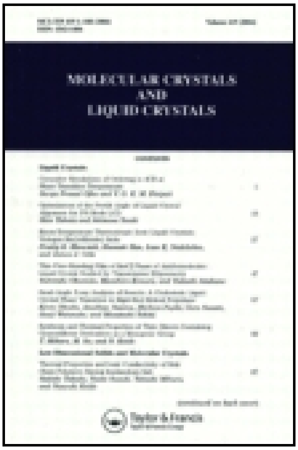

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Pressure Phenomena in Spectral Hole Burning

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PRESSURE PHENOMENA IN SPECTRAL HOLE BURNING

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Abstract We investigate the response of spectral holes to isotropic pressure variations for quite a series of systems: alcohol glasses, long chain molecular aggregates and polymorphic systems. The latter one can be brought into the crystalline as well as into the amorphous phase. From the results, detailed conclusions on the relevant molecular interactions, on the elastic behavior as well as on fundamental features of crystals and glasses can be drawn.

Keywords: hole burning, aggregates, amorphous, crystalline, probe-lattice interaction

INTRODUCTION

One of the most important practical aspect of the hole burning technique is its high sensitivity to external perturbations brought about by electric, magnetic or strain fields[1,2]. The high sensitivity allows the experimentalist to work with perturbations which are orders of magnitude smaller than typical probe-lattice interactions. A measure for the average probe-lattice interaction is the solvent shift. Its fluctuation is reflected in the inhomogeneous widths of the associated spectral bands.

In this paper we focus on external perturbations as induced by isotropic pressure variations[3]. From the behavior of burnt-in holes under pressure variations we will be able to unravel important aspects on the probe-lattice interactions and on the elastic properties of the lattice as reflected in the respective compressibility[4]. We will compare the behavior of organic crystals and glasses[5] and will discuss the specific aspects of long chain molecular aggregates[6].

ASPECTS OF THE EXPERIMENTAL PROCEDURE

As a rule, a hole burning system consists of a host material which is doped with a photoreactive guest molecule in a rather low concentration. The host material can be a glass, a polymer, a crystal or even a protein[7].

If the photoreactive probe is bleached at sufficiently low temperatures, a hole will appear in the inhomogeneously broadened absorption spectrum at the laser frequency. Since its width can be close to the natural width of the transition involved, it can be extremely narrow, e.g. in the MHz to GHz-range. Hence, extremely low pressure levels are required to induce line shifts or broadening phenomena of the order of the original hole width. A typical pressure level is 1 MPa. Because of this sensitivity, pressure experiments can be done at temperatures below the λ-point of ^{4}He, which solidifies above a pressure level of 2.4 MPa.

In samples which are solids at room temperature, the experimental procedure is straightforward: The external pressure is transmitted via He-gas and the response of the burnt-in hole to pressure is measured. Samples which are liquids at room temperature are more difficult to handle[4]. We usually put them into small plastic bags to prevent them from sticking to the walls of the pressure chamber during freezing. This procedure ensures isotropic pressure conditions.

The quantities extracted from the experiment are the pressure induced shift of the hole and the associated broadening. As to the broadening it is assumed that a hole experiences a Gaussian broadening under pressure. This Gaussian kernel is deconvoluted numerically from the measured hole shape.

SOLVENT-SHIFT AND PRESSURE-SHIFT IN GLASSES

The response of spectral holes to pressure was extensively treated by Laird and Skinner[8]. Let us consider a probe molecule in a glassy solvent and let $\nu(R)$ be a differential potential which describes the change of the absorption frequency of the isolated probe molecule due to a solvent molecule at a distance R. Then, if pressure Δp is applied, we have

$$\nu(R, \Delta p) = \nu(R) + \alpha(R)\, \Delta p \tag{1}$$

with $\alpha(R)$ given by

$$\alpha(R) = -\frac{\kappa}{3} R \frac{\delta \nu}{\delta R} \tag{2}$$

with κ being the isothermal compressibility. Here, we have provided that the sample is homogeneous and isotropic. In addition to homogeneity and isotropy it is assumed that the N-particle density correlation can be factorized in a product of two particle correlation functions g(R). Then, the pressure shift s and the pressure broadening Γ of a burnt-in hole can be directly calculated within the Gaussian approximation:

$$s = \left[N \langle\alpha\rangle + \frac{\langle\alpha\nu\rangle}{\langle\nu^2\rangle} (\nu_b - \nu_o) \right] \Delta p, \tag{3}$$

$$\Gamma = \left[N \langle\alpha^2\rangle (1 - \rho^2) \right]^{1/2} \Delta p. \tag{4}$$

