively.

^bFrom reference 9. ^cFrom reference 12.

^dFom from reference 25.

is more prominent for the poly-HEMA sample. This in part is due to the increased integrated hole area of the poly-HEMA ZPH but more importantly due to a narrower anti-hole site distribution.

Hole widths were measured from fitting Lorentzians to the ZPH of a series of holes burned a few gigahertz apart at a burn temperature, T_B . After measuring those holes, the temperature was raised and the holes re-measured. This continued until the holes were too shallow to measure accurately. At this point, a new set of holes was burned at a higher T_B and the process continued. In the course of the measurements, it was verified that the widths measured at some temperature, T , above T_B , were the same as the width of a hole burned at T , if the holes were burned with the same fluence. At 70 K and above, as shown in Figure 2, although it was still possible to detect the hole, the ZPH was not well-resolved from the accompanying pseudo- and real-phonon sideband holes (indicated by the arrows in the figure). However, it was still possible to measure the ZPH width with reasonable accuracy up to ~ 80 K. At higher temperatures, the overlap between ZPH and sideband holes prevented accurate measurement. See, for example, the $T_B = 100$ K hole profile in Figure 2, where the real and pseudo-PSBH are indicated by arrows.

Hole widths, expressed as $(\Gamma_h/2 - \Gamma_0)$ are plotted versus temperature in Figure 3. Here, Γ_h is the measured hole width and Γ_0 is the lifetime limited linewidth of the zero-phonon line, $\Gamma_0 = 1/(2\pi\tau_{fl}) = 25$ MHz. The fluorescence lifetime (τ_{fl}) was measured as 6.5 ns at 77 K for HGW deposited at 77 K. At temperatures < 25 K, the hole widths are determined by extrapolating the hole widths at several fluences to the zero fluence value. Above 25 K, the values shown are the narrowest value recorded at each temperature. The solid line is a fit to the data using the expression:

Figure 2. Hole spectra for APT in water-saturated poly-HEMA. The upper spectrum was burned and detected at 70 K, while the lower spectrum was burned and detected at 100 K. Vertical arrows are displaced $\pm 24\text{ cm}^{-1}$ from the burn wavelength and mark the real- and pseudo-phonon sideband holes.

Figure 3. Temperature dependence of the ZPH width for APT in water-saturated poly-HEMA. The data points were measured as described in the text. The solid line is the fit to Eq. 1.

$$\Gamma_h/2 - \Gamma_0 = aT^\alpha + b\bar{n}(\omega) \quad (1)$$

which follows in the slow modulation limit of exchange coupling in the Jackson-Silbey theory.¹⁹ The first term in Eq. 1 describes dephasing from coupling of the electronic transition to the intrinsic two-level systems (TLS_{int}) of the glass host. The TLS_{int} correspond to bistable intermolecular potentials.²⁰ For a wide variety of probe molecules in amorphous hosts, $\alpha \approx 1.3$,^{21, 22} as is also found here, see Table 2. This term dominates the low temperature dephasing ($T < 8$ K), while the second term is associated with dephasing due to exchange coupling with a pseudo-localized phonon, of frequency ω . $\bar{n}(\omega)$ is the thermal occupation number of the mode. The phonon relaxation time (τ) is given in the low temperature limit by $(bc\pi)^{-1}$ with $c = 3 \times 10^{10}$ cm s⁻¹.²¹ Values obtained from fitting Eq. 1 to the hole width data are given in Table 2.

Figure 4 compares hole burning for APT in water-saturated poly-HEMA to hole burning of APT/poly-HEMA in which the polymer was saturated with a solution of APT in D₂O. The hole spectra shown for the two samples are quite similar. However, the spectra were burned with significantly different fluences. For the deuterated sample, a burn intensity of 50 mW cm⁻² was used while for the protonated sample the burn intensity was 0.2 mW cm⁻². For both samples, the burn time was 30 s. This difference in burn rates is reflected in the hole growth kinetics curves, labeled H₂O and D₂O in the figure. As is commonly observed for NPHB, the growth rates are non-exponential.²³ This is primarily due to a distribution of tunneling rates for the TLS_{ext} involved in the hole burning process.^{23, 24} Curve D in the figure is the D₂O curve with the time axis compressed by a factor of 15. This compression results in the D₂O and H₂O curves overlapping, exactly. (The D₂O curve is

Table 2. Dephasing Parameters for APT in Various Matrices.

	a	b_1	b_2	ω_1	ω_2	α	τ_1	τ_2
	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)		(ps)	(ps)
HGW, Annealed ^a	0.0002	6.9	11.1	50	182	1.3	1.5	1.0
HGW Fresh ^a	0.0010	7.0	53	53	179	1.3	1.5	0.2
Wet p-HEMA	0.0018	2.6	--	42	--	1.3	4.1	--

^aFrom reference 16. Fresh HGW refers to a film deposited at $T \approx 5$ K, while annealed refers to a film which is warmed to a temperature near T_g before cooling to the measurement temperature.

Figure 4. Hole growth kinetics for APT in H_2O - and D_2O -saturated poly-HEMA. Curve D is the D_2O data with time axis compressed 15-fold and slightly shifted along the ordinate so as not to obscure the H_2O curve. Also shown are the saturated hole spectra for APT in the two samples. The hole spectra were burned at the same wavelength (689 nm) but have been shifted for clarity. Burn fluence was 1.5 J cm^{-2} for D_2O and 6 mJ cm^{-2} for H_2O ; $T = 4.5 \text{ K}$.

shifted slightly along the ordinate for clarity.) However, the D₂O growth curve was obtained with a power density of 15 $\mu\text{W cm}^{-2}$ and the H₂O growth curve with 0.7 $\mu\text{W cm}^{-2}$. Based on the burn intensity difference and the 15x compression factor, the D₂O sample burns ~320 times slower than the H₂O sample.

4. Discussion

A. Transition energies and Q_x - Q_y splittings

As can be seen in Figure 1A, the fluorescence excitation spectrum of APT in poly-HEMA is red-shifted from the corresponding spectrum for APT in HGW. In Table 1, are shown the low temperature Q_x -transition energies for APT in several glasses as measured from the fluorescence excitation spectra. The room temperature values for the corresponding liquids as measured from absorption spectra are given in the caption. The Q_x - Q_y splittings (ΔQ_{xy}) and the peak phonon frequencies (ω_m) as determined from hole spectra of APT in those glasses are also tabulated. From the Table, it can be seen that APT in wet poly-HEMA has a Q_x energy similar to that of APT in HGE, while for dry poly-HEMA the absorption is further red-shifted.

Before discussing the poly-HEMA data, it is instructive to compare the data from Table 1 for the liquids and their hyperquenched glasses. Consider first the values for ΔQ_{xy} (uncertainty of $\pm 15 \text{ cm}^{-1}$). The value of 230 cm^{-1} for HGW is close to the value of 215 cm^{-1} determined from molecular mechanics and ZINDO calculations.¹⁷ This value is for two water molecules ligated to the central aluminum of APT and oriented with the water hydrogens aligned with the bridging nitrogens and the two water molecules (on opposite sides of the macrocycle) so as to preserve the σ_h symmetry plane. It is this structure that gives the

maximum value for ΔQ_{xy} . The value for hyperquenched glassy ethanol (HGE) and hyperquenched glassy methanol (HGM) are somewhat lower than the value for HGW. As discussed in ²⁵, similar values for the three glasses are expected since the ethanol and methanol contain ~1 % water. That is, water molecules are expected to be ligated to the central aluminum in methanol and ethanol. Hydrogen bonding between the ligated water and ethanol (methanol) molecules would be expected to have some effect on ΔQ_{xy} . The significant difference between the frequencies (ω_m) of the Franck-Condon active phonons for the three glasses are consistent with such hydrogen bonding, *vide infra*.

Consider next the Q_x transition energies. At room temperature, the energies in methanol and ethanol are nearly identical while water is blue shifted $\sim 100 \text{ cm}^{-1}$. In ²⁶, it was estimated on the basis of a pressure dependent study of the zero-phonon holes of APT in HGW, that the Q_x transition of APT in the gas phase is at roughly $15,000 \text{ cm}^{-1}$. Thus, the solution values for the Q_x transition of ethanol and methanol are red-shifted from the vapor value. The situation for water is less clear. Upon the formation of HGE, the Q_x transition barely changes, while HGW and HGM undergo a blue shift. Given that the permanent dipole change of APT's $S_0 \rightarrow Q_x$ transition is very small, $< 0.1 \text{ D}$ as determined by Stark hole burning spectroscopy it seems unlikely that dipole (solvent)-induced dipole (APT) interactions make a significant contribution to the solvent shifts.²⁷ It is likely that dispersion and hydrogen bonding interactions are the major contributors to the solvent shifts. The results are consistent with hydrogen bonding in water and HGW being stronger than in methanol (HGM) and ethanol (HGE) and, furthermore, they are consistent with hydrogen bonding resulting in a blue shift of the of the Q_x transition in going from the vapor to the condensed phase. This is in line with the observation that formation of HGW from water

results in a blue shift. Since dispersion interactions are expected to result in red-shifting²⁸, it appears that in methanol (HGM) and ethanol (HGE) they dominate the hydrogen bonding interactions, while the opposite is true for water (HGW).

The phonon frequencies (ω_m) in Table 1 provide some support for this. In ²⁵, it was proposed that Franck-Condon active phonons in the hole spectra most likely represent librational motions of APT hydrogen bonded to the glass network. Thus, one expects ω_m of HGW (38 cm⁻¹) to be higher than the value for HGM and HGE, as is observed. However, it is not apparent why the value of 17 cm⁻¹ for HGM is significantly lower than the value of 26 cm⁻¹. MM/QM calculations might shed light on this.

Turning now to the values for APT in wet poly-HEMA (Table 1), the evidence seems to indicate that the APT is located such that it interacts both with the non-freezable water and with the hydroxyethyl groups that line the polymer pores. In ¹², it was proposed that APT in poly-HEMA must be located at least partially in contact with the non-freezable (bound) water based on two factors: that hole burning of APT did not cease after annealing the sample above the crystallization temperature of the freezable water, and that the APT dimensions would require the molecule to be nearly perfectly centered in a pore to avoid interaction with the bound water and hydroxyethyl groups. In HGW, it has been reported that hole burning ceases after the sample is annealed at temperatures sufficient to cause transformation of the HGW to cubic ice.¹⁵ This is also as expected from the current understanding of the NPHB mechanism.^{29, 11} Based on the size of APT (20 Å lateral dimension) compared to the average poly-HEMA pore size (30 Å diameter) some interaction between APT and bound water and the hydroxyethyl groups of the polymer is expected.

Given the size of APT, it is possible that APT prevents crystallization of the freezable water in the pores.

Regarding the values of ΔQ_{xy} for the polymer, the large splitting in the wet polymer is puzzling as it is expected that two water molecules are still ligated to the aluminum in this sample. The larger splitting here must reflect, to some extent, interactions between APT and bound water and the hydroxyethyl groups. Interestingly, the ΔQ_{xy} splitting and red-shift of the Q_x transition for dry poly-HEMA are the largest for all the systems studied. The drying procedure is expected to remove freezable and bound water from the pores. However, the Al-ligated water may not have been removed. The large red-shift is most likely due to weakening of hydrogen bond interactions between the host medium and APT due to removal of most of the water molecules. Again, hydrogen bonding leads to blue-shifting of the Q_x -transition. The low value of 25 cm^{-1} for ω_m is consistent with this. The large ΔQ_{xy} value of 340 cm^{-1} may be due to collapse of the polymer about APT that occurs upon drying. This collapse could conceivably result in an APT structure that is different from that in the three glasses and in wet poly-HEMA.

