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PERSISTENT INFRARED SPECTRAL HOLE BURNING
OF THE SULFUR–HYDROGEN VIBRATIONAL MODE IN HYDROGENATED As$_2$S$_3$ GLASS

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Persistent infrared spectral hole burning is observed for the sulfur–hydrogen vibrational absorption in hydrogen-doped As$_2$S$_3$ glass, the first observation of non-electronic spectral persistence in a glassy host. A dramatic increase in hole width with decreasing burn frequency demonstrates a strong correlation between the inhomogeneous broadening perturbation at a given center and that center's excited state lifetime. Holes are observed to narrow as they spontaneously refill. The non-exponential decay of the integrated hole area over a wide dynamical range and four decades in time is well described by a Gaussian distribution of tunnelling parameters.

Persistent spectral hole burning in the visible has been employed to study the dynamics of amorphous systems, in effect using the impurity center as a microscopic probe of the glassy environment [1]. All persistent spectroscopic effects observed to date in glassy hosts have involved electronic excitation of the defect center, with the hole burning attributed either to photochemical modification of the defect itself, or to rearrangement of the host atoms around the defect. Because of the electronic excitation, however, the observed behavior is not necessarily representative of the glass near its ground state configuration. By using a vibrational excitation in the electronic ground state in the hole burning process, it should be possible to study behavior which is more representative of the pure, unperturbed glass. Since persistent IR spectral hole (PIRSH) burning through defect reorientation has been observed for vibrational modes of some defects in ionic crystals and van der Waals matrices [2] a search was initiated for a similar effect in glasses.

In this paper we report the first observation of PIRSH burning of an impurity vibrational mode in a glassy host, namely the SH stretching mode in hydrogen-doped As$_2$S$_3$ glass, demonstrating that spectral persistence can occur in covalently bonded glasses even when the system remains in the electronic ground state. In addition to its non-electronic na-

ture, this newly discovered PIRSH system displays unique properties which distinguish it from other systems. First, the large asymmetry of the inhomogeneous broadening mechanism for this defect allows the connection between the inhomogeneous broadening perturbation and the excited state lifetime to be studied. Second, the spectral holes become narrower as they spontaneously refill, which, to our knowledge, has not previously been observed for any system. Finally, the convenient timescale on which this refilling occurs permits it to be monitored over a much wider dynamic range than in previous work, leading to a more accurate determination of the functional form of the hole decay, which is found to be well described by a Gaussian distribution of tunnelling parameters.

Samples are prepared by melting As$_2$S$_3$ glass in a sealed quartz tube filled with hydrogen gas at roughly 1 atm. By heating to 500°C for 30 min and quenching in air, a strong infrared absorption band in the sulfur–hydrogen stretch mode region is produced. PIRSH burning experiments are carried out using a tunable semiconductor diode laser (SDL) focused to an intensity typically on the order of 10 mW/cm^2 at the sample, which is enclosed in an optical access cryostat equipped with ZnSe and NaCl windows. A single SDL is used as both pump and probe; a persistent hole is first burned by holding the laser fre-

quency constant for several seconds to several minutes, then probed by sweeping the laser frequency through a region centered on the burn frequency.

Fig. 1 shows the infrared absorption spectra of two samples prepared in the manner described above, one doped with hydrogen, the other with deuterium. The hydrogen-doped sample displays an absorption band peaked at 2485 cm^{-1} with a full width at half maximum (fwhm) of 74 cm^{-1} at 1.5 K. In the deuterated sample the absorption maximum is at 1807 cm^{-1} and the width is 51 cm^{-1}. The isotope shift by a factor of 1.375, approximately the square root of the ratio of the masses, confirms that these absorptions are vibrational in nature. The sharp line at 2323 cm^{-1} appearing in both spectra is due to a defect unrelated to that responsible for the broad bands; the ratio of the strengths of the broad and sharp absorptions varies widely from sample to sample. Also, no analogous isotope-shifted feature appears in the deuterated sample. No PIRSH has been observed for the sharp 2323 cm^{-1} line.

Both the SH and the SD absorption bands exhibit persistent hole burning, and the behavior of the two isotopes is qualitatively similar. Holes have been burned throughout the SH band at temperatures ranging from 1.5 up to 47 K. All holes can be erased by heating above 60 K for a few minutes.