Here, N is the number of solvent molecules, ν_b the frequency of the burning laser and ν_o the maximum of the inhomogeneous band. The brackets indicate averaging procedures, for example

$$\langle\alpha\rangle = V^{-1} \int \alpha(R)\, g(R)\, d\vec{R} \tag{5}$$

V is the volume. $V^{-1}g(R)$ is the probability of finding a solvent molecule at a distance R from the probe.

ρ^2 is the square of the degree of correlation between $\alpha(R)$ and $\nu(R)$

$$\rho^2 = \frac{\langle\alpha\nu\rangle^2}{\langle\alpha^2\rangle\langle\nu^2\rangle} \; ; \; 0 \leq \rho^2 \leq 1, \tag{6}$$

and is a measure for the similarity of the solute-solvent interaction pattern with and without pressure.

Note that the shift s (Eq. 3) varies in a linear fashion with burn-frequency whereas the broadening Γ (Eq. 4) is independent of it.

All the averages in Eqs. (3) and (4) depend on the solute-solvent interaction. This interaction may be quite complicated: there are attractive, repulsive, short range and long range terms. The question is which term dominates.

Eq. (3) attains a very simple, yet useful form, if $\nu(R)$ goes like - $1/R^n$. In this case $\alpha(R) = \frac{n}{3}\kappa\,\nu(R)$ and the pressure shift s becomes[9]

$$s = \frac{n}{3}\kappa\,(\nu_b - \nu_{vac})\,\Delta p \qquad (7)$$

with ν_{vac} being the so-called vacuum absorption frequency, i.e. the absorption frequency of the isolated probe. The most reasonable choice for n is 6, which holds for dispersion or higher order electrostatic interactions. We call the special case which leads to Eq. (7) the pressure shift - solvent shift model, because both quantities are proportional[10]. Eq. (7) has two parameters: κ, which characterizes the solvent and ν_{vac} which characterizes the probe. These parameters can be determined by performing the pressure tuning hole burning experiments for various burn-frequencies ν_b within the inhomogeneous band: A plot of $ds/d\Delta p$ vs ν_b yields a straight line whose slope is determined by 2 κ. In addition, there is a well defined frequency, namely ν_{vac}, where s vanishes and changes sign.

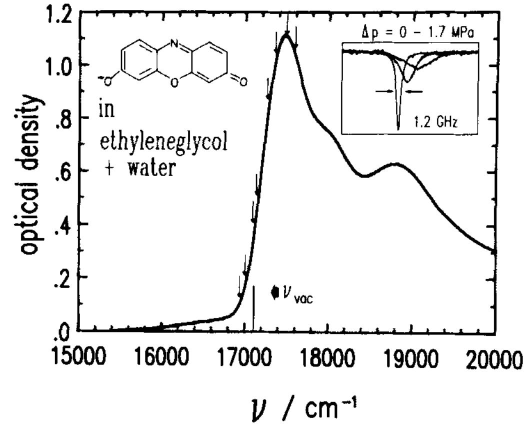

FIGURE 1: Broadband absorption spectrum (4.2 K) of resorufin in ethylenglycol/water glass. Arrows mark the hole burning frequencies.

Hence, the important question is whether $\nu(R) \sim 1/R^6$ really describes the situation correctly, and, if so, why can the other terms be neglected.

Note that there is one obvious problem with a $1/R^6$- potential: Since, in this case, $\alpha \sim \nu$, it follows immediately from the definition of ρ^2

$$\rho^2 = 1$$

and, according to Eq. (4), a $1/R^6$ potential would not lead to a pressure broadening, a conclusion which disagrees with experiments. Hence, Laird and Skinner considered a Lennard-Jones potential to account for a shift as well as for a broadening, as observed in the experiments.