B. Temperature dependence of pure dephasing of APT in wet poly-HEMA

The temperature dependence of the dephasing is shown in Figure 3. The solid line is a fit to the experimental data, using Eq. 1. The values of the fitting parameters are given in Table 2 along with the corresponding data for APT in fresh and annealed HGW.¹⁶ The first term of Eq. 1 describes dephasing due to diagonal modulation associated with the electron-TLS_{int} interaction. At temperatures $\lesssim 8 \text{ K}$, this term dominates the dephasing. For

molecular systems, α is typically 1.3, as previously reported for APT/HGW¹⁶ and as found here for APT/poly-HEMA. The $b\bar{n}(\omega)$ form for the exchange coupling applies in the slow modulation limit, $\delta < \tau^{-1}$, where δ is the difference in frequency of the pseudo-local mode for the ground and excited electronic states of the probe and τ^{-1} , the relaxation frequency, is given by

$$\tau^{-1}(T) = 2\pi g(\omega)D(\omega)[\bar{n}(\omega) + 1]. \quad (2)$$

Here ω is the effective frequency of the pseudo-local mode, $g(\omega)$ is the density of states of modes which couple to the pseudo-local mode and $D(\omega)$ is the coupling function. In the slow modulation limit, $\tau(0 \text{ K}) = (bc\pi)^{-1}$ where b is in cm^{-1} and c is the speed of light. For APT in wet poly-HEMA, $\tau(0 \text{ K}) = 4.1 \text{ ps}$. The corresponding value for APT/HGW is 1.5 ps. Whether or not the longer lifetime in poly-HEMA is due to a decrease in the value of $g(\omega)$ or a decrease in $D(\omega)$ or a combination of both is unclear.

From Table 2, note that the electron-TLS_{int} dephasing for poly-HEMA is similar to that of APT in fresh HGW. In HGW, the ZPH width at 5 K decreases by a factor of 5 if the sample is annealed at $\sim 130 \text{ K}$.¹⁵ This width decrease is indicative of a 5-fold decrease of the density of TLS_{int} in the sample.¹⁵ This TLS_{int} density decrease is mirrored in the amplitude of the TLS_{int}-electron dephasing term that also decreases $5 \times$ on annealing. For the poly-HEMA sample, annealing of a quickly cooled sample does result in a decrease in the ZPH width.¹² However, in the present work, the samples were slowly cooled and the initial widths at 5 K were comparable to those reported for annealed samples in ¹². Comparing the amplitude of the TLS-electron dephasing for poly-HEMA and fresh HGW, the values differ by somewhat less than a factor of two while the ZPH widths at 5 K are a factor of two

different, *vide infra*. An important point is that the TLS_{int} that dictate pure dephasing in bulk glasses at low temperatures also exist in confined glassy solids and are active in dephasing. It seems likely, however, that the bound water is involved in the structures of at least a fraction of the TLS_{int} .

Note that for APT/HGW, as described in ¹⁶, two phonon modes at 53 cm^{-1} and 180 cm^{-1} were used to fit the dephasing data over the range from 5 K to 100 K, although only a single mode at 53 cm^{-1} was sufficient up to 70 K. In the case of APT/poly-HEMA, the data is only available up to 80 K, and here also, only a single mode with energy 42 cm^{-1} is needed to obtain a good fit.

As in the case of APT/HGW and also APT in HGE,²⁵ the pseudo-local mode active in dephasing differs in frequency from the mode that appears (as a phonon sideband hole) in the hole spectra. As pointed out in ¹⁶, the phonon sideband hole arises due to linear electron-phonon coupling (with coupling strength given by the Huang-Rhys factor, S), while the mode causing dephasing through the exchange mechanism occurs via diagonal quadratic electron-phonon coupling. For HGW, the two modes (53 and 180 cm^{-1}) needed to fit the dephasing data can be identified with known modes of liquid water. Although the dynamical nature of these modes is the subject of current research, there appears to be general agreement that they are acoustic (translational) in nature. Walrafen³⁰ assigns the 50 and 180 cm^{-1} modes as transverse (shear-like) and longitudinal (dilatational) in character, respectively, with the latter corresponding to O-O stretching of O-H...O units in a T_d arrangement (in a time averaged sense). Shear motion of two water molecules leads to O-O-O bending and center of mass motion. Both modes are viewed as standing waves associated with hydrogen bonded

structures whose spatial extent in the glass is expected to be limited because of structural disorder.

For ethanol, only a single mode (47 cm^{-1}) was needed to fit the dephasing data. The similarity between the HGW and HGE mode frequencies, together with similar values for the maxima in spectral densities of the two liquids, and similar vibrational dynamics suggests an identification of the exchange coupled modes with the spectral density maxima.²⁵ In contrast, the phonon sideband frequencies for APT in HGW and in HGE are not similar (37 cm^{-1} in HGW and 26 cm^{-1} in HGE), showing that the linearly coupled modes cannot be identified with the quadratically coupled modes. In ²⁵, it was proposed that the phonon sideband mode is a libration of APT with the differences in mode frequencies for HGW and HGE reflecting difference in hydrogen bonding strength in the two glasses.

With reference to APT/wet poly-HEMA, by analogy with HGW, the 42 cm^{-1} mode causing dephasing would be expected to show up as a maximum in the spectral density for water saturated poly-HEMA. The reduction from the water value of $\sim 50\text{ cm}^{-1}$, then is indicative of the disruption of the water structure in the polymer relative to bulk water. The mode at 32 cm^{-1} observed as a phonon sideband hole is also most likely due to APT libration with a frequency between the mode frequency of HGW and HGE indicating that the average hydrogen bonding to APT in wet poly-HEMA is weaker than in HGW but stronger than in HGE.

C. Dispersive hole growth kinetics of APT in wet poly-HEMA

Further evidence for the structure of glassy water about APT in poly-HEMA being a disrupted form of the APT environment in HGW comes from the deuteration data shown in Figure 4. As has often been observed, deuteration of the host in NPHB does not effect the ZPH width or phonon frequency but does greatly decrease the hole burning efficiency.²⁰ The absence of a deuteration effect on hole widths indicates that the TLS_{int} are spatially extended with only small amplitude proton motion.²² However, the rate-determining step in NPHB involves extrinsic two level systems associated with the probe and its inner shell of host molecules and large amplitude proton motion.²⁹ As shown in the figure, a 15x time compression of the data for the deuterated sample results in coincidence of the deuterated and protonated results. Taking into consideration the difference in burn fluences used for the two samples, the deuterated sample burns 320 times slower than the protonated sample.

The kinetics data were fit by the expression²⁴

$$D(t) = 1.5 \int d\lambda f(\lambda) \int d\alpha \sin \alpha \cos^2 \alpha \cdot e^{-P\sigma_{LT}^p \phi(\lambda) \cos^2 \alpha t} \quad (3)$$

In this equation, $D(t)$ is the fluorescence excitation signal at holeburning time, t ; λ is the tunnel parameter for TLS_{ext} and $f(\lambda)$ is its Gaussian distribution function centered at λ_0 with standard deviation σ_λ ; α is the angle between burn laser polarization and the transition dipole; P is the photon flux in number of photons $\text{cm}^{-2} \text{s}^{-1}$; σ_{LT}^p , is the peak absorption cross section at low temperature ($5.5 \times 10^{-11} \text{ cm}^2$); and $\phi(\lambda)$ is the NPHB quantum yield given by

$$\phi(\lambda) = \frac{\Omega_0 \exp(-2\lambda)}{\Omega_0 \exp(-2\lambda) + \tau_f^{-1}} \quad (4)$$

In eq. 4, τ_f is the fluorescence lifetime and Ω_0 is the prefactor in the Fermi Golden rule expression for the TLS relaxation rate for nonphotochemical hole burning, $R = \Omega_0 \exp(-2\lambda)$.²² As in ^{15,31}, a value of $7.6 \times 10^{12} \text{ s}^{-1}$ was used for Ω_0 . In fitting data using Equation (3), the data must be scaled with the Huang-Rhys factor, S , which limits the maximum ZPH depth to $\exp(-S)$.²³ Thus, the fractional ZPH depth, $d(t)$, is given by $d(t) = (1 - D(t)) \cdot e^{-S}$. The parameters resulting from fitting the protonated and deuterated data of Figure 4 are given in Table 3, along with the corresponding data for APT in protonated and deuterated HGW.

In Table 3, the values $\langle R \rangle$ and $\langle \phi \rangle$ are the average TLS tunneling rate, $\langle R \rangle = \Omega_0 \exp(-2\lambda_0) \exp(2\sigma_\lambda^2)$, and the average quantum yield for hole burning, $\langle \phi \rangle = \langle R \rangle / (\langle R \rangle + \tau_f^{-1})$, respectively. The ratio of the values of $\langle R \rangle$ for the deuterated and protonated poly-HEMA samples is ~ 330 , nearly the same as determined from curve D of Figure. 4. The ratio of $\langle \phi \rangle$ for the protonated and deuterated samples is not the same because the two fluorescence lifetimes differ. As stated previously, fluorescence lifetimes were determined for APT in HGW and deuterated HGW at 77 K. In protonated HGW, $\tau_f = 6.5 \text{ ns}$, while in deuterated HGW, $\tau_f = 9.2 \text{ ns}$. These values were used for fitting the hole growth kinetics curves in HGW and in poly-HEMA. The ratio of $\langle R \rangle$ values for HGW, protonated and deuterated, is ~ 800 , a little more than twice the value for poly-HEMA. A factor of ~ 2 difference between poly-HEMA and fresh HGW was also noted in the low temperature dephasing data. However, in contrast to the dephasing data for which poly-HEMA seems to be similar to fresh HGW films, the values of λ_0 and σ_λ for poly-HEMA are more like the values for annealed HGW. Note that while the dephasing data are dependent on the density of states of TLS_{int} , the kinetics parameters reflect the tunneling rate for TLS_{ext} .

Table 3. Hole Growth Kinetics Parameters for APT in Wet poly-HEMA and in HGW^a

	S	λ_0	σ_λ	$\langle\phi\rangle$	$\langle R \rangle, s^{-1}$
HGW, ^b protonated (fresh/annealed)	0.55	8.2/8.3	1.3/0.9	0.78/0.015	$1.3 \times 10^7 /$ 2.4×10^6
HGW, deuterated (fresh/annealed)	0.60	11.0/11.0	1.0/0.85	$1.4 \times 10^{-4} /$ 8.2×10^{-5}	$1.6 \times 10^4 /$ 9.0×10^3
Wet p-HEMA, protonated	0.44	9.2	0.8	.0048	2.8×10^5
Wet p-HEMA, deuterated	0.55	12.1	0.8	7.7×10^{-6}	8.4×10^2

^aFrom ref 31. ^bLower values of S , λ_0 , and σ_λ for protonated HGW were reported in ref 11.

The values listed here from reference 31 were determined by a method similar to that used for the poly-HEMA measurements.

Thus, although the TLS_{int} density of states for poly-HEMA is similar to that of fresh HGW, the inner solvent shell around the APT molecule appears to be as highly ordered as it is in annealed HGW. Comparing the λ_0 and σ_λ values for protonated and deuterated poly-HEMA, note that the σ_λ values are the same while the λ_0 values are different. The ratio of $\lambda_0^{\text{D}}/\lambda_0^{\text{H}}$ is 1.3, the same as for the HGW ratio and nearly equal to the isotopic mass ratio $\sqrt{2}$, which indicates that it is proton tunneling that is involved in the TLS_{ext} .

5. Concluding Remarks

As discussed in the Introduction, understanding of the properties of water in confined spaces is an important step toward understanding the role and properties of water in biological systems. Here, spectral hole burning has been used to probe the environment of the APT chromophore confined to the pores of the poly-HEMA polymer. These pores are lined with hydroxyethyl groups and are water filled. Thus, the hole burning properties of the APT-water-polymer system were compared to the hole burning properties of HGW and of HGE. From this comparison, it is concluded that the APT molecule is located so that it interacts with both the bound (unfreezable) water and with the hydroxyethyl groups.

