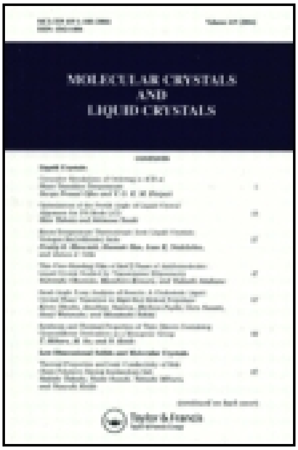

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Persistent IR Spectral Hole Burning of the Vibrational Modes of $H_2O$ in Chalcogenide Glasses

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To cite this article: Gi. Schneider , B. Uebbing & A. J. Sievers (1996): Persistent IR Spectral Hole Burning of the Vibrational Modes of $H_2O$ in Chalcogenide Glasses, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 291:1, 235-240

To link to this article: http://dx.doi.org/10.1080/10587259608042752

*Mol. Cryst. Liq. Cryst.*, 1996, Vol. 291, pp. 235–240
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# PERSISTENT IR SPECTRAL HOLE BURNING OF THE VIBRATIONAL MODES OF $H_2O$ IN CHALCOGENIDE GLASSES

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**Abstract** The nonradiative relaxation behavior of water molecules across the Ge-As-Se glass series has been studied by persistent IR spectral hole burning and picosecond IR saturation spectroscopy. The bending and stretching modes of the guest molecule are found to display relaxation times in the range between 100 ps and 400 ps. When the vibrational lifetimes of the $H_2O$ modes are compared for different chemical compositions of these ternary compounds, it is found that these times are not correlated with the chemical environment but instead with the glass network topology as given by the average number of covalent bonds per atom.

## INTRODUCTION

One of the best glass formers in nature is the Ge-As-Se covalent network. This glass series has attracted attention as a way of testing in some detail the topological constraint theory originally proposed by Phillips.[1,2] Using his approach it follows that a mechanical critical point should occur for covalently bonded glasses constrained by bond stretching and bond bending forces and that the mean coordination number $\langle r \rangle$, which is the average number of covalent bonds per atom, could be used to characterize glass forming and elastic properties.[3-6] A key feature of the constraint counting mean field theory applied to Ge-As-Se is that a stiffness threshold occurs at $\langle r \rangle = 2.4$, where the lattice changes from an under constrained network containing a large number of low lying floppy vibrational modes to a rigid over constrained glassy matrix. This threshold has been looked for in a number of physical properties of glasses ranging from inelastic neutron scattering to activation energies for viscosity with some success.[6] In this paper we review our study of the nonradiative relaxation properties of the mechanical vibrations of guest molecules in ternary Ge-As-Se host glasses in the vicinity of the mechanical stiffness threshold region and demonstrate that for $H_2O$ the vibrational lifetime does depend on the topological rather than the chemical environment.

## EXPERIMENTAL RESULTS

The chalcogenide glasses are quite transparent in the IR with a window extending from about 800 $cm^{-1}$ to 12,000 $cm^{-1}$ making them ideal hosts in which to explore the dynamical properties of molecules in their electronic ground states.[7] When such glasses are doped with molecular impurities, especially those containing hydrogen, inhomogeneously broadened vibrational bands appear. Both persistent IR spectral hole burning[8] (PIRSH) and saturation spectroscopy[9] have been employed to compare the two techniques for determining the vibrational lifetime of the S-H stretch mode in vitreous $As_2S_3$. (Low temperature lifetime $\tau$ and hole width $\Gamma$ are related by $\Gamma = 1 / \pi\tau$ in the small hole limit if there is no spectral diffusion.) Since the two techniques yield the same linewidth here, we continue to use both to determine the homogenous linewidth in the glass series.

Experimentally, the mean coordination number for Ge-As-Se alloys, which is given by $\langle r \rangle = 4X_{Ge} + 3X_{As} + 2X_{Se}$ (where X is in mole fraction), can be varied from $\langle r \rangle =$ 2.0 up to values of $\langle r \rangle = 3.2$. PIRSH measurements of the Se–H stretch vibration in Ge-As-Se glasses have shown that the hole refilling rate decreases dramatically with increasing coordination number, by more than three orders of magnitude,[10] suggesting that topological constraints indeed govern some energy transfer processes in these glasses. Additional measurements of the homogeneous linewidth as a function of mean coordination number appear to indicate a definite minimum near $\langle r \rangle = 2.4$ although more glasses need to be tested.[11]

So far only the results for diatomic stretch modes have been studied in any detail. Triatomic guest molecules provide the opportunity to examine how the mechanical relaxation versus mean coordination number depends on the symmetry of the excited vibrational mode. We now describe our studies of the mechanical relaxation for both the bending and stretching modes of $H_2O$ molecules across the glass series.