We tested the simple pressure shift - solvent shift model with quite a series of very different dye molecules in organic glasses. Fig. 1 - 3 show as an example resorufin in an ethylenglycol/water-glass. From these figures it is obvious that, on a qualitative level, the model works quite well[5]. Fig. 1 shows the inhomogeneous absorption with the spectral positions (arrows) where hole burning experiments were performed. Fig. 2 shows the shift per pressure as a function of burn-frequency. According to Eq. (7), this quantity should depend in a linear fashion on burn-frequency, which is indeed the case. Around 17100 cm^{-1} the shift vanishes and changes sign, if the burning laser is tuned across this frequency. Within the frame of the simple pressure shift - solvent shift model, this frequency has to be identified with ν_{vac} (Eq. 7). In Fig. 3 (insert) it is demonstrated that a hole burnt right at this frequency does not shift. Yet, there is pressure broadening.

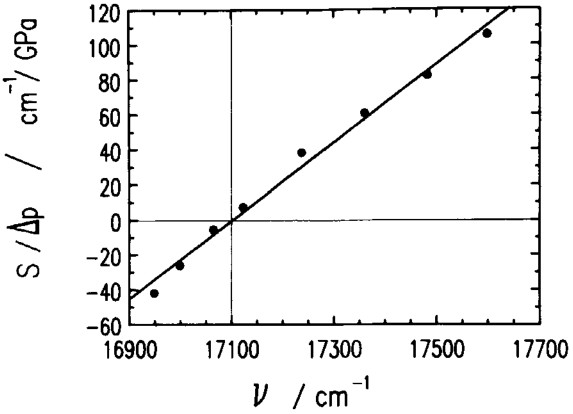

FIGURE 2: Hole shift per pressure as a function of burn-frequency. Sample: resorufin in ethylenglycol/water glass.Temperature 1.5 K.

Although all these features agree very well with Eq. (7), we stress that Eq. (3) shows the same qualitative behavior and, hence, additional experiments are required in order to decide whether Eq. (7) works on a quantitative level, too.

The results of such experiments are shown in Fig. 4. We investigated the influence of pressure variations on spectral holes of a series of rather different dyes in the same solvent, namely ethanol/methanol glass[11]. There are small and large probes, polar ones and charged ones. If the specific probe solvent interaction played a role in the pressure tuning of spectral holes, it would influence the degree of correlation (Eq. 6) and, hence, would show up in the slope of the shift vs burn-frequency (Eq. 3). The data in Fig. 4 convincingly demonstrate that this slope does not depend on the probe but rather seems to be a property of the solvent. This is the case only, when $\nu(R) \sim R^{-n}$. Then, Eq. (3) turns into Eq. (7) and the slope is determined solely by the compressibility κ of the host material.

We stressed above that the only reasonable choice for n is 6. This choice pertains to the dispersion and to higher order electrostatic interactions. The point is that the dispersion interaction always leads to a red shift whereas the electrostatic interaction usually leads to a blue shift. Hence, there may be a situation where both forces compensate. If so, the solvent shift will be zero. According to the pressure shift - solvent shift model (Eq. 7), which is based on the assumption that these two quantities are proportional, the pressure shift will vanish, too. That this is indeed the case is clearly seen in Figs. 2 and 4. For instance, in Fig. 2 a hole burnt at 17100 cm^{-1} does not shift at all under pressure, yet it broadens (Fig. 3). We stress that molecules absorbing at ν_{vac} do, of course, interact with the solvent. However, the interaction is very specific in the sense that it influences the excited state and the groundstate in the same way.

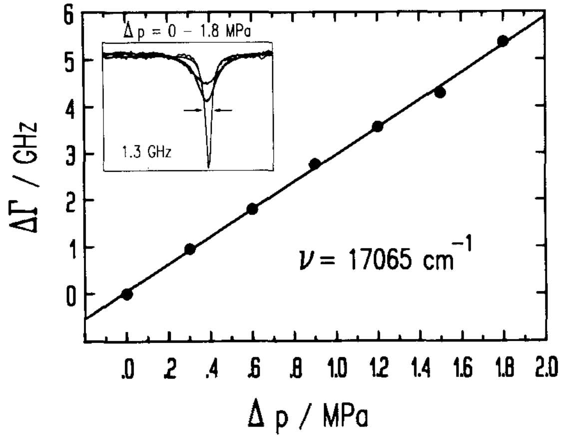

FIGURE 3: Pressure broadening of a hole burnt close to the "vacuum absoprtion frequency" (17100 cm^{-1}). Sample: resorufin in ethylenglycol/water glass. Temperature: 1.5 K. Insert shows the shape of the hole as it deforms under pressure