The results presented further establish that nonphotochemical hole burning (NPHB) can be used to distinguish between a probe molecule in confined and bulk glassy environments. The properties of Al-phthalocyanine tetrasulphonate (APT) in wet poly-HEMA films (pore size ~ 30 Å) investigated include: (1) T -dependence of pure dephasing due to electron-TLS coupling and quadratic electron-phonon coupling; (2) the linear electron-phonon coupling (Huang-Rhys factor S and peak phonon frequency ω_m) that results

in phonon sideband hole structure; (3) zero-phonon hole growth kinetics; and (4) the energy of APT's $S_0 \rightarrow S_1$ origin transition. The results were compared with those of APT in bulk hyperquenched glassy water (HGW, fresh and annealed), APT in bulk hyperquenched glasses of ethanol (HGE) and APT in "dry" poly-HEMA. Concerning (1), the basic mechanisms of dephasing in poly-HEMA are the same as in HGW with electron-TLS_{int} coupling dominating the dephasing below 8 K. At higher temperatures the dephasing in poly-HEMA is dominated by quadratic electron-phonon coupling to a 42 cm⁻¹ mode that correlates with the active 50 cm⁻¹ mode in HGW. The latter had been assigned to the transverse acoustic mode of glassy water. It is not clear if the decrease to 42 cm⁻¹ is entirely due to the effects of the bound water and hydroxyethyl groups of the pore surface. That is, APT with its 20 Å lateral dimension might also affect the acoustic mode energy of the freezable (unbound) water. Concerning (2), $\omega_m = 32$ cm⁻¹ for wet poly-HEMA, compared with values of 38 cm⁻¹ and 26 cm⁻¹ for HGW and HGE, respectively. The intermediate value of 32 cm⁻¹ suggests that APT interacts to some degree with the hydroxyethyl groups. That the value of $\omega_m = 25$ cm⁻¹ for dry poly-HEMA and that the Q_x transition energy of APT in wet poly-HEMA is equal to that in HGE provide support for interactions with the hydroxyethyl groups. Comparison of the Q_x transition energies of the systems studied indicates that H-bonding with APT, which is strongest for water, leads to a blue-shifting of the Q_x state that counteracts the red-shifting due to dispersion interactions.

As discussed herein, the APT/poly-HEMA system does not possess hole burning properties (ZPH width, Huang-Rhys factor, mean phonon frequency) as well suited to hole burning at higher temperatures as the APT/HGW system. Nevertheless, ZPH in the polymer

system can be resolved up to 80 K. APT in other matrices containing confined water has previously been studied both by hole burning^{13, 14} and by fluorescence line narrowing spectroscopy³². Galaup and co-workers, have studied APT in water confined in the pores of a xerogel and in a porous glass (Vycor)^{13, 14}. In the Vycor matrix, ZPH were detectable up to 80 K¹⁴. That system was characterized by a peak phonon frequency of 32 cm⁻¹ and a Huang-Rhys factor of 0.13. However, the reported 80 K hole width was 9 to 10 cm⁻¹ while for APT/poly-HEMA the 80 K width is ~ 7 cm⁻¹. In the APT/xerogel studied in that work, the phonon frequency was 25 cm⁻¹ and the Huang-Rhys factor, 0.26. In the xerogel, ZPH were not detectable above 60 K. APT in a poly(acrylamide) gel was studied by Saikan and co-workers by fluorescence line narrowing spectroscopy³². For that polymer, zero phonon lines in emission were measurable up to 110 K. For the hydrolyzed gel, the phonon frequency was 38 cm⁻¹. Although a Huang-Rhys factor was not reported, the electron-phonon coupling was described as weak.

References

1. Bhattacharyya, K.; Bagchi, B. *J. Phys. Chem. A*, **2000**, *104*, 10603.
2. Crupi, V.; Majolino, D.; Migliardo, P.; Venuti, V. *J. Phys. Chem. A*, **2000**, *104*, 11000.
3. Bellisent-Funel, M. C. *J. Phys.-Condens. Matter*, **2001**, *13*, 9165.
4. Beckstein, O.; Biggin, P. C.; Sansom, M. S. P. *J. Phys. Chem. B*, **2001**, *105*, 12902.
5. Nandi, N.; Bhattacharyya, K.; Bagchi, B. *Chem. Rev.* **2000**, *100*, 2013.
6. Pal, S. K.; Peon, J.; Bagchi, B.; Zewail, A. H. *J. Phys. Chem. B*, **2002**, *106*, 12376.
7. Pathmanathan, K.; Johari, G. P. *J. Polym. Sci. B, Polym. Phys.*, **1990**, *28*, 675.
8. Corkhill, P. H.; Jolly, A. M.; Ng, C. O.; Tighe, B. J. *Polymer*, **1987**, *28*, 1760.

9. Hofer, K.; Mayer, E.; Johari, G. P. *J. Phys. Chem.* **1990**, *94*, 2689.
10. Hallbrucker, A.; Mayer, E.; Johari, G. P. *J. Phys. Chem.* **1989**, *93*, 7751.
11. Reinot, T.; Small, G. J. *J. Chem. Phys.* **2001**, *114*, 9105.
12. Hayes, J. M.; Reinot, T.; Small, G. J. *Chem. Phys. Letters*, **1999**, *312*, 362.
13. Galaup, J.-P.; Fraigne, S.; Landraud, N.; Chaput, F.; J.-P. Boilot *J. Luminesc.* **2001**, *94-95*, 719.
14. Galaup, J.-P.; Fraigne, S.; Landraud, N.; Chaput, F.; J.-P. Boilot *J. Luminesc.* **2002**, *98*, 189.
15. Kim, W.-H.; Reinot, T.; Hayes, J.; Small, G. J. *J. Phys. Chem.* **1995**, *99*, 7300.
16. Reinot, T.; Kim, W.-H.; Hayes, J. M.; Small, G. J. *J. Chem. Phys.* **1996**, *104*, 793.
17. Reinot, T.; Hayes, J. M.; Small, G. J.; Zerner, M. C. *Chem. Phys. Letters*, **1999**, *299*, 410.
18. Furusawa, A.; Horie, K.; Mita, I. *Japan, J. Appl. Phys.* **1989**, *28*, Suppl. 28-3, 247.
19. Jackson, B.; Silbey, R. *Chem. Phys. Letters*, **1983**, *99*, 331.
20. Jankowiak, R.; Hayes, J. M.; Small, G. J. *Chem. Rev.*, **1993**, *93*, 1471.
21. Völker, S. in *Relaxation Processes in Molecular Excited States*, Funfschilling, J., Ed., (Kluwer: Dordrecht, **1989**) p. 113.
22. Narasimhan, L. R.; Littau, K. A.; Pack, D. W.; Bai, Y. S.; Elschner, A.; Fayer, M. D. *Chem. Rev.* **1990**, *90*, 439.
23. Kenney, M. J.; Jankowiak, R.; Small, G. J. *Chem Phys.* **1990**, *146*, 47.
24. Reinot, T.; Dang, N.; Small, G. J. *J. Luminesc.* **2002**, *98*, 183.
25. Reinot, T.; Hayes, J. M.; Small, G. J. *J. Chem. Phys.* **1997**, *106*, 457.
26. Hayes, J. M.; Reinot, T.; Shields, P.; Small, G. J. *Rev. Sci. Instrum.* **1999**, *70*, 2455.

27. Reinot, T. *unpublished results*.
28. McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562.
29. Shu, L.; Small, G. J. *J. Opt. Soc. Am. B*, **1992**, *9*, 724.
30. Walrafen, G. E. *J. Phys. Chem.* **1990**, *94*, 2237.
31. Kim, W.-H.; Reinot, T.; Hayes, J. M.; Small, G. J. *J. Chem. Phys.*, **1996**, *104*, 6415.
32. Mikami, M.; Ueta, T.; Kobayashi, D.; Koreeda, A.; Saikan, S. *J. Luminesc.* **2000**, *86*, 257.

CHAPTER 7

TEMPERATURE DEPENDENCE OF HOLE GROWTH KINETICS IN
ALUMINUM-PHTHALOCYANINE-TETRASULPHONATE IN HYPERQUENCHED
GLASSY WATER

Manuscript for submission

N. C. Dang¹, J. M. Hayes,² T. Reinot,² and R. Jankowiak³

Ames Laboratory-USDOE and Department of Chemistry,

Iowa State University, Ames, IA 50011

Abstract

The temperature dependence of hole growth kinetics (HGK) of aluminum-phthalocyanine tetrasulphonate in fresh and annealed hyperquenched glassy water is given in temperature ranges of 5 to 20 K using the model described in [*J. Chem. Phys.*, 2000, Vol. 113, p. 10207]. We argue that the hole-burning rate is significantly less dependent on temperature when temperature-induced absorption rate is considered. A slightly slower growth rate of persistent holes with temperature increase is associated with thermal hole filling, which prevents faster-burning chromophores forming persistent spectral hole. To

¹ Graduate student

² Research advisor

³ Major professor

account for HGK at temperatures higher than 15 K, the two-level system model for non-photochemical hole burning becomes insufficient.

1. Introduction

The phenomenon of photochemical and non-photochemical hole burning (NPHB) in the electronic absorption band of a frozen glassy solution was first reported in [1,2]. It was proposed shortly thereafter that NPHB was common to glassy media and was due to the interaction of the absorber with the low-frequency excitations responsible for the anomalous properties of glasses at low temperatures [3]. These low-frequency modes [4,5] were thought to be rearrangements of the glass molecules between two nearly isoenergetic configurations, typically described by a double potential well, and referred to as two level systems (TLS). The original NPHB model [3] proposed that hole burning occurs due to a reduced barrier between the potential minima of a TLS coupled to an absorber in its excited state. Phonon-assisted tunneling between the potential minima leads to energy of the excited molecule, resulting in the "burning" of a spectral hole. The original hole-burning mechanism assumed a *static* distribution of TLS induced by the probe molecules (extrinsic TLS, TLS_{ext}) [3]. A number of experimental findings invalidated this assumption [6], leading to a refined mechanism proposed by Shu and Small [7]. These authors suggested that NPHB is the result of a hierarchy of configurational tunneling events triggered by electronic excitation of the probe. These events begin in the outer shell of the probe involving relaxation of the faster, intrinsic TLS (TLS_{int}), which originate from the disordered nature of glassy environments and terminate in the inner shell. This outside-in chain of events results in the migration of

excess free volume around the probe that leads to the final and rate-determining step: tunneling of TLS_{ext} in its excited state ($\text{TLS}_{\text{ext}}^*$).

It has been known for two decades that the kinetics of NPHB, as well as those of spontaneous hole filling, are highly dispersive. The original model was based assumed that the dispersive kinetics were due to structural disorder and stemmed mainly from the distribution of tunneling rates for the TLS, called λ -distribution; and that a Gaussian shape for λ -distribution is physically reasonable [8]. Dispersion due to photo-selection caused by the laser polarization, i.e. the α -distribution [9,10] and the ω -distribution [11] caused by off-resonant absorption were later considered to account for better HGK fits. The importance of the aforementioned distributions was analyzed in detail in Ref. 12, where it was demonstrated that the λ - and α - distributions were the most and least important, respectively. The latter HGK model was further improved by incorporating the contribution from the photoproduct [13].

In a previous study of Oxazine 720 in glassy glycerol matrix from 1.6 to 7 K [6], the temperature-dependent HGK was modeled using only λ -distribution. It was concluded that the temperature dependence of the induced absorption rate (i.e., the change of homogeneous linewidth of the ZPL) fully accounts for the temperature dependence of the ZPH growth kinetics, and that the tunneling relaxation rate, R , is independent of temperature despite the fact that phonon-assisted tunneling as the rate-determining step should show to increase with increasing temperature. That no increase of R was observed in [6] can be explained by the fact that the chosen temperature range – thermal occupation numbers of phonons at 1.6 and 7 K – were practically the same, and HGK differences were buried under the noise. On the

other hand, hole burning, which ceases above a certain temperature, will slow down before it comes to a complete stop.

In order to see an increase (or decrease) in the HGK rate, we chose a higher and broader temperature range, 5 to 20 K, and used another non-photochemical hole-burning system, aluminum phthalocyanine tetrasulphonate (APT) in fresh and annealed hyperquenched glassy water (HGW), which we have previously and extensively studied [12-16]. The T -dependence of the single-site absorption spectrum was introduced using electronic dephasing data from Ref. 15. The T -dependence of the tunneling rate was estimated from the experimental data. Thermal hole filling (THF) becomes observable in APT/HGW above 10 K; it leads to an additional slowdown of HGK and it was accounted for using a simple model modification. Note that the range available for temperature studies is limited due to rapidly vanishing ZPL intensity with increasing temperature. The significant decrease of the ZPH intensity requires higher burn fluences to detect ZPH, which complicates modeling of the HGK as the contribution from PSBH and photoproduct must be considered.

2. Experiment

Aluminum phthalocyanine tetrasulphonate (APT) purchased from Porphyrin Products and nanopure water ($R \approx 18 \text{ M}\Omega \text{ cm}^{-1}$) were used for sample preparation. A solution of APT in water with a concentration of $2 \times 10^{-5} \text{ M}$ was made by extensive mixing followed by filtering. The room temperature absorption spectra of APT in water were recorded, which allowed the integrated absorption cross-section (σ) of the Q_x absorption band to be determined.