In a typical amorphous hole burning system, spectral diffusion causes the hole width to increase with time after burning has ceased [3,4]. As can be seen in fig. 2, however, in the As$_2$S$_3$:H system the hole
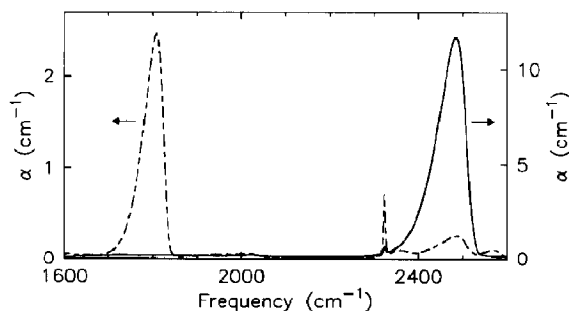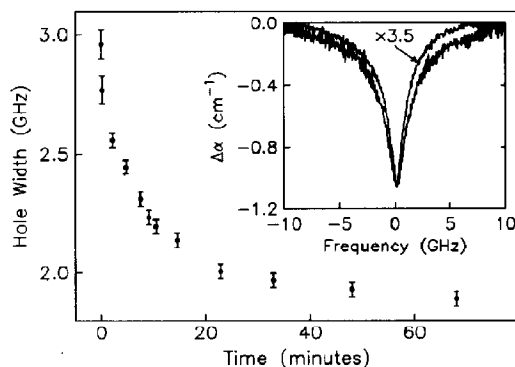

Fig. 2. Time evolution of the 1.5 K hole width (fwhm) after the burning laser is removed for a hole burned at 2504 cm^{-1}. The inset shows the hole 5 s (broader hole) and 48 min (narrower hole) after burning was stopped. Plotted is the change in absorption versus the difference between the probe and burn frequencies. The vertical scale for the narrower hole was expanded by a factor of 3.5 to facilitate comparison of widths.

actually becomes narrower as it refills. The simplest explanation for the hole narrowing behavior is that the excited state lifetimes and dephasing rates, and hence the homogeneous widths, are not the same for all centers absorbing at a given frequency, and that those centers with the largest homogeneous linewidths return most rapidly to the original unburned configuration [1]. The effect is seen only for relatively long burn times (several minutes) or high intensities; the broad, quickly relaxing contribution to the hole takes longer to build up than the slowly relaxing narrow contribution. Since the time evolution of the hole width is the opposite of that expected for spectral diffusion, it seems likely that spectral diffusion does not contribute significantly to the hole width. Hence the measured width in the low intensity, short burn time limit reflects the true homogeneous width, which for Lorentzian lineshapes is half the hole width.

A striking feature of the SH and SD IR absorption bands is their highly asymmetric shape, with a sharp high frequency cutoff and long low frequency tail. This lineshape has been observed to be concentration independent for concentrations ranging over almost three orders of magnitude, thus ruling out interactions between defects as a factor determining

Fig. 1. Infrared absorption spectra of the doped As$_2$S$_3$ glass. The spectra, measured at 1.5 K with 1 cm^{-1} resolution, show the vibrational absorption bands which appear when As$_2$S$_3$ glass is prepared by melting in hydrogen gas (solid line) or in deuterium gas (dashed line).

[1] Ref. [5] presents a model which under certain conditions can lead to hole narrowing through asymmetric hole filling. Asymmetric filling, however, is not evident in the present work.

the lineshape. At the high frequency limit of these bands, the SH and SD stretch frequencies in As_2S_3 are only about 2% lower than published gas phase values for free SH and SD radicals [6–8] (2598.77 and 1885.8 cm^{-1}, respectively). The absorption maxima, however, occur at a shift of about 4% from the gas phase values, and the low frequency tails extend to shifts of several times this amount. Since all observed SH absorption in the glass occurs at frequencies lower than for free molecules, and since there exists a sharp high frequency cutoff, it seems reasonable to interpret the asymmetric shape of the inhomogeneous band as arising from a perturbation which can only act to reduce a center's vibrational frequency. Absorption on the high frequency side of the band would then be due to relatively unperturbed centers, while strongly perturbed centers would give rise to the low frequency tail of the band.