PRESSURE INDUCED BROADENING IN GLASSES

There is a big problem with a R^{-n} interaction which was pointed out by Laird and Skinner: Since, in this case, $\rho^2 = 1$, the pressure induced broadening of the hole vanishes (Eq. 4). Yet, this is generally not the case. Holes do broaden under pressure and in many cases the scale is of the same order of magnitude as the shift.

How can this observation be reconciled with the simple pressure shift - solvent shift model? There are several ways out of this dilemma, for instance, there can be forces, such as random dipolar forces, which cannot contribute to a shift but can lead to line broadening. However, the most reasonable way to interprete the broadening is by taking into account the angular degrees of freedom ϕ (Ω) of the R^{-6}- type potentials.

$$v(R) = aR^{-6}\ \phi\ (\Omega) \qquad (8)$$

This interpretation can account for the common scale in the broadening and shift via the R-dependent factor which is often observed. (Note that this scaling argument fails in case electrostatic and dispersion forces show strong cancelling tendencies). Second, it can account for the fact that the broadening depends on the size of the probe molecules (Fig. 5): The broadening is largest for the smallest molecule dimethyl-s-tetrazine, and it is smallest for the largest molecule protoporphyrin-IX[11]. This behavior reflects the fact that the number fluctuation of nearby solvent molecules is larger for small probes. This observation excludes dipolar forces. Their interaction is essentially of infinite range and the argument of number fluctuations would be meaningless.

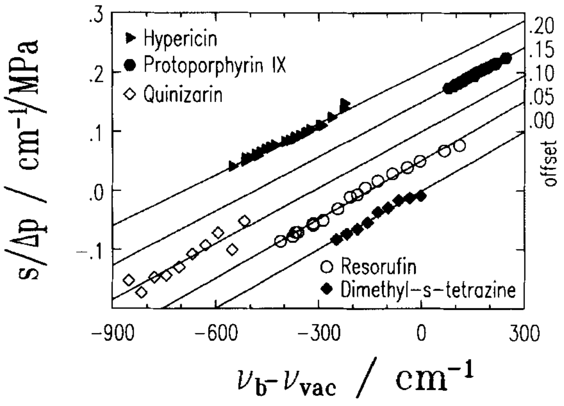

FIGURE 4: Hole shift per pressure as a function of burn-frequency for a series of probe molecules in ethanol/methanol. Temperature: 1.5 K. Probes are shown in Fig. 5

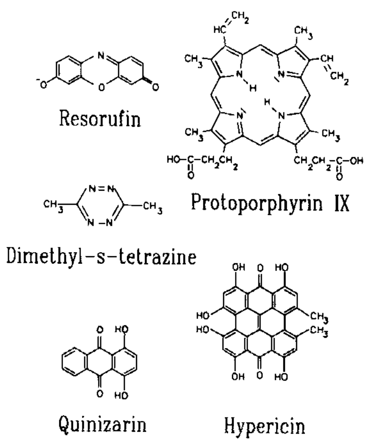

FIGURE 5: Probe molecules used for the experiment shown in Fig. 4

PRESSURE PHENOMENA IN LONG-CHAIN MOLECULAR AGGREGATES

Pressure phenomena in holes burnt into long chain molecular aggregates show novel features[6]: The pressure shift is quite large, 0.2 cm^{-1}/MPa. Yet, the broadening within the experimental accuracy is close to zero. This is demonstrated in Fig. 6 for pseudoisocyanine chlorid aggregates. The broadening of a hole in the aggregate spectrum is compared with a hole in the respective monomer spectrum. Contrary to the aggregate, the hole in the monomer spectrum broadens quite strongly.