The apparatus used to prepare hyperquenched glassy films of water containing APT and the optical setup is described in detail in Ref. 15. Briefly, hyperquenched films were produced by thermospray deposition of the sample onto a polished copper substrate attached to the cold finger of a Janis ST-100 continuous flow helium cryostat. The substrate temperature was measured by a silicon diode (Lake Shore Cryogenics, DT-470) mounted on the back of the copper substrate. The temperature was monitored and stabilized by a temperature controller (Lake Shore 330 Autotuning Temperature Controller). The lowest temperature obtained was 5.0 K. The body of the cryostat was mounted in a vacuum chamber, which was continuously pumped using a turbomolecular pump. The lowest pressure obtained was $\approx 2 \times 10^{-7}$ Torr. The thermospray was inserted into the chamber through a vacuum fitting. Inlet and outlet temperatures of 80°C and 180°C of the thermospray resulted in solution droplets of $\approx 2 \mu\text{m}$ diameter. Films with thicknesses of $\approx 10 \mu\text{m}$ were obtained on the substrate using a reciprocating plunger pump. Films deposited at 5.0 K are referred to as *fresh* HGW while films deposited at 5.0 K and annealed at temperature T_A for time t_A are referred to as *annealed* HGW. In this experiment, $T_A = 140$ K and $t_A \approx 1$ hour. After annealing the film was cooled to 5.0 K for spectroscopic measurements. For higher temperature measurements, the temperature controller was used to heat the sample to the desired temperature.

The optical setup consisted of an actively stabilized ring dye laser (Coherent 699-29, long term linewidth < 10 MHz, laser dye: LD-688 (Exciton)) pumped by a 6W Ar-ion laser (Coherent, Innova-90). The intensity of the laser beam was stabilized electro-optically (Brockton Electro-Optics Corp., LPC). A beam expander was used and the signal was

attenuated using a set of neutral density filters. The fluorescence, detected with a photomultiplier tube (Hamamatsu, R2949) followed by a photon counter (Stanford Research SR400), was collected through a long wavelength pass filter (Omega Optical, AELP-730). Hole growth kinetics curves were obtained by monitoring the decrease in fluorescence intensity as a function of burn time. Different channel times were used in data acquisition to ensure detection of the early events in the hole-burning process.

3. Standard hole growth kinetics model

The “standard” hole growth kinetics model is given by [12,14]:

$$D(\Omega, t) = 1.5 \int d\omega L(\Omega - \omega) G(\omega) \int d\lambda f(\lambda) \int d\alpha \sin \alpha \cos^2 \alpha e^{-P\sigma\phi(\lambda)L(\omega - \omega_B) \cos^2(\alpha)t}, \quad (1)$$

$D(\Omega, t)$ is the absorption as probed at frequency Ω following a burn time of t at ω_B . For HGK detection, $\Omega = \omega_B$. ω is the frequency of the zero phonon line (ZPL), $G(\omega)$ is a Gaussian distribution of ZPL frequencies (the site-distribution function), α is the angle between the laser polarization and the transition dipole vectors, λ is the tunnel parameter for the TLS_{ext} , and $f(\lambda)$ is its normalized Gaussian distribution function centered at λ_0 , with a standard deviation of σ_λ . σ is the integrated absorption cross-section ($\text{cm}^2 \text{s}^{-1}$) and P is the photon flux (photons $\text{cm}^{-2} \text{s}^{-1}$). The NPHB quantum yield, $\phi(\lambda)$, is given by $\phi(\lambda) = \frac{R}{R + \tau_f^{-1}}$,

where τ_f is the excited state lifetime of the chromophore and R is the phonon-assisted tunneling rate. The non-photochemical hole-burning rate is determined by tunneling in the $\text{TLS}_{\text{ext}}^e$; the corresponding relaxation rate, R , is calculated assuming that two eigenstates of the TLS become coupled via modulation of TLS potential, which is caused by the elastic wave in the medium, i.e., a phonon. Downward processes (with creation of one phonon)

should be prevalent at low temperatures; TLS-TLS interaction is neglected and weak electron phonon coupling is assumed ($S < 1$). For a single $\text{TLS}_{\text{ext}}^e$ the phonon-assisted tunneling rate becomes [17,6]

$$R = \left(\frac{3f^2 W^2 E}{16\pi\rho c^5 \hbar^5} \right) (\bar{n}(E) + 1). \quad (2)$$

Where, ρ is local sample density around the probe, c is an average sound velocity, and the f parameter is related to TLS_{ext} deformation potential difference. The thermal occupation number is given by $\bar{n}(E) = (\exp(E/kT) - 1)^{-1}$, and the tunnel splitting, E , is given by $E^2 = \Delta^2 + W^2$ (where Δ is the asymmetry parameter and W is the tunneling frequency, $W = \omega_0 \exp(-\lambda)$). Because the tunneling frequency, W , depends exponentially on the tunnel parameter, λ , one can write Eq. 2 as $R = \Omega_0 \exp(-2\lambda) (\bar{n}(E) + 1)$. It has been argued that a broad range of λ is responsible for the distribution of relaxation rates, which, in turn, has been argued to have Gaussian shape [8]. Thus, λ -distribution can be described by its centervalue (λ_0) and standard deviation (σ_λ), which can be obtained from fitting experimental HGK curves with Eq. 1.

$L(\Omega - \omega)$ in Eq. (1) is the normalized, single-site absorption spectrum, which consists of the ZPL and phonon sideband (PSB). In order to model temperature-dependent hole growth kinetics, single-site absorption spectrum is expressed as:

$$L(\Omega - \omega) = L_{\text{ZPL}}(\Omega - \omega) \times FC + L_{\text{PSB}}(\Omega - \omega) \times (1 - FC), \quad (3)$$

where the L_{ZPL} is the normalized Lorentzian profile of the ZPL given by:

$$L_{\text{ZPL}}(\Omega - \omega) = \frac{1}{\pi} \times \frac{\Gamma_H(T)}{(\Omega - \omega)^2 + [\Gamma_H(T)]^2}. \quad (4)$$

FC is Frank-Condon factor:

$$FC = \exp \{-S[2\bar{n}(\omega_m) + 1]\}, \quad (5)$$

where $\bar{n}(\omega_m)$ is the thermal occupation number for a phonon with mean phonon frequency ω_m , and S is the Huang-Rhys factor due to low frequency phonons centered at ω_m . L_{PSB} is the one-phonon profile of the phonon side band (PSB), which is approximated by a Gaussian on the low-energy side and a Lorentzian on the high-energy side [18]. $\Gamma_H(T)$ in Eq. 4 is given by [19,20]:

$$\Gamma_H(T) = \Gamma_0 + aT^\alpha + b_1\bar{n}(\omega_1), \quad (6)$$

where $\Gamma_0 = 1/(2\pi\tau_h)$ is the lifetime limited width of the ZPL. The second term describes dephasing due to the electron-TLS_{int} coupling. The third term is associated with dephasing due to exchange coupling with pseudo-localized mode of frequency ω_1 [19]. The values specific to APT in HGW used in above equations are summarized in Table 1.

To calculate the temperature-dependent relaxation rate, the values of asymmetry (Δ) and tunneling parameter ($\mathcal{W}$) of the TLS_{ext}^e, must be estimated. Following Ref. 14 we assume that the tunneling pre-factor $\omega_0 \approx \Omega_0 = 7.6 \cdot 10^{12}$ Hz [6], that leads to $\mathcal{W} \approx 0.1 \text{ cm}^{-1}$ for $\lambda_0 = 8$. The values of Δ_g and Δ_e , for the ground and excited state of TLS_{ext} were estimated as follows: The average frequency difference between photoproduct and educt, $\Delta_d = |\Delta_g - \Delta_e|$, was determined from the experiment. Photoproduct from ZPH is not observable in APT in HGW for all burn fluences. It is negligible compared to the photoproduct originating from the

Table 1. Parameters used to fit hole growth kinetics data for APT in fresh and annealed HGW.

FWHM of site distribution function $G(\omega)$, Γ_I (cm^{-1})	356
Peak phonon frequency, ω_m (cm^{-1})	37
Phonon sideband (half) widths, Γ_G/Γ_L (cm^{-1})	15.5/23.5
Tunnel splitting E (cm^{-1})	27
Burn time, t_B (s)	1000
Fluorescence lifetime, τ_f (ns)	6.5
Integrated absorption cross-section, σ (cm^2s^{-1})	1.75×10^{-2}
Pre-factor of tunneling rate, Ω_0 (s^{-1})	7.6×10^{12}
Dephasing parameters for fresh / annealed HGW (Equation 6) ^a	
Amplitude a (cm^{-1})	0.0011 / 0.00022
Amplitude b_I (cm^{-1})	7 / 6.9
Exponent α	1.30 / 1.30
Phonon frequency ω_1 (cm^{-1})	53 / 50

^a From Ref.19. Due to low temperature ($T < 20$ K) only the lowest frequency phonon-mode ($\sim 50\text{cm}^{-1}$) was used.

PSBH (see inset in Fig. 1). In our hole burning spectra, the blue-shifted photoproduct is always more abundant. Therefore, the value for average frequency change at hole burning was taken $\Delta_d = 120 \text{ cm}^{-1}$. It was assumed that $\frac{\Delta_g}{\Delta_e} \approx \frac{V_g}{V_e}$, where V_g and V_e are barrier heights in ground and excited TLS. The tunnel parameter for the $\text{TLS}_{\text{ext}}^g$ was $\lambda_{0,g} = 18.9$ [23], and for $\text{TLS}_{\text{ext}}^e$, $\lambda_{0,e} = 8.0$. Using Gamov's formula:

$$V = \lambda^2 \hbar^2 / 2md^2, \quad (7)$$

where d is the distance involved in tunneling and m is the mass of the tunneling entity. The ratio $V_g / V_e \approx 5.5$ and also $\Delta_g / \Delta_e > \approx 5.5$. For a TLS_{ext} having photoproduct at 120 cm^{-1} from initial absorption frequency this provides $\Delta_g = 147 \text{ cm}^{-1}$ and $\Delta_e = 27 \text{ cm}^{-1}$.

4. Results

Fluorescence excitation spectrum of APT in fresh HGW is shown in Fig. 1. The spectral range used for hole growth kinetics (HGK) studies was 676.9-680 nm. The low-energy side of the APT's Q_x -band was chosen to avoid excitation of the Q_y states, for which hole burning is significantly slower due to the competing process of $Q_y \rightarrow Q_x$ relaxation [16]. A hole profile of APT in fresh HGW, which was obtained by subtracting the pre-burn spectrum from the post-burn spectrum, is presented in the inset of Fig. 1. The hole was burned at 673 nm with 15 mJ/cm^2 at 5 K. For smaller burn fluences (i.e. $\leq 1 \text{ mJ/cm}^2$) the contribution from PSBH is negligible and the photoproduct from ZPH is buried within the experimental noise. Thus, the majority of visible photoproduct originates from the pseudo-PSBH. The average distance of blue and red photoproduct from the PSBH is 120 cm^{-1} and

Figure 1. Pre-burn (A) and post-burn (B) fluorescence excitation spectrum of APT in fresh HGW ($2 \cdot 10^{-5}$ M) at 5 K; Q_x and Q_y mark two components of the lowest electronically excited band of APT. The curve (B-A) shows (3 times multiplied) hole profile burned at 5K with 15 mJ/cm^2 at 673 nm. The distances between PSBH peak and the mean values of the blue and red photoproduct (indicated with arrows) are $\sim 120 \text{ cm}^{-1}$ and 100 cm^{-1} , respectively.

100 cm^{-1} , respectively. At this burn fluence there is ~ 4 times more blue-shifted photoproduct than red-shifted photoproduct.