A typical low temperature absorption spectrum, here for $Ge_{0.078}As_{0.144}Se_{0.778}$, $\langle r \rangle = 2.3$ at a temperature of T = 1.7 K is shown in Figure 1. The lines with peaks at 1580 $cm^{-1}$, 3515 $cm^{-1}$ and 3612 $cm^{-1}$ are the $H_2O$ bending, symmetrical stretching and asymmetrical stretching modes, respectively. The bending mode frequency is only slightly shifted from the free molecule, $\nu_2$, and the broadening is less than 25 $cm^{-1}$, whereas the stretching modes are shifted by more than 100 $cm^{-1}$ and their linewidth is broadened to over 100 $cm^{-1}$, hence the bending mode is less strongly perturbed by the host glass. The fact that ice particles appear for a sample doped with water molecules follows because for low coordination numbers, the glass temperature is below the

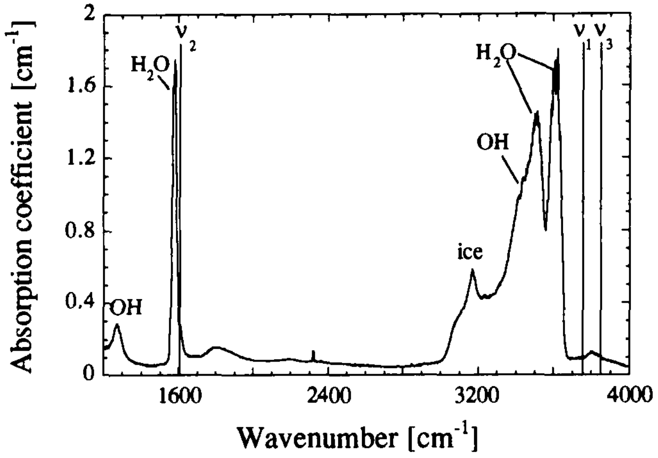

FIGURE 1 Absorption spectrum of $H_2O$ doped $Ge_{0.078}As_{0.144}Se_{0.778}$. The temperature is 1.7 K and <r> = 2.3. The normal mode markers $\nu_1$, $\nu_2$ and $\nu_3$ for free water molecules are also shown.

boiling point of water.[12] The particle signature is the absorption peak centered around 2300 $cm^{-1}$ and increased opacity due to light scattering.[13] This limits the range of the study with $H_2O$ impurities somewhat although the range of coordination numbers still extends from $2.1 < r < 2.8$.

Figure 2 shows the relaxation rate for $H_2O$ in the stretch mode region as measured by

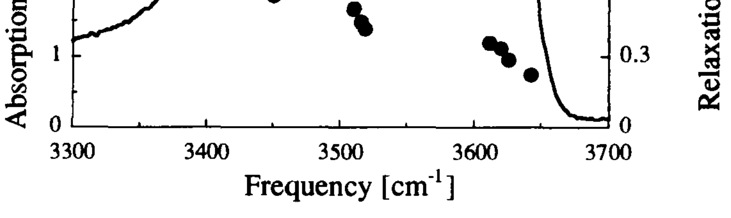

FIGURE 2 Absorption spectrum of $H_2O$ doped $Ge_{0.078}As_{0.144}Se_{0.778}$,(solid line) and relaxation rate as determined by transient saturation spectroscopy (●) at T= 5K. <r> = 2.3. The three branches of the rate are: OH stretching mode (3350 $cm^{-1}$ - 3450 $cm^{-1}$), the symmetric (3450 $cm^{-1}$ - 3525 $cm^{-1}$) and the asymmetric (3600 $cm^{-1}$ - 3650 $cm^{-1}$) stretching modes of $H_2O$.

the ps pump-probe technique.[14] Note that the measurements are as a function of frequency for a representative sample $Ge_{0.078}As_{0.144}Se_{0.778}$, <r> = 2.3. Three distinct branches appear in the measured relaxation rate shown in Figure 2 which identify the detailed relaxation properties of the inhomogeneously broadened vibrational modes both of the OH and $H_2O$ impurities. Note that the larger the red shift of the particular mode frequency, the larger the relaxation rate, and hence the larger is the coupling of that particular mode to the host glass.

Figure 3 depicts the measured frequency dependence of the PIRSH hole width throughout the bending mode frequency interval of $H_2O$. Only a slight increase in linewidth with red shift, about 15 MHz / $cm^{-1}$ is observed here , compared to a value of 50 MHz / $cm^{-1}$ at the center of the higher frequency stretching mode. Samples with <r> $\geq$ 2.4, i.e., above the rigidity percolation threshold have hole widths of about 2 GHz, identical to the relaxation rate of the stretching mode, those with <r> < 2.4 show an increasing hole width with decreasing <r>.