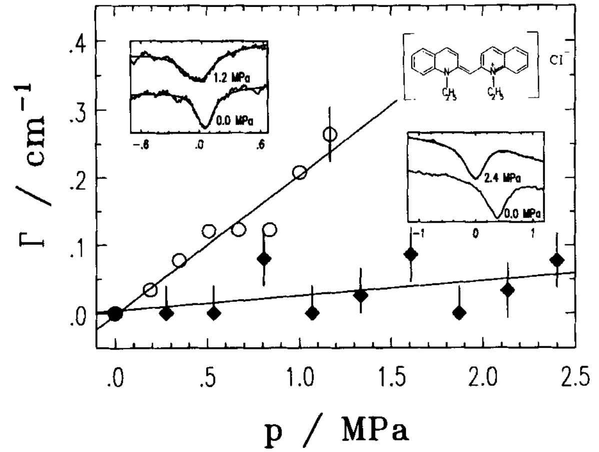

FIGURE 6: Pressure broadening of a spectral hole burnt into monomers and aggregates of pseudoisocyanine chlorid. Solvent: ethylenglycol/water. Temperature: 1.5 K. The frequency scale for the inserts is in wavenumbers.

How can this peculiar behavior be understood? There are to possible views. The first one follows directly from Eq. (4): Pressure broadening vanishes if the degree of correlation approaches 1. Hence, the conclusion is that ρ^2 ~ 1 must hold for the aggregates. This conclusion is obvious, if the size of the aggregates is large as compared to the scale of the structural fluctuations in a glass. Typically this scale is of the order of 10 nm. Within this length scale the fluctuations decay to zero. If the aggregate is much larger, its environment can be considered as being perfectly homogeneous. In other words, two different aggregates see essentially the same environment. Consequently, the degree of correlation $|\rho|$ ~ 1, and there is no broadening.

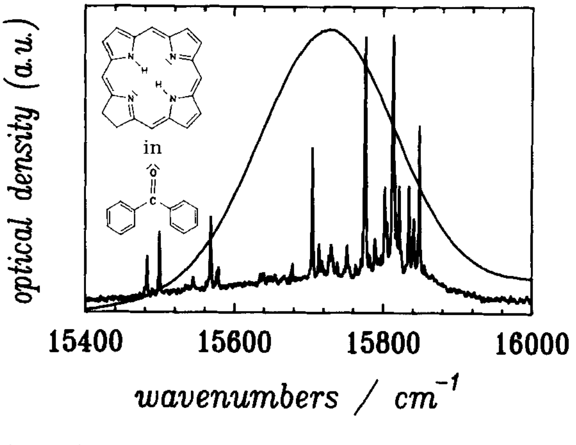

FIGURE 7: Absorption spectrum of chlorin in benzophenone. Broad band: Glassy phase. Narrow bands: Crystal phase. Temperature: 1.5 K.

The second view is also closely related to the size of the aggregate or, more precisely, to the coherence length of the excited state. The monomers in the aggregates are strongly coupled in the excited state, so that the excitation energy is not anymore localized on a specific monomer but extends over N centers. This situation is equivalent to an exciton traveling down the aggregate chain. The traveling exciton reduces all inhomogeneities by roughly a factor of $1/N^{1/2}$ through motional narrowing. Since pressure induced broadening is inhomogeneous in nature, it is strongly reduced in the aggregates as compared to the monomer.

Narrowing phenomena of this type were also observed for other salts of pseudoisocyanine. There is a subtle point to be stressed: Whereas a large coherence length leads to a narrowing of inhomogeneous line broadening, it leads to a broadening of the homogeneous width via the influence of molecular superradiance on the radiative lifetime. Hence, the initial hole width is very large (on the order of 0.5 cm^{-1}), and, as a consequence, the experimental accuracy in measuring the pressure broadening is reduced. The ratio of the respective slopes between monomer and aggregate is about 10. From this, we estimate the number of monomers within the coherence length to about 100.

PRESSURE PHENOMENA IN POLYMORPHIC SYSTEMS: CRYSTALS AND GLASSES WITH HIGH FRAGILITY

Glasses with high fragility show a strong tendency toward polymorphic behavior: They can easily be brought into the glassy as well as into the crystalline state. Hence, they offer the possibility to investigate pressure phenomena on spectral holes in both states for the same system. The higher the fragility of a glass, the larger is the deviation of its viscosity from an Arrhenius-type behavior, and the closer is its behavior to a pronounced Vogel-Fulcher-Tamman law[12]. As a consequence, there is a rather low viscosity regime in the supercooled liquid state, in which the system can order within reasonable time scales. We performed experiments in benzophenone with chlorin as a probe molecule[5]. Fig. 7 shows the absorption spectrum of the glassy and of the crystalline phase. Note that chlorin is a rather bulky dopand which obviously does not fit very well into the benzophenone crystal lattice. As a consequence, the spectrum in the region of the electronic origin consists of a large number of sites whose energies almost span the same spectral region as the inhomogeneously broadened band in the glassy phase.