Normalized HGK data (noisy curves) for APT in fresh and annealed HGW in the temperature range 5-20 K are shown in Figs. 2 and 3. Each hole was burned at a slightly different wavelength (0.1 nm apart) in the range of 676.9 - 679.7 nm. It was verified that ZPH did not overlap, since it would have modified the HGK. Our model (see Eqs. 1 and 11) accounts for the wavelength dependence of induced absorption rate; nevertheless, the ZPH were burned in a narrow spectral range. Burn intensity (I_B) and burn time (t_B) were 82 nW/cm² and 1000 s, respectively. A burn fluence ($I_B \times t_B$) of 82 $\mu\text{J}/\text{cm}^2$ was chosen to ensure that phonon-sideband holes (PSBH) does not interfere with during the course of the burn process, and to ensure that HGK spans several decades of time to ensure good fits.

The smooth curves in left panel of Fig. 2 are the fits using the parameters given in Table 1 and Eq. 1 to the experimental data. Perfect fits to the HGK curves at different temperatures were obtained using λ_0 , σ_λ , and S as free parameters, although a gradual increase of the S factor from 0.23 up to 0.55 was required. The temperature-dependent Huang Rhys factor was considered non-physical since S is temperature independent in this model. Therefore, the S factor was fixed to the value found from fitting 5K HGK data, and the fits shown in the right panel of Fig. 2 were calculated with only two free parameters: λ_0 , and σ_λ . Note that fits at $T > 5\text{K}$ were "poor." The limit for ZPH depth is determined by the FC of the ZPL (see Eqs. 3 and 5), which depends on Huang-Rhys factor. Consequently, S appears to increase when the ZPH are burned with the same fluence, but have decreasing depth. The latter is caused by thermal hole-filling of ZPH, as illustrated in Fig. 4 (curve a). First, a ZPH with fractional depth of

Figure 2. Normalized experimental and calculated HGK curves for APT in fresh HGW. Curves were obtained at different temperatures and at different wavelengths ($\lambda_B = 679.7 - 676.8$ nm); burn intensity and time were $I_B = 82$ nW/cm² and $t_B = 1000$ s, respectively. Left and right panels show the same experimental curves, which are fitted differently (see text for details).

Figure 3. Normalized experimental and calculated HGK curves for APT in fresh (left) and annealed (right) HGW. Curves from bottom to top were obtained at different temperatures 5, 7, 9, 11, 13, 15, 18, and 20 K, respectively. Each curve was burned at different wavelength in the range 679.7-676.8 nm (see text for details). Burn intensity and burning time were $I_B = 82 \text{ nW/cm}^2$ and $t_B = 1000 \text{ s}$, respectively.

Figure 4. A ZPH with fractional depth of 0.48 was burned into APT in fresh HGW at 680.2 nm with $I_B = 70 \text{ nW/cm}^2$, $t_B = 60 \text{ s}$, and at $T = 5 \text{ K}$. This fractional hole depth (curve a) is followed as a function of time as different temperature excursions are made; sample temperature as a function of time is shown with the curve b. Vertical arrows mark moments fractional hole depths were recorded, the latter were used to calculate relative thermal hole filling (see text for details).

0.48 was burned for 60 s in APT in fresh HGW at 680.2 nm with 70 nW/cm^2 , ($T = 5 \text{ K}$). The laser was kept at burn frequency with the intensity reduced to 6 nW/cm^2 ; the fluorescence was then detected as a function of time, while the sample temperature was cycled as shown in Fig. 4 (curve b). This allowed measurement of the ZPH depth at 5 K before and after each thermal cycle as illustrated with a series of arrows in curve a of Fig. 4. A relative loss of ZPH depth can be calculated as a ratio of the corresponding ZPH depths, which were 2, 6, 8, 24, 45, and 65%, after thermal cycling to 10, 13, 15, 19, 25, and 30 K, respectively. Note that ZPH depth starts to recover after the thermal cycle as the thermally filled sites are quickly burned away. In fact, the HGK of partially filled hole is very fast in the beginning and slows down remarkably as initial hole depth is reached, i.e. its HGK is different when compared to that of 'unaffected' sites burned at 5 K in a "virgin" sample (data not shown). This is most likely caused by different distributions of hole-burning sites.

5. Discussion

It is clear from Fig. 2 that hole growth kinetics in both annealed and fresh HGW slows down remarkably as temperature increases. The broadening of the zero phonon line and increasing Frank-Condon factor from the PSB are the primary causes of the slowdown of the HGK. For example, neglecting the temperature dependence of the absorption profile, $L(\omega - \omega_B)$, in Eq. 1 will lead to increase of λ_0 from 8.1 to 10.2 at 20 K. However, if HGK data is fitted with Eq.1, λ_0 increases from 7.8 to 8.1 (± 0.03) for fresh and from 7.85 to 8.1 (± 0.03) for annealed HGW, respectively, indicating additional slowing down of kinetics as an increase of λ_0 by 0.3 would lead to a decrease of R by a factor of 1.8. Fitting HGK curves as

a function of temperature resulted either in “poor” fits or required a gradual increase of the S factor from 0.23 up to 0.55.

The slowdown of HGK and the temperature-dependence of S are most probably caused by neglecting the photoproduct and, subsequently, the interference of photoproduct i.e. spontaneous hole filling (SHF) in the ground state, light-induced hole filling (LIHF) and temperature-induced hole filling (THF). The latter starts to influence HGK in APT in HGW already above 10 K (see Figure 4 curve **a**), where ZPH signal loss after a thermal cycle can be observed (the height difference between two leftmost arrows). Interference between HB and THF leads to non-physical temperature dependence of fitting parameters, especially Huang-Rhys factor. THF is a ground state, thermally activated process that returns hole-burned sites with low barrier heights back to their origin state. If it happens at the time HGK is detected, then the detected HGK is slower and the resulting ZPH is shallower. A simple modification of Eq. 1 will account for the THF processes in case of low burn fluences (i.e. when PSBH and product band are not observed in absorption spectrum, *vide infra*). To start, we note, that the barrier heights of TLS_{ext} and tunneling rates are related, $V \sim \lambda^2$ (see Eq. 7). Sites with faster kinetics (with small λ) have also lower barriers, allowing separation of the λ -distribution (as well as Eq. 1) into two parts (fast and slow). We define a temperature dependent step-function:

$$H(T) = \left(1 + \exp \left[\frac{\lambda_{\text{step}}(T) - \lambda}{c} \right] \right)^{-1}, \quad (8)$$

where λ_{step} is a function of temperature defined so that $H(T) = 0$ for $\lambda < \lambda_{\text{step}}$ and $H(T) = 1$ for $\lambda > \lambda_{\text{step}}$. c provides a finite width to the step. A percentile, given by $p(T) = \int d\lambda f(\lambda) H(T)$,

provides a fraction of sites that persistently burn at a given temperature. Secondly, $p(T)$ gives the fraction of photon flux, which burns a persistent hole. Thus, equation Eq. 1 can be rewritten as: $D(\Omega, T, t) = D_{slow}(\Omega, T, t) + D_{fast}(\Omega, T, t)$, where

$$D_{slow}(\Omega, T, t) = 1.5 \int d\omega L(\Omega - \omega) G(\omega) \int d\lambda f(\lambda) H(T) \int d\alpha \sin \alpha \cos^2 \alpha e^{-Pp(T)\sigma\phi(\lambda)L(\omega-\omega_B)\cos^2(\alpha)t} \quad (9)$$

$$D_{fast}(\Omega, T, t) = 1.5 \int d\omega L(\Omega - \omega) G(\omega) \int d\lambda f(\lambda) (1 - H(T)) \int d\alpha \sin \alpha \cos^2 \alpha e^{-P(1-p(T))\sigma\phi(\lambda)L(\omega-\omega_B)\cos^2(\alpha)t} \quad (10)$$

Eq. 9 is the absorption spectrum of sites that hole burn, and Eq. 10 describes the absorption spectrum of sites that hole burned and then rapidly filled thermally. Hole burning quantum

yield, $\phi(\lambda)$ is given for both equations with: $\phi(\lambda) = \frac{H(T)\Omega_0 \exp(-2\lambda)}{\Omega_0 \exp(-2\lambda) + \tau^{-1}}$. Eq. 10 can be

simplified because the $\phi(\lambda) = 0$ for $\lambda < \lambda_{step}$ (i.e. the exponent equals to 1) and the coefficient $(1-H(T)) = 0$ for $\lambda > \lambda_{step}$:

$$D_{fast}(\Omega, T, t) = \int d\omega L(\Omega - \omega) G(\omega) (1 - p(T)) \quad (11)$$

and it provides temperature dependent, constant in time i.e. “non-burning” background. The temperature dependent HGK curves presented in Fig. 4 were modeled with:

$$D_b(\Omega, T, t) = \int d\omega L(\Omega - \omega) G(\omega) \times \left(1 - p(T) + 1.5 \int d\lambda f(\lambda) H(T) \int d\alpha \sin \alpha \cos^2 \alpha e^{-Pp(T)\sigma\phi(\lambda)L(\omega-\omega_B)\cos^2(\alpha)t} \right) \quad (12)$$

$p(T)$ were found from thermal cycling experiment (Fig. 4); values: 0, 0.01, 0.02, 0.04, 0.07, 0.10, 0.17, and 0.25 were used at 5, 7, 9, 11, 13, 15, 18, and 20 K, respectively. For fresh APT in HGW fitting resulted in constant $\lambda_0 = 8.25 \pm 0.02$ and constant Huang Rhys factor $S = 0.23 \pm 0.01$. For APT in annealed HGW fitting resulted in $\lambda_0 = 8.15 \pm 0.02$ and Huang

Rhys factor $S = 0.24 \pm 0.01$. However, σ_λ increased from 0.85 to 1.1 in fresh and from 0.75 to 1.1 in annealed HGW when temperature increased from 5 to 20 K. The increase is apparent and is most likely due to simplified treatment of the photoproduct in Eq. 11. Another factor is that the TLS model gradually loses its applicability with increasing temperature (*vide infra*).

Eq. 11 (and single TLS_{ext} model) is not suitable for high and medium fluence hole burns. For example, to observe $\sim 70\%$ deep ZPH (e.g. at 5 K) requires holeburning of all resonant TLS_{ext} . After a thermal cycle to 50 K, such ZPH fills 100%; in other words those TLS, that contributed to the $\sim 50\%$ deep hole burned at 5K do not burn persistently above 50 K. However, even at 78 K 45% deep ZPH can be burned in APT in HGW [25] and hole burning is possible up to 125 K. The possibility to burn deep holes above 50 K requires, therefore, more than one TLS_{ext} per single chromophore, i.e. one needs to incorporate a multiple-level system (MLS) model for hole burning. MLS model for NPHB was first introduced in [14] to explain very sharp and intense blue-shifted photoproduct and deep ($\sim 85\%$) PSBH at high burn intensities, features that were impossible to model numerically using only single TLS_{ext} . One possible realization of MLS is shown in the right frame of Fig. 5. The third level has a much lower tunneling rate and would be responsible for processes that irreversibly trap the hole-burning site at higher energies compared to the burn laser frequency. Since multiple potential wells would couple with the same chromophore, different tunneling coordinates leading to distinctly different λ -distributions could characterize different pairs of TLS. We emphasize that the latter concept is not the same as one very broad and/or non-Gaussian distribution. In the TLS model, a persistent hole saturates when competing hole growth and filling rates become equal due to SHF, THF,

Figure 4. Frames A and B show schematics of the extrinsic TLS model and multiple level system model for non-photochemical hole burning, respectively. Indices e and g indicate chromophore in its excited and ground state. ω_B is the burn frequency, W is the tunneling frequency, Δ is asymmetry, d is distance and V denotes TLS barrier height. I, II, III, and N denote different chromophore-host configurations where I is the pre-burn configuration and II,...,N are post-burn configurations. For each pre- and post-burn configuration pair ($i = 1, 2, \dots, n$), correspond different tunneling parameters (W , Δ , V , d , R and λ) forming different distributions.

and/or LIHF processes. In contrast, in the three-level model such balance is expected at higher fluences. In the multiple-level model such balance may not occur. This prediction is consistent with our experimental data obtained for APT in HGW, where we were unable to saturate the hole growth for fluences ranging from nJ/cm² up to kJ/cm². When the TLS model works well, i.e., at low temperatures and at moderate and low-burn intensities, the fluence is a good characteristic for hole growth (i.e. two holes are identical if burned with the same fluence but using different burn times and intensities). As a consequence of multiple levels and several competing growth and filling processes, fluence alone is not a good parameter to fit HGK, which depends on burn intensity and time in a more complicated manner.