If this picture is correct, then an SH defect's frequency shift downward from the high frequency cutoff is a measure of the host–defect coupling strength for that site. Since both the optical dephasing rate and the excited state lifetime depend on how strongly the defect is coupled to the host, one would expect larger dephasing rates, shorter lifetimes, and hence greater hole widths, the lower the burn frequency. Fig. 3 shows that this is indeed the case, and the effect is quite dramatic. Plotted is the hole width as a function of burn frequency in the short burn time

limit for holes burned at 1.5 K. For burn frequencies above the absorption peak, the hole width is roughly constant, varying from 0.8 GHz at 2525 cm^{-1} to 0.9 GHz at 2497 cm^{-1}. Below this, however, the hole width increases sharply with decreasing burn frequency, growing by an order of magnitude by 2445 cm^{-1} and eventually exceeding the SDL's 0.5 cm^{-1} continuous tuning range.

A clue to the mechanism responsible for this dramatic hole broadening with decreasing burn frequency comes from the dependence of the hole width of the burn temperature. Fig. 4 shows the hole width $\Delta \nu$ as a function of temperature between 1.5 and 47 K at two burn frequencies for which the hole widths at 1.5 K differ by roughly 2.8 GHz. As the burn temperature is increased, this difference between the hole widths for the two frequencies remains constant. The 2503 cm^{-1} data are fit with the function $\Delta \nu (T) = \Delta \nu_0 + bT^{1.97 \pm 0.1}$, with $\Delta \nu_0 = 0.8$ GHz and $b = 3.4 \times 10^{-3}$ $GHz/K^{1.97}$. The 2462 cm^{-1} data are fit with the same function, with $\Delta \nu_0$ increased to 3.6 GHz. The most reasonable interpretation of these results is that the temperature-dependent contribution to the width, which appears independent of frequency, is due to dephasing processes, while the zero temperature width is the excited state lifetime limited width [9], although in glasses a zero temperature dephasing process cannot be ruled out [1]. Thus, since the
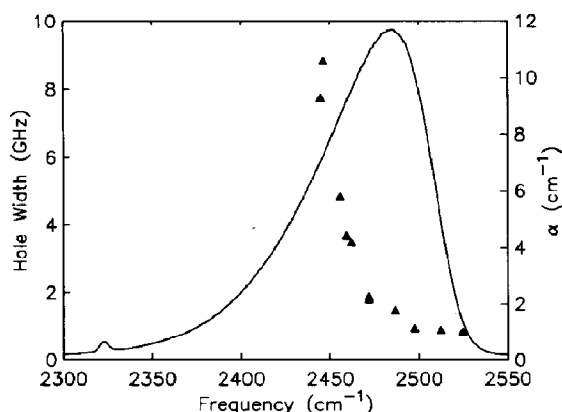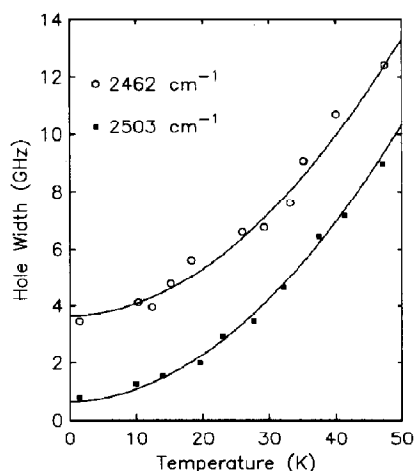

Fig. 3. Hole width (fwhm) in the short burn time, low intensity limit as a function of burn frequency (triangles, refer to left scale). The solid curve shows the unmodified infrared absorption coefficient of the SH band (refer to scale on right).

Fig. 4. Hole width as a function of burn temperature for holes burned at 2503 and at 2462 cm^{-1}. All widths are measured at the burn temperature. Solid lines are fits described in the text.

width at 1.5 K is essentially the low temperature limit, the hole broadening with decreasing frequency shown in fig. 3 is a reflection of a lifetime which is drastically reduced as the coupling to the host is increased. The interesting puzzle here is what decay mechanism gives rise to such short (≈ 20 ps for the broadest holes to ≈ 400 ps for the narrowest) vibrational lifetimes. Multiphonon decay is apparently ruled out for the following reason. The narrowest hole width observed for the SD band is 0.6 GHz, compared to 0.8 GHz for SH. Since multiphonon decay would be an eight-phonon process for SH and a five-phonon process for SD, this mechanism should lead to an SD hole width which is markedly greater than the SH hole width, in contradiction to the experimental result.