We performed the same type of experiments as described above, namely burning holes at various frequencies in the electronic origin and measuring their broadening and their frequency shift under pressure. For the crystalline phase, this means that we measured the behavior of holes under pressure in quite a large number of discrete sites.

The results show interesting features characteristic for the two different phases: In the benzophenone glass, broadening is strong and compares well with what we measured in alcohol glasses. In the crystal, although broadening under pressure occurs as well, it is by two orders of magnitude smaller. Generally speaking, such a behavior is expected for a well ordered system. The reason is the perfect N-particle correlation of the molecules building the crystal lattice so that the corresponding density distribution is well represented by a sum of δ-functions. Yet, the fact that the crystal retains its order during pressurizing is not at all trivial for such a heavily distorted system as chlorin in benzophenone. The distortion is obvious from the many sites in the absorption spectrum, as shown in Fig. 7.

The most interesting outcome of the comparative investigation of pressure phenomena in the glass and crystal phase is shown in Fig. 8. Here, the frequency dependence of the shift of the hole per pressure is compared for the two phases.

The broken line represents the behavior of the glass. It perfectly reflects the features of the model outlined above: a linear color effect with a slope given by the compressibility κ. The order of magnitude obtained for κ, namely 0.1 GPa^{-1} fits nicely into the scenario known from organic glasses.

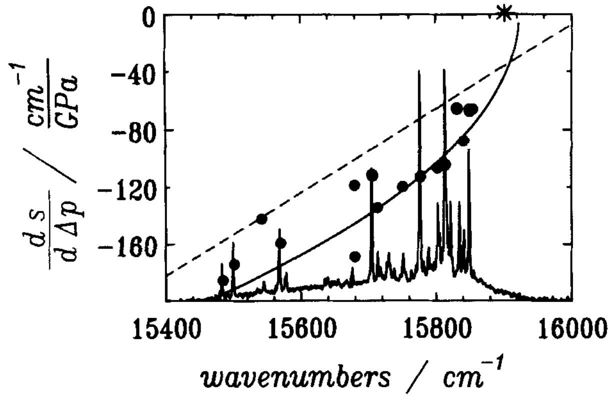

FIGURE 8: Frequency dependence of the pressure shift in the crystal phase as compared to the glass phase (broken line). The fit curve is based on Eq. (10). Sample: chlorin in benzophenone.

The crystal shows quite a different behavior: First, for all sites investigated, the shift per pressure is larger than in the glass. Second, there is a color effect, yet, it shows a nonlinear tendency. Third, contrary to the smooth behavior of the data for the glass, the data for the crystal shows kind of a stochastic scatter around the general trend behavior.

How can this be understood? Suppose we could perform pressure experiments on spectral lines of individual molecules in the glassy phase. What would we expect? We would expect some molecules to respond strongly to pressure because their respective environment is easy to compress, whereas others would respond weakly to pressure because their respective environment is hard to compress. In other words, we would associate with local environments local compressibilities. Since the environments selected vary in a stochastic fashion, the associated compressibilities would vary in a stochastic fashion and consequently the spectral response to pressure would vary in a stochastic fashion.

However, our experiment measures an ensemble of molecules. The important point with glasses is the fact that there is no correlation between absorption frequency and local environment. Consequently, the experiment averages over all environments and all individual features vanish. The characteristic quantity measured is the bulk compressibility.

The situation in the multisite crystal is quite different. Each individual site corresponds with a specific environment as is obvious from the negligible pressure broadening. Hence, contrary to glasses, pressure tuning hole burning spectroscopy in multisite crystals offers the possibility to probe individual environments in addition to the general behavior. As a consequence, the observed scattering in the pressure shift of the individual sites reflects the stochastic variation in the local elastic properties. For some sites, this stochastic variation is quite large, yet as compared to the broadening in the glass, it is by more than a factor of 2 smaller.