One way to incorporate multiple levels into Eq. 12 is to introduce different λ -distributions (λ_i) with $i = 1, \dots, n$. In this case Eq. 12 can be re-written in the following way:

$$D(\Omega, T, t) = \int d\omega L(\Omega - \omega) G(\omega) \times \prod_i \left(1 - p_i(T) + 1.5 \int d\lambda_i f(\lambda_i) H_i(T) \int d\alpha \sin \alpha \cos^2 \alpha e^{-P p_i(T) \sigma \phi(\lambda_i) L(\omega - \omega_B) \cos^2(\alpha) t} \right) \quad (13)$$

where index i labels normalized Gaussian distribution functions $f(\lambda_i)$, with different center-values λ_{0i} and standard deviations $\sigma_{\lambda i}$. MLS model becomes necessary at temperatures above 15K. However, for all burn fluences of interest (at $T > 15$ K) the photoproduct and the PSBH appear in the spectrum and interfere with the ZPH. This interference rapidly progresses with increasing fluence and/or temperature and becomes a major hole shape determining factor. Therefore photoproduct needs to be considered simultaneously with MLS.

The theoretical hole-burning model, which automatically takes into account photoproduct [13], exists. It was based on Eq 1. Briefly, educt and photoproduct sites were

treated separately and were both regarded as capable of interacting with a burn laser. A hole-burned educt site changed its frequency and formed photoproduct. A hole-burned product site changed its absorption frequency and returned to its origin frequency, i.e. it populated educt sites. The major improvement of this model is that it provides HB sites with the memory of their origin frequency in agreement with experimental observations [21]. The site-distribution function (SDF, $G(\omega)$ in Eq. 1) was substituted with two-dimensional (2D) time-dependent SDF, $G(\omega_j, \omega_i, t)$, where the second frequency coordinate labeled the origin frequency of each site and t was the holeburning time. In order to hole burn, the last two integrals in Eq. 1 were calculated once for each $G(\omega_j, \omega_i, t)$. The full absorption spectrum, $D(\Omega, t)$, at time t and at frequency Ω , was found by summing the number of SDF sites with the same energy, ω_j , followed by a convolution with single-site absorption profile. The 2D model could be incorporated into the MLS model and both thermal and spontaneous hole filling processes could be taken into account. This improvement, however, is beyond the scope of this manuscript and will be published elsewhere.

6. Conclusions

The temperature dependence of hole growth kinetics in aluminum phthalocyanine tetrasulphonate in hyperquenched glassy water was studied in the temperature range ($T = 5 - 20$ K). As expected, changes in the relative intensity of the zero phonon line vs. phonon sideband cause significant slowing in kinetics. If the phonon sideband is considered, an additional slowdown becomes evident, which is attributable to the onset of the thermal hole-filling processes. Filling processes inhibit faster tunneling sites from taking part in burning a persistent hole, leading to the slowdown of overall hole growth. The growth of a persistent

hole slows further because of the reduced burn photon flux at the expense of those TLS_{ext} , which hole burn transiently i.e., which were rapidly thermally filled. Thermal filling processes, which begin at ~ 10 K in APT in hyperquenched water glass, lead to the breakdown of the two-level system model for non-photochemical hole burning at $T \sim 15$ K. The utilization of the multiple-level model becomes necessary if holes are burned at $T \sim 15$ K. Additional potential energy wells give rise to additional distribution(s) of hole burn rates. Due to competing filling and burning processes as well as multiple rate distributions, hole parameters such as hole depth cease to depend on burn fluence, depending instead on burn intensity and time in a more complicated manner.

Acknowledgements

Authors dedicate this paper to their good friend, colleague, and teacher, Professor Gerry Small who passed away on August 7, 2004. This research was supported by the Solid State Chemistry and Polymers Program of NSF under Grant No. DMR-9908714.

References

1. A. A. Gorokhovskii, R. Kaarli, and L. A. Rebane, *JETP Lett.*, **20**, 216 (1974).
2. B. M. Kharlamov, R. I. Personov, and L. A. Bykovskaya, *Opt. Commun.* **12**, 191 (1974).
3. J. M. Hayes and G. J. Small, *Chem. Phys.* **27**, 151 (1978).
4. P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.* **25**, 1 (1972).
5. W. A. Phillips, *J. Low Temp. Phys.* **7**, 351 (1972).
6. Kenney, M. J.; Jankowiak, and R.; Small, G. J. *Chem Phys.* **146**, 47 (1990).

7. L. Shu and G. J. Small, *Chem. Phys.* **141**, 447 (1990).
8. R. Jankowiak, R. Richert and H. Bässler, *J. Phys. Chem.* **89**, 4569 (1985).
9. W. Köhler, W. Breinl and J. Friedrich, *J. Phys. Chem.* **89**, 2473 (1985).
10. A. Elschner and H. Bässler, *Chem. Phys.* **123**, 305 (1988)
11. W. Köhler and J. Friedrich, *Chem. Phys. Lett.* **134**, 200 (1987).
12. T. Reinot, and G. J. Small, *J. Chem. Phys.* **113**, 10207 (2000).
13. T. Reinot, N. C. Dang, and G. J. Small, *J. Chem. Phys.* **119**, 10404 (2003).
14. T. Reinot, and G. J. Small, *J. Chem. Phys.* **114**, 9105 (2001).
15. T. Reinot, J. M. Hayes, and G. J. Small, *J. Chem. Phys.* **106**, 457 (1997).
16. T. Reinot, J. M. Hayes, G. J. Small, and M. C. Zerner, *Chem. Phys. Lett.* **299**, 410 (1999).
17. J. Jäckle, L. Piche, W. Arnold, and S. Hunklinger, *J. Non-Cryst. Sol.* **20**, 365 (1976).

R. Jankowiak, J. M. Hayes, and G. J. Small, *Topics in Current Physics, Persistent Spectral Hole Burning: Science and Applications*, W. E. Moener, ed., Springer, Berlin, 1987, p. 153
18. Jankowiak, R., Hayes, J. M. and Small, G. J., *Chem. Rev.* **93**, 1471 (1993).
19. R. Silbey and K. Kassner, *J. Lumin.* **36** 283 (1987).
20. W.-H. Kim, T. Reinot, J. M. Hayes, and G. J. Small, *J. Chem. Phys.* **104**, 793 (1996).
21. T. Reinot, J. M. Hayes, and G. J. Small, *J. Chem. Phys.* **110**, 4820 (1999).

CHAPTER 8

CONCLUDING REMARKS

The standard non-photochemical hole burning (NPHB) mechanism, which involves phonon-assisted tunneling in the electronically excited state, was originally proposed to explain the light-induced frequency change of chemically stable molecules in glassy solids at liquid helium temperatures by this research group more than two decades ago. The NPHB mechanism was then further elucidated and the concept of intrinsic to glass configurational relaxation processes as pre-mediating step to the hole burning process was introduced. The latter provided the theoretical basis for NPHB to evolve into a powerful tool probing the dynamics and nature of amorphous media, which aside from 'simple' inorganic glasses may include also 'complex' biological systems such as living cells and cancerous/normal tissues.

Presented in this dissertation are the experimental and theoretical results of hole burning properties of aluminum phthalocyanine tetrasulphonate (APT) in several different matrices: i) hyperquenched glassy water (HGW); ii) cubic ice (I_c); and iii) water confined into poly(2-hydroxyethylmethacrylate) (poly-HEMA). In addition, results of photochemical hole burning (PHB) studies obtained for phthalocyanine tetrasulphonate (PcT) in HGW and free base phthalocyanine (Pc) in ortho-dichlorobenzene (DCB) glass are reported. The goal of this dissertation was to provide further evidence supporting the NPHB mechanism and to provide more insight that leads to a better understanding of the kinetic events (dynamics) in glasses, and various dynamical processes of different fluorescent chromophores in various amorphous solids and the liquid that exist above the glass transition temperature (T_g). The

following issues are addressed in detail: 1) time evolution of hole being burned under different conditions and in different hole burning systems; 2) temperature dependent hole profile; and 3) the structure/dynamics of water in confined space, which has been studied, in part because of the importance of non-freezable water in biological systems. The main results of this work are:

- 1) Hole burning properties of two very similar molecules, i.e. APT and PcT in HGW and in cubic ice were explored. The NPHB in APT in cubic ice was found to be several orders of magnitude less efficient than in HGW while PHB in PcT in cubic ice was as efficient as in HGW. This is consistent with the prediction of NPHB mechanism that hole burning should cease upon formation of a crystalline phase while PHB should not.
- 2) Hole growth kinetics (HGK) in APT and PcT in HGW revealed similar dispersive kinetics, contrary to the common sense prediction that HGK should be significantly less dispersive in PHB system. Highly dispersed kinetics was attributed to structural disorder of water, which due to strong hydrogen bonding of water molecules to the inner shell of PcT results in distribution of barrier heights.
- 3) HGK was studied in Pc embedded in DCB glass, which has significantly reduced hydrogen bonding network. As expected, the dispersion of HGK was found to be significantly reduced, due to relatively weaker Cl...H bonding between host matrix and inner shell of Pc.
- 4) A new hole burning model for hole burned spectra and kinetics was developed. The model takes into account photoproduct and explains observed photo-memory effects; the model was successfully applied to PHB system - Pc in DCB.

- 5) The 'standard' HGK model containing all three distributions - the λ -, α - and ω -distributions – was used to study fluence broadening in matrices characterized by a different degree of structural disorder (i.e. dispersive vs. non-dispersive system). It has been established that the fluence broadening of the ZPH at the early stage of hole burning is considerably stronger than that in non-dispersive system. In a dispersive hole burning system, a subset of sites burns significantly faster than the average burn rate, while center value of the burning rates determines the rate constant in non-dispersive system. Therefore, at early stage of hole burning fluence broadening is more important for a dispersive system than the equivalent non-dispersive system. For example, in the narrow laser linewidth limit and for a fractional hole depth of 0.10, the contribution from fluence broadening to the ZPH width can be expected to be at least 30% while for a non-dispersive system the value is about 10%. Thus, it was established that for a typical uncertainty in a holewidth measurement of $\pm 10\%$, fractional hole depths less than 0.1 are required to eliminate the contribution from fluence broadening dispersive systems while the required fractional hole depths for the non-dispersive case are up to 0.3.
- 6) HGK, electron phonon coupling, and pure dephasing were studied in APT in water confined into poly-HEMA. It was shown that confined water exists in two forms, freezable (free water with properties similar to those of unconfined bulk water) and non-freezable (water in contact with the polymer inner surfaces via hydrogen bonding). HGK of APT in poly-HEMA confinement was found to be more similar to that of annealed HGW. However, the confinement prevents significant decrease of

TLS_{int}. The mechanism of hole burning was found to involve proton tunneling, as hole growth slowed remarkably upon deuteration.

- 7) The 'standard' HGK was used to study kinetics in APT in HGW in the temperature range of 5 to 20 K. It was found as expected that, kinetics slows down significantly due to the temperature dependence of the induced absorption rate. At ~ 10 K, an additional slowdown of hole growth rate was observed and it was assigned to the onset of thermal hole filling (THF) processes. The modified HGK (taking THF into account) provide excellent fits to the experimental HGK data. However, we have proposed that THF processes may eventually lead to the breakdown of the two level system model of NPHB at temperature near 15 K, a temperature onset where multiple level model (that also includes photoproduct) must be taken into account.

Finally, the Appendix addresses the nature of water above its glass transition temperature (T_g) using polarization-resolved single molecule spectroscopy (SMS). A single Rhodamine 700 (Rh700) molecule was also studied in supercooled liquid ethanol matrix. It was found that single Rh700 molecule starts to rotate only ~ 2 K above T_g of ethanol. In contrast, no rotation of Rh700 was observed in the water in the temperature range from 110 to 170 K. This result provides strong evidence that the nature of water above $T = 136$ K (i.e. a widely stated value for T_g of hyperquenched water and vapor deposited glassy water) is not a fragile liquid. Although our evidence is highly suggestive it is still not clear whether water above 136 K constitutes a glass or "ultraviscous" strong liquid; therefore, a set of additional experiments has been proposed. In addition, it has been proposed that future studies of rotational motion of single molecules (e.g. Rh700 molecule) in supercooled liquid matrices

(e.g. ethanol) could provide better insight into the nature of heterogeneous dynamics of supercooled liquids.