In the As_2S_3:H system, spontaneous refilling of holes takes place on an experimentally accessible time scale from a few seconds to several hours, with a substantial fraction of the decay occurring in the first minute after burning ceases. Since the SDL frequency can be swept through the hole at kHz rates, the hole can easily be monitored at these short times. Fig. 5 shows the non-exponential decay of the integrated hole area, proportional to the number of centers N_H remaining in the burned configuration, as a function of time after burning for two consecutive burn/decay experiments carried out at 1.5 K. The data presented here extend from 1 s to 158 min, dur-
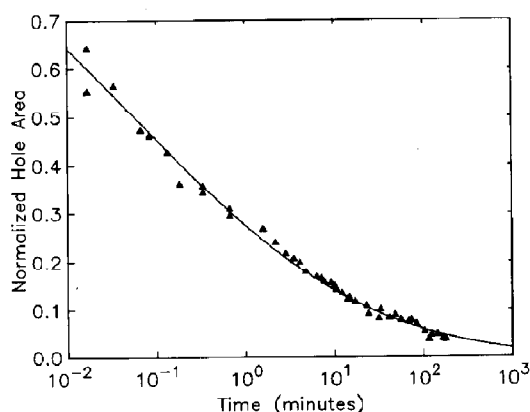

Fig. 5. Integrated hole area as a function of time after the burning laser is removed. The burn frequency is 2504 cm^{-1} and the temperature is 1.5 K. Data points from two consecutive burn/decay sequences are superimposed here. The solid line is a fit to a Gaussian distribution of tunnelling parameters described in the text.

ing which time the hole area decreases by a factor of 15. Although non-exponential spontaneous hole filling has previously been reported for tetracene [3] and quinizarin [10] in methanol/ethanol glass, due to the very long timescale of this decay, the data did not cover a sufficient dynamic range and had too much scatter to distinguish between the various proposed models. Reasonable fits to the quinizarin data, for example, have been obtained both with a form linear in log t derived [9] using the tunnelling rate distribution of Jäckle [11], and with a model which assumes a Gaussian distribution of tunnelling parameters [12]. Similarly, recent hole decay data for rare earth ions and dyes in poly(vinyl alcohol) covered a small dynamic range and could be fit well with either a simple exponential form or with a Gaussian distribution of tunnelling parameters, and less satisfactorily with a logarithmic decay law [5]. The data for the present system, because of its large dynamic range, put more severe restrictions on the functional form used to describe the decay. The decay is clearly not linear in log t, nor is it well described by a power law or an exponential form. The data can be fit very well, however, using a Gaussian distribution of the parameter λ, where the rate at which a given center relaxes from the burned to the unburned configuration is given by $\Gamma = \Gamma_0 \exp(-\lambda)$. Γ_0 is an attempt frequency, assumed to be on the order of a phonon frequency. For a barrier height V, the parameter λ is equal to V/kT if the decay proceeds by thermal hopping of the barrier. If the hole decay proceeds by tunnelling from the burned to unburned configuration, λ is the tunnelling parameter, of the general form $(2mV)^{1/2}d/\hbar$, where m is the mass of the tunnelling entity and d is the width of the barrier. The absence of strong temperature dependence in the observed decay between 1.5 and 8 K indicates that the second mechanism, tunnelling, is responsible for the hole decay at low temperatures. Following Jankowiak et al. [12,13], we assume that Γ_0 is the same for all centers and that λ has a Gaussian distribution about some center value λ_0,

$$g(\Delta\lambda) = (1/\pi^{1/2}\sigma) \exp[-(\Delta\lambda)^2/\sigma^2], \qquad (1)$$

where $\Delta\lambda = \lambda - \lambda_0$ and the distribution is normalized so that the integral over all $\Delta\lambda$ is equal to one. Thus if N_0 is the total number of centers initially in the hole-burned state, the number of centers with