The obvious conclusion is that the scattering of the pressure shift in the crystal and the broadening in the glass are of different origin. It gives strong evidence that pressure broadening in glasses is due to the orientational factors in the dispersion and higher order electrostatic interactions, as suggested above, and does not originate from an interplay between attractive and repulsive parts of the Lennard-Jones potential.

How can we understand the non-linear tendency of the color effect in the crystal and how can we reconcile this with the linear behavior in the glass?

For a crystal, the harmonic approximation is usually very good. Hence, we associate with the ground and excited state of the probe molecule two harmonic oscillators which differ in their force constant and in their equilibrium position. They describe the lattice degrees of freedom. In an harmonic potential, the force, and hence the pressure, goes linearly with the displacement. Consequently, the transition frequency ν_p varies with pressure as

$$\nu_p = \nu_o' - \alpha^2 (\Delta p + p_o)^2. \tag{9}$$

ν_o', α and p_o are model parameters. From our results, which show a linear variation of ν_p with Δp, we have to conclude that p_o is much larger than Δp. We interprete p_o as an internal pressure caused by the crystal strains. It is subject to variations in the various sites. If there is neither internal strain nor external pressure, $\nu_p = \nu_o'$. Hence, we can identify ν_o' with the absorption frequency of the isolated probe, which we called above the vacuum absorption frequency. From Eq. (9), we get for the frequency dependence of the pressure shift.

$$\frac{ds}{d\Delta p} = -2\,\alpha \left[\nu_o' - \nu\right]^{1/2} \tag{10}$$

This is the fit curve shown in Fig. 8. Note that it extrapolates to a value ν_o' which is very close to the experimental vacuum frequency (star in Fig. 8) as measured for chlorin in a jet experiment.

What remains to be answered is the question why the theory for the crystal fails to describe the behavior of the glass.

To answer this question, we note that in a glass the correlation among the glassforming molecules is rather low, and is well described by two particle correlations. Within this approximation, the solvent molecules are independent. Consequently, the parameters in Eq. (9) do not characterize the whole system, like in crystals, but rather characterize the individual solvent molecules (as seen from a certain probe molecule). As a consequence there is a distribution of such parameters.

The point is that the glass transition is not a well defined phase transition but is rather characterized by a broad temperature range where the liquid is in a supercooled state. Although relaxation is slow in this transition regime, it still occurs. Hence, the solvent molecules have a chance to adapt the solvent cage to the geometry of the probe molecule, properly. In a crystal this possibility does not exist. Consequently, the internal strains (p_o) are large. In the glassy state, on the other hand, we may consider the first solvent shell molecules as fully relaxed and associate with them a p_o-value close to zero. In this limit, the first shell contributes to the pressure shift only in a quadratic fashion ($\sim\Delta p^2$). Since Δp is very small, we can neglect this contribution in line with the assumption made above that it is the attractive part of the Lennard-Jones potential which plays the dominant role in the pressure shift. The rest of the solvent molecules are shifted away from the minimum of the probe-solvent interaction potential. Within the frame of Eq. (9), this means that they feel a finite p_o-value and, hence, the linear terms dominate. The large strain (and, hence, the large p_o-values) in the crystal may also be responsible for the larger pressure shift in the crystal as compared to the glass (Eq. (9)). There is one point to be stressed: Although the nearest neighbour molecules may not significantly contribute to the pressure shift, they contribute, of course, to the solvent shift. This could be a possible explanation for the observation that the compressibilities fit quantitatively pretty well into the scenario known, the vacuum absorption frequencies and, hence, the average solvent shifts usually fit much worse to values known from supersonic yet experiments.

SUMMARY

Pressure phenomena in hole burning spectroscopy are very specific for the host-guest systems under investigation: crystals, glasses, aggregates. From pressure tuning, bulk as well as local compressibilities can be determined by purely optical techniques. From pressure broadening fundamental aspects of the solute-solvent statistics can be elucidated. In the case of long chain molecular aggregates this aspect can be viewed as a motional narrowing phenomenon. Finally, single site pressure phenomena in fragile crystals reflect the aspects of a single molecule pressure experiment. It also shows the basic differences between the amorphous and the ordered phase. Aspects of a unified view are discussed.

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