APPENDIX

DYNAMICAL PROPERTIES OF GLASSY WATER AND ETHANOL STUDIED WITH POLARIZATION-RESOLVED SINGLE MOLECULE SPECTROSCOPY

(Preliminary results)

1. Introduction

Water is a simple, stable molecule - two hydrogen atoms strongly bonded to an oxygen atom. Liquid water is the foundation of our life and has been under intense study for over a hundred years. Water exists in a wide range of solid forms – some crystalline, some amorphous. It is believed that the most common state of water in the universe is in amorphous solid form, as a film on dust particles and on comets [1]. A detailed review of the known experimental facts and theoretical and computational studies of the thermodynamic and transport properties of supercooled and glassy water are given in Refs. 1 and 2. However, the subject of the glass transition temperature (T_g) of water, as well as the nature of water above and below T_g is still a matter of current debate (see Chapter 1). Consensus has been reached that at atmospheric pressure and below 136 K water exists as a glass, at ~ 155 K a transition to cubic ice takes place, and that it is one of the most fragile liquids around 273 K. Three glass transition scenarios are possible for water at normal pressures in the temperature range 130-170 K. First, water's T_g is 165 K i.e. water is in the glassy state below 155 K (above 155 K water is in the crystalline form); in this case the real glass transition of water cannot be observed. Second, water's T_g is 136 K i.e. water is in glassy state below 136 K and a fragile liquid above T_g up to the crystallization temperature, T_c . A third possibility

is that water is a strong liquid above its T_g , 136 K. The last two possibilities raise a number of interesting questions about the nature of water between 155 K and 273 K.

Unlike water, ethanol is known to be a glass forming fragile liquid [3] that has three phase-transitions from the supercooled liquid below melting point ($T_m = 159$ K) to glassy state below 95 K [4]. Below 159 K ethanol exists as a supercooled liquid, a plastic crystal, and as an orientational or ordinary glass. An orientational glass is structurally similar to an orientationally-disordered mixed crystal and *shows* a glass transition like structurally disordered glass. A plastic crystal has translational symmetry but gives molecules rotational freedom. Below 95 K, ethanol is either orientational or ordinary glass; the form depends on cooling rate below its T_m . Cooling rates faster than 20 K/min and cooling from above 159 K to below 95 K are required to obtain the ordinary glass while cooling from plastic crystal phase to below 95 K at the same rate provides orientational glass. When ordinary glass is heated, a phase transition occurs at 95 K (the glass transition temperature) – the orientational or ordinary glass enters into a supercooled liquid state. At further heating the supercooled liquid enters into plastic crystal phase at 105 – 110 K. The next transition occurs at 125 K into another supercooled liquid.

Polarization-resolved spectroscopy has the capability to reveal the molecular rotation of water and ethanol glasses. For example an anisotropy can be created by photobleaching a subensemble of guest molecules with prevalently one polarization. Further, the anisotropy decay due to molecular rotation can be studied as a function of temperature. Specifically, a hyperquenching cooling technique can be used to provide structurally disordered glasses consisting of a large number of droplets. Unfortunately, many droplets seem to efficiently depolarize the exciting laser light and/or emitted fluorescence; therefore, attempts to create

anisotropy in bulk hyperquenched ethanol and water have been unsuccessful so far with this method.

However, polarization-resolved single fluorescent molecule spectroscopy (SMS) and/or the anisotropy loss study in a single glassy droplet have potential to reveal the rotational motion in ethanol and water and to overcome the inherent problems with bulk polarization measurements. Polarization-resolved SMS experiments were planned as follows to investigate this potential application of SMS. In these experiments, linearly polarized laser light excites a single molecule (with large transition dipole moment) embedded in glassy matrix, and the fluorescence from the single molecule is collected at constant temperature and as a function of time. At the same time laser polarization is intermittently toggled between two angles at 90 degrees difference by using an electrical polarization rotator; consequently, a pair of orthogonal signals are obtained. Depending on the molecule's orientation, the contrast between two signals thus obtained can range from zero to one. If the molecule starts to rotate, at least one signal will change, but most often anti-correlated changes in fluorescence intensities are expected to occur. In Ref. 5 the rotation of Rhodamine 6G single molecule in ortho-terphenyl (a fragile glass former) was observed at 2-3 K above T_g of o-terphenyl. At temperatures close to T_g , the guest molecule's rotation can be often characterized as a sequence of flips between two different 'allowed' orientations. If more than one but only a few molecules are present in a glassy droplet, then it is possible to find a droplet where the majority of molecules are oriented similarly. The anisotropy decay can then be studied similarly (as described above), toggling the laser polarization in time at different temperatures.

Because ethanol is a fragile glass-former (as is o-terphenyl), a similar onset of rotational motion for a guest molecule in timescale of many seconds is expected in the range of 97 to 100 K. At higher temperatures the rotation is expected to speed up into sub-second timescales – too fast for the detection method. Also, three different phases above the glassy state may provide three temperature ranges with different guest molecule rotational dynamics.

For water, if rotational motion is observed in water below 155 K, then glass transition occurs at 136 K. If the onset of rotation is fairly close to T_g then water is a fragile liquid as well. If water is glass until 155 K no rotation should be observed. However, rotation may not be observed below 155 K if water is very a strong liquid above 136K. In case rotation is not observed in water, then the rotation onset should be measured in known strong glass-former, a supercooled liquid in large temperature range above its T_g chosen to be close to 140K.

Below, a detailed description of our SMS experimental apparatus followed by preliminary experimental results of rotational properties of single Rhodamine 700 molecule in hyperquenched glassy water (HGW) and hyperquenched glassy ethanol (HGE) are presented.

2. Experimental

Rhodamine 700 (Rh700) was purchased from Exciton Inc, and used as received. The molecule was selected because of its planar elongated shape, good solubility in water and ethanol, high fluorescence quantum yield and durability (Rh700 is a very efficient laser dye), and absorption maximum at 648 nm. Nanopure water ($R \approx 18 \text{ M}\Omega \text{ cm}^{-1}$) was locally

purified. A solution of Rh700 in water with concentration of 10^{-4} M was made by extensive mixing, the solution was then further diluted to a concentration of 10^{-9} M followed by filtering. A similar dilution method was used for a 10^{-9} M solution of Rh700 in absolute ethanol. The size of hyperquenched water and ethanol droplets were estimated to be $\sim 2 - 4$ μm , thus the concentration of 10^{-9} M provides a few dye molecules per droplet. The room temperature absorption spectra of Rh700 in water and ethanol were recorded before and after filtering to ensure that no aggregation occurred.

The optical setup (see Fig.1) was based on the confocal microscope configuration; the fluorescence excitation detection arrangement was used. The excitation source was a Coherent 699-29 dye laser (Exciton DCM Special dye; 610-710 nm) with a line width of ~ 0.1 cm^{-1} (without intra-cavity assembly) pumped by a 6W Ar-ion laser. A short-pass filter (Omega Optical; 3rd Millennium SP700) was placed just before the laser power stabilizer (Brockton Electro-Optics Corp, LPC) in order to suppress broadband fluorescence of the laser dye. The intensity of the laser beam was stabilized by a laser power stabilizer and attenuated using neutral density filters; typically, ~ 5 W cm^{-2} of laser intensity was used to excite the selected molecules. The laser beam was delivered using a polarization maintaining single mode fiber, the tip of which formed the first pinhole. The laser beam was further collimated by $f = 100$ mm biconvex lens and passed through electrically controlled polarization rotator made from two nematic-effect variable retarders (Meadowlark Optics). The collimated beam was reflected from the dichroic beamsplitter (Omega Optical, DRLP 680) and then from a computer controlled scanning mirror. The latter allowed positioning (raster-scanning) of the illuminated spot on the sample; the estimated field of view on the

Figure 1. Optical setup of confocal microscope for SMS. M - mirror, NDF - neutral density filters, APD - avalanche photo diode, CCD - charged coupled device camera.

sample was 0.1 x 0.1 mm. Lastly, the beam was further focused to a $\sim 1\ \mu\text{m}$ diameter spot in the sample plane by using a Newport 60x 0.85 NA objective (0.3 mm working distance), which was mounted on a cold finger inside a vacuum chamber.

Emission of the selected molecule was collected by the same microscope objective and was passed through the dichroic beamsplitter. Residual laser light was then filtered out by a long-pass filter (Omega Optical, AELP 680) and focused on a detector with identical biconvex lens ($f = 100\ \text{mm}$). The identity of two collimating lens and their equal distance from detectors was crucial for the microscope operation. A flipping mirror allowed to guide the fluorescence into a liquid nitrogen cooled charged couple device (CCD) camera or into an avalanche photodiode (APD, Perkin-Elmer, dark count $< 25\ \text{s}^{-1}$). The CCD camera was used to focus the microscope, the APD was used to collect the fluorescence signal. The total magnification of the microscope was 38 $\times$, thus $1\ \mu\text{m}$ spot on the sample was converted $\sim 40\ \mu\text{m}$ spot on the APD. The small size of APD, $180\ \mu\text{m}$, functioned adequately as the second pinhole, which is required for confocal microscope to spatially reject out-of-focal-plane light, thus reducing unwanted background signals. In addition, a $50\ \mu\text{m}$ pinhole was included before APD to further reduce the background.

In general, a typical experiment was operated in the following manner. First, the light focused on random spot with the help of the CCD camera. The signal of the focused spot was then redirected to the APD and optimized by fine-tuning the focus and aligning the APD to the optimal position. Next, a raster-scan was performed with exciting laser at $\sim 650\ \text{nm}$ and at a temperature below the T_g . The raster-scan provided the pseudo-image (and coordinates) of spots with increased emission on the sample. The scanning mirror was then positioned to one 'hot spot' and its spectrum was recorded in order to identify that if the

signal of that “hot spot” was of the probed molecule. In other word, in doing so we can eliminate artifacts, unwanted high signals, such as spots with elevated background signal. The polarization resolved excitation was then used to find optimal angles and several curves with different laser polarization were recorded simultaneously at various temperatures.

The apparatus used to prepare hyperquenched glassy films is described in detail in [6, 7], was adapted for these SMS experiments. Briefly, hyperquenched glassy films are produced by forcing a liquid of study through a small nozzle (0.1 mm) into the vacuum chamber. The liquid flow conditions – liquid temperature and pressure are chosen to obtain highly turbulent flow, so that liquid forms a large number of micron-sized droplets. These droplets further impinge on the cold copper cryoplate where they are cooled with rates of 10^6 K/s. The only modification to the thermospray apparatus for SMS detection is the design the sample holder which will be discussed in more detail (see below).

The most challenging and difficult task for SMS experiments is to design a working sample holder, with often-contradictory requirements. Namely, the major challenges that we have to deal with are as the following. The sample and the objective need to be mechanically and thermally fixed to each other with sub-micron precision and to the rest of the optical system with better than 20 μm precision. The objective must be 0.3 mm away from sample but sample needs to be made in vacuum by spraying. Thus the objective cannot be cooled since it will break or be covered with the sprayed solvent, rendering the objective opaque. Due to low thermal conductivity of glasses in vacuum, if using glass plate as the sample substrate, the difference in temperature between the sample substrate and the sample holder is large. For obtaining accurate data, the agreement in temperature between the sample and the sample holder must be within 2 K. Thus, glass plate in vacuum will not satisfy that

requirement. Copper and sapphire, which exhibit higher thermal conductivity, give relatively too large background, burying the signal of single molecules.

The modified sample holder for hyperquenched glassy matrix in SMS is shown in Fig. 2. To avoid the problem of breaking the microscope objective at low temperature, the objective frame is kept at 297 K at all times using temperature controller and heater (Lakeshore Cryotronics, M330). The objective holder is connected to the sample holder using a door-like construction with two plastic hinges and is thermally separated from the rest of the holder with a small styro-foam spacer. In this construction, the open position (see Fig. 2) enables sample deposition without the obstructing objective. The sample substrate is a 0.04" thick copper plate, which functions as a leaf spring, with its top portion fixed to the sample holder. The substrate is also covered with thin layer of commercial black spray-paint to suppress back-reflected scattered laser light. The background from painted surface was found to be smaller than from front surface of sapphire or glass plate. The temperature of substrate is measured with calibrated temperature diode and controlled by the Lakeshore Cryotronics, M330. Final temperature calibration uses spectroscopic changes in the actual sample (see below). Before each deposition the old paint was removed and new coat of paint was applied. The painted substrate was checked for unwanted high signals that come from micro-holes formed by air bubbles during painting and/or fluorescent impurities before each deposition by rasterscanning the substrate. Thermal stability was obtained by physically attaching the substrate, the objective, and the focusing device to each other, and by making linear dimensions of all components as small as possible and by using the same material, copper. A permanent magnet and an electromagnet are used to control sample's distance from the objective. During the sample deposition, the objective holder is flipped out away

Figure 2. Sample holder for single molecule spectroscopy in hyperquenched glassy films.