burned to unburned relaxation rates between $\Gamma_0 \exp[-(\lambda_0 + \Delta\lambda)]$ and $\Gamma_0 \exp\{-[\lambda_0 + \Delta\lambda + d(\Delta\lambda)]\}$ is $N_0 g(\Delta\lambda) \, d(\Delta\lambda)$. The number of centers with this relaxation rate remaining after time t is

$$N_0 g(\Delta\lambda) \, d(\Delta\lambda) \exp\{-\Gamma_0 t \exp[-(\lambda_0 + \Delta\lambda)]\}, \quad (2)$$

and thus the total number of hole-burned centers remaining at time t is obtained by integrating over all $\Delta\lambda$:

$$\frac{N_H(t)}{N_0} = \frac{1}{\pi^{1/2}\sigma} \int_{-\infty}^{\infty} \exp[-(\Delta\lambda)^2/\sigma^2]$$

$$\times \exp\{-\Gamma_0 t \exp[-(\lambda_0 + \Delta\lambda)]\} \, d(\Delta\lambda). \quad (3)$$

A fit using this function [*2], with fit parameters $\Gamma_0 \exp(-\lambda_0) = 0.167 \text{ s}^{-1}$ and $\sigma = 6.56$, is shown in fig. 5. Since significant hole decay occurs in the time between the end of burning and the first data point at 1 s, N_0 is unknown, and is an additional fit parameter, used to normalize the data so the fit extrapolates to unity at $t = 0$. Assuming that Γ_0 is on the order of a phonon frequency, roughly 10^{13} s^{-1}, the fit yields a value for the center of the distribution $\lambda_0 = 31.2$, approximately five times the value of σ. Although there is some ambiguity in the choice of N_0, and hence in the value of $\Gamma_0 \exp(-\lambda_0)$, the fact that λ_0 lies in the exponent means this uncertainty does not significantly affect the value obtained for λ_0. For all reasonable fits the ratio of the width to the center value falls in the range $\sigma/\lambda_0 = 0.20 \pm 0.03$ for assumed value of $\Gamma_0 = 10^{13}$.

It should be noted that the decay parameters are not uniquely determined by the burn frequency and temperature; the observed hole decay behavior is also dependent upon the laser intensity used to burn the hole. Holes burned with high intensity display more rapid initial decay than those burned with a lower intensity. In fact, the intensity is the dominant factor determining the characteristic rate $\Gamma_0 \exp(-\lambda_0)$.

This behavior can easily be understood if one examines the rate equation governing the hole burning

process. If one considers an optically thin system with N centers at the burn frequency and a single relaxation rate Γ, then the rate of hole burning is given by

$$dN_H/dt = (N - N_H)\sigma\eta(I/h\nu) - N_H\Gamma, \quad (4)$$

where N_H is the number of centers in the hole-burned configuration, σ the absorption cross section, η the quantum efficiency of the hole burning process, $h\nu$ the photon energy, and I the incident intensity. Hole growth ceases when N_H grows large enough so that $(N - N_H)\sigma\eta I/h\nu = N_H\Gamma$. Clearly, for a given relaxation rate there exists a minimum intensity below which the size of the hole, N_H, will be unmeasurably small at the steady state condition. Thus for a system having a distribution of relaxation rates, hole burning at a particular intensity selects out only those centers which relax slowly enough to make a detectable contribution to the hole. This sort of intensity-dependent relaxation behaviour should occur to some extent for any hole burning system with a broad distribution of relaxation rates.

In conclusion, the observation of PIRSH burning for the SH defect in As_2S_3 shows that vibrational hole burning is not restricted to ionic and van der Waals solids, but can occur in covalently bonded glasses as well. The time dependence of the spontaneous hole relaxation is well described by a Gaussian distribution of tunnelling parameters, but is strongly dependent upon the intensity used to burn the hole. The temperature dependence of the hole width suggests that the low temperature width is dominated by the excited state lifetime. The remarkable increase in the hole width with decreasing burn frequency is thus a consequence of a sharp reduction of the excited state lifetime with increasing host–defect coupling.

[*2] The data are also well described by the ubiquitous stretched exponential form $N(t) \propto \exp[-(t/\tau)^\beta]$, which even over this relatively large dynamic range is almost indistinguishable from the fit to eq. (3). This empirical fit to the data gives a characteristic time $\tau = 2.9$ s, and an exponent $\beta = 0.15$.

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