At left, the front view of the sample holder in detection position. At center, the front view of the sample holder in deposition position, the objective holder is flipped away (the 'door' is open). At right, the side view of the sample holder in detection position. Pulling permanent magnet fixed to lower part of leaf-spring/sample holder into the electromagnet focuses the sample.

from the substrate and hidden behind a protective shield. After the deposition the 'door' is closed and objective frame is held against the rest of the sample holder by the attractive forces of the three pairs of permanent magnets.

3. Preliminary Results and Discussions

Rh700 in hyperquenched glassy water (HGW). In the process of approaching the single molecule detection in our SMS experiment, the probe concentration was reduced step by step (from 10^{-6} – 10^{-9} M). In this process, a very good anisotropy signal was obtained when a solution with 10^{-8} M concentration was used (see Fig. 3). In this figure, the fluorescence signals were detected simultaneously with two orthogonal polarized laser lights. It was estimated that the focal point probes $\sim 5 - 50$ molecules at such concentration. There also were several different locations in the same sample showing anisotropy of fluorescence, but to the lesser degree, and also, the angles of orientation were different. Based on the principle of polarization resolved spectroscopy discussed in the introduction that, if one can select out in isotropic bulk HGW an anisotropic sub-ensemble (several probed molecules have the same orientation), rotational motion of the probed molecules can be then studied by observing the anisotropy decay in time and at different temperatures, thus rotational dynamics of the probed Rh700 in HGW can be studied using the above observations. In what follows, the results of such a study is discussed.

As is clearly evident from Fig. 3, there is no loss of anisotropy as the temperature of the sample holder was increased from 110 to 170 K, within 20 minutes, i. e. there is no rotational motion of Rh700. This indicates that HGW structurally remains unchanged in the

Figure 3. Temperature dependence of anisotropic emission from few (~ 20) Rh700 molecules in hyperquenched glassy water. Laser-beam polarization was intermittently rotated between two 90 degrees different angles (20 and 110 degrees from vertical direction); simultaneously two emission signals were detected. The temperature of the sample was increased within 20 minutes from 110 K to 170 K. Laser intensity was $\sim 10 \text{ W/cm}^2$ at 650 nm.

temperature range between $T_g = 136\text{K}$ and $T_c = 155\text{ K}$. Hence, it allows us to make important conclusion that if water's T_g is 136 K, water is not an ultra-viscous fragile liquid above its $T_g = 136\text{ K}$. Instead, water is an ultraviscous strong liquid at the temperature above T_g . On the other hand, if water's T_g is 165 K, the substance remains in glassy state up to crystallization temperature. This finding is in agreement with recent dielectric studies by Minoguchi et al. [8].

Rhodamine 700 in hyperquenched glassy ethanol (HGE). Fig. 4 shows fluorescence excitation spectra of the single Rh700 molecule in HGE. All spectra were scanned from lower energy towards higher energy at 80 K. Spectrum C (the last spectrum recorded) represents the unwanted background, arising due to contamination with unknown impurity molecules. Similar background signal is obtained from all locations on the sample. Spectra A and B are shifted apart for clarity, to visualize their background a smooth thin curve – the ‘fit’ of C is placed under curves A and B. Spectrum A is the first scan of the molecule with vertically polarized laser light. Next, two spectra (labeled B) were simultaneously detected; the laser light polarization being toggled between two, 90 degrees different polarization. In the middle of the recording (when detection is at $\sim 654\text{ nm}$) only the background signal remains. Abrupt loss of absorption is a typical behavior of single molecule and it is well-known in SMS. As the scan C demonstrates, Rh700 molecule has photo-bleached and has lost the absorption at all frequencies.

In Fig. 5, Rh700 fluorescence signal was monitored as a function of time at temperatures close to the T_g of ethanol ($97 \pm 2\text{ K}$). The fluorescence was excited at 654 nm; excitation polarizations were orthogonal. It is estimated that a few Rh700 molecules (3–10) are probed. At the beginning part of detection signals show cross-correlated nature – a

Figure 4. Fluorescence excitation spectra of the same single Rhodamine 700 molecule in ethanol at $T=80\text{K}$, curves are shifted apart for clarity. All spectra were scanned from lower energy towards higher energy. The smooth lines are baselines for single molecule spectra representing 'unwanted' background signal. Spectrum A was scanned first. Two partially overlapping spectra (B) are detected simultaneously with 90 degrees different polarization. A single Rhodamine molecule photobleaches in the middle of detection (at $\sim 654\text{ nm}$). Curve C is detected after curves A and B.

Figure 5. Fluorescence excitation signal kinetics of few (3-10) Rhodamine 700 molecules, detected at 97 ± 2 K. Two simultaneously detected curves are shifted apart for clarity. Molecules were excited with intermittently rotated (by 90 degrees) laser beam; upper curve is excited with horizontal, lower with vertical polarization. The excitation was $\sim 5 \text{ W/cm}^2$ at 654 nm. Symbols mark the signal from two differently oriented rotation events – ‘*’ marks rotation of one Rhodamine 700 molecule in plane perpendicular to the laser beam, ‘o’ marks rotation in horizontal plane (in lab coordinates).

typical sign of reorientation of single-molecule. The equal intensity of jumps marked with ‘*’ points that a single Rh700 molecule rotates almost in the plane perpendicular to the laser beam. Shortly after the horizontal polarization loses signal in a jump-like manner (‘o’), which indicates another molecule is rotating in the horizontal plane, i.e. this particular molecule’s dipole does not have significant vertical projection. The reason for signal loss can be rotation almost perfectly out of the plane or that the molecule is blinking. A blinking is also a well-known single molecule effect and it changes molecule’s absorption frequency in jump-wise manner i.e. it is a molecular analogue to hole burning followed by light induced hole filling.

Temperature dependent dynamics of a single Rh700 molecule in ethanol glass is presented in Fig. 6. The temperature was set to increase and two cross-polarized signals from the same molecule were detected as a function of time (total collection time was 900 s, excitation was at 654 nm, and with $\sim 5 \text{ W/cm}^2$), similarly as is described above. In the upper panel of the Fig. 6, the collected signal pair has a “common” slow component ($\sim 60 \text{ s}$) subtracted and shown separately in the lower panel. The key phase transition temperatures are marked in the lower panel. Quite often the fluorescence signal reflects phase transitions taking place in the sample; either the whole spectrum shifts or the light scattering properties of the sample change resulting in fluorescence intensity changes, this leads to the “common” slow component signal. The fluorescence intensity changes with phase transitions of a sample with known phase transition temperature can be (and were) used to fine-tune the temperature-detector for further calibrating the sample temperature. Similar intensity changes have been also observed in bulk aluminum phthalocyanine tetrasulfonate in ethanol samples deposited on a thick copper substrate (results not shown), in which conditions

Figure 6. Temperature dependence of single Rhodamine 700 molecule dynamics in hyperquenched ethanol (HGE). The single molecule signal was collected at 654 nm, simultaneously increasing the sample temperature from 90 to 145K (increase is non-linear). In the top panel there are two cross-polarized components of single molecule emission; the common slow component depicted in the bottom panel is subtracted from both curves. With vertical lines and labels in the bottom panel are marked temperatures, which correspond to: 1st glass transition at 95 - 97 K, plastic crystal transition at 107-100 K, and 2nd glass transition at ~125 [4] (see text).

temperature readings are significantly more reliable.

The upper panel presents the difference signal from a single molecule. Anti-correlated flipping is evidencing that molecule starts to rotate above $T_{g1} = 97$ K. Flipping frequency rapidly increases which is a proof of decreasing viscosity and increasing rotational freedom. Above ~ 102 K the rotation rate becomes faster than signal detection time (1 s) and the two signals of the fast rotating molecule appear as random oscillations around the same center value. The total Rh700 molecule signal was not lost or significantly reduced in the temperature range 97 to 107 K, which agrees with the observation that the translational relaxation rates are hundreds of times slower than rotational rates above T_g [8]. At approximately 107 K a transition from supercooled liquid into plastic crystal occurs, and it has been argued that in plastic crystal (ethanol) molecule has rotational but no translational freedom [9]. The dynamics of difference signal shows significantly reduced noise, which is interpreted that rotation of single Rh700 molecule stopped, since Rh700 being significantly larger than ethanol molecule is locked in the cage of host crystal. As the ethanol is further heated above the $T_{g2} = 125$ K a second onset of rotation is observed. Note, that the temperature increase in the Fig. 6 was not linear.

4. Conclusions

Polarization-resolved SMS experiments demonstrate that one is able to observe single molecules and their dynamics when embedded into hyperquenched glasses. Single Rh700 molecule rotation starts immediately above glass transition in a fragile glass former - ethanol. Rotation speeds up rapidly as the viscosity of supercooled ethanol decreases. A similar onset of rotation was not observed in hyperquenched glassy water. The latter observation strongly

suggests that that water is not a fragile liquid above $T = 136$ K; water is most likely either a strong liquid or glass in temperature range 136 and 155 K.

Work is currently in progress to detect rotational onset of Rh700 molecule embedded into neohexanol glass, which is a known strong glass-former with $T_g = 143$ K. Such measurements should answer the question: Should one expect rotational motion at $T \sim 150$ K in HGW i.e. a few degrees below ice transition and ~ 15 K above its widely accepted $T_g = 136$ K. If the answer is positive then longer-lasting SMS experiments in HGW are necessary. In addition, when extensive SM studies have provided statistically enough data, the heterogeneous dynamics of supercooled ethanol can be characterized and compared with bulk data using the method described in Chapter 2, section 2.7.

References

1. Angell, C. A., *Chem. Rev.*, 2002, **102**, 2627.
2. Debenedetti, P. G., *J. Phys.: Condens. Matter*, 2003, **15**, R1669.
3. Angell, C. A., *J. Non-Cryst. Solids*, 1991, **131-133**, 13.
4. Talon, C., et. al., *Phys. Rev. B*, 1998, **58**, 745.
5. Deschenes, L. A and Vanden Bout, D. A., *J. Phys. Chem. B*, 2001, 105, 11978.
6. Kim, W.-H.; Reinot, T.; Hayes, J. M. and Small, G. J. *J. Chem. Phys.*, 1995, vol. 99, p.7300.
7. Kim, W.-H., Reinot, T., Hayes, J. M. and Small, G. J. *J. Chem. Phys.*, 1996, vol. 104, p. 793.
8. Minoguchi, A., Richert, R. and Angell, C. A., *Phys. Rev. Lett.*, 2004, **93**, 215703-1.
9. Eguchi, T., Soda, G. and Chihara, H., *Mol. Phys.*, 1980, 40, 861.

ACKNOWLEDGMENTS

I sincerely thank my Research Advisors, Professor Gerald J. Small and Professor Ryszard Jankowiak, who suggested and patiently helped me in the completion of this project. Thanks are also extended to Dr. Tonu Reinot and Dr. John Hayes, with whom I worked closely on all of my projects and for what I have learned from them in the course of scientific discussions during my graduate studies.

Mr. (soon becomes Dr.) Kerry Riley provided considerably helpful discourse and suggestions. I certainly appreciate both his scientific help and my informal discussions with him.

Also, I would like to thank my Co-major Professor Klaus Schmidt-Rohr who helped and suggested me in finalizing this dissertation.

Finally, I would like to acknowledge the support of the Graduate School and the Department of Chemistry at Iowa State University.

The United States Government has assigned the DOE Report number IS-T 2674 to this thesis. Notice: This document has been authored by the Iowa State University of Science and Technology under Contract No. W-7405-ENG-82 with the U.S. Department of Energy. The U. S. Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this document, or allow others to do so, for U. S. Government purposes.