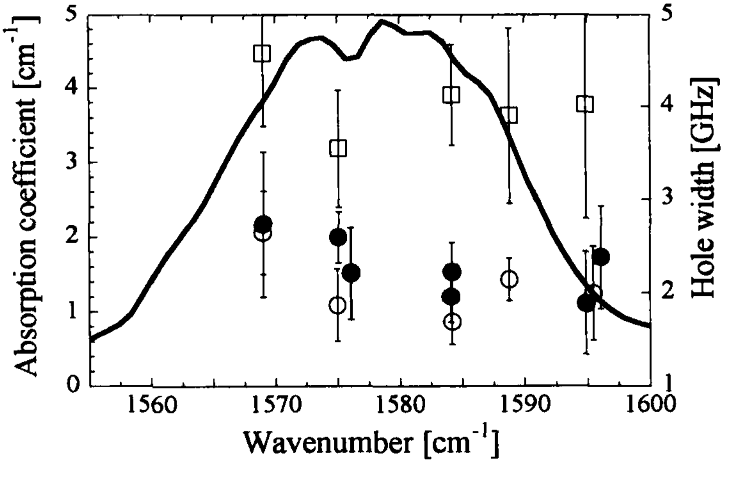

FIGURE 3 Absorption spectrum of the $H_2O$ bending mode (solid line) in $Ge_{0.078}As_{0.144}Se_{0.778}$, <r> = 2.3 and persistent hole width spectrum for different chalcogenide glasses for 30 s burntime at 40 mW/$cm^2$. Symbols: for $Ge_{0.042}As_{0.116}Se_{0.842}$, <r> = 2.2 (□), for $Ge_{0.177}As_{0.146}Se_{0.677}$, <r> = 2.5(●) and for $Ge_{0.233}As_{0.233}Se_{0.534}$, <r> = 2.7 (O).

## DISCUSSION

How do our relaxation results above connect with the constraint theory of covalent networks? To distinguish between topological and chemical contributions to the mechanical relaxation rate of the different modes of $H_2O$ in the glasses, we summarize our measurements in four different ways in Figure 4. The results are presented both for the same coordination number <r> (either open symbols, <r> = 2.4, or solid symbols, <r> = 2.6, ) and different chemical composition as well as for the same Se-, As- and Ge-content but different values of <r>. The hole width (or relaxation rate) of the low frequency bending mode (open and solid diamonds) and the higher frequency symmetric (open and solid circles) and asymmetric (open and solid triangles) stretch are shown versus the molar fraction of the glass constituents and the coordination number. When the diamonds, circles, or triangles are close together on the abscissa, they should also be close together on the ordinate for a particular figure frame to illustrate a good correlation. Clearly the best correlation is found for the frame which displays the relaxation rate of each mode versus coordination number, that is, the data indicate that samples with the same coordination number but different composition show similar relaxation times for each of the different symmetry modes.

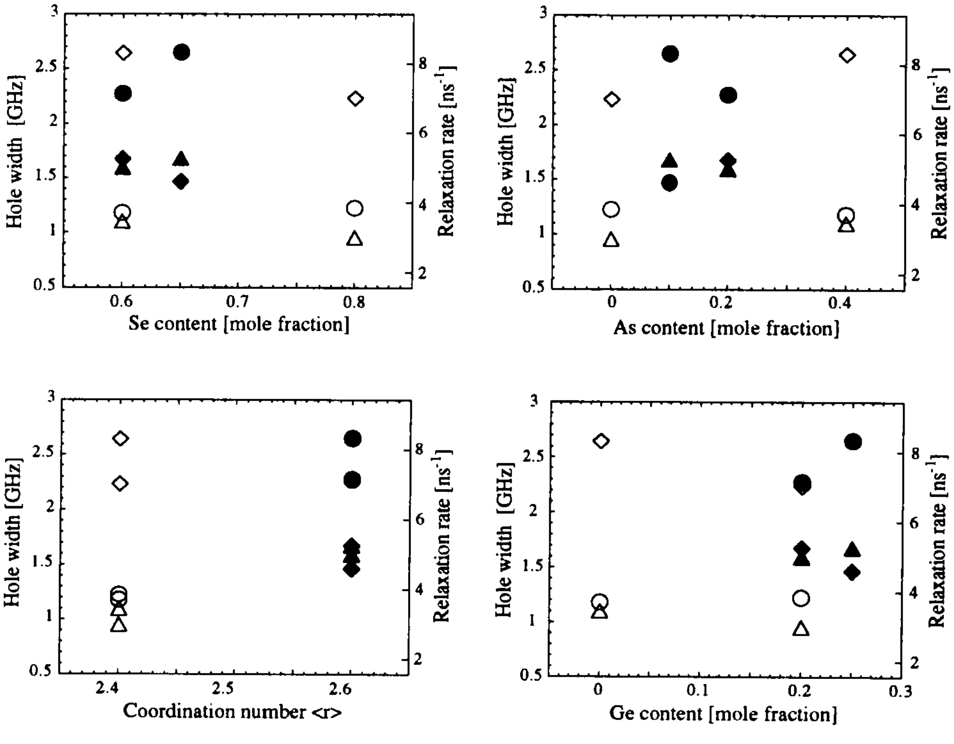

FIGURE 4 Hole width as a function of Se, As, Ge content and of coordination number. Diamonds denote results of hole burning of the bending mode at 1584 cm$^{-1}$ for 30s at 40 mW/cm$^2$. Values from saturation spectroscopy are shown as circles for the symmetric stretch mode at 3515 cm$^{-1}$ and triangles for the asymmetric stretch mode at 3612 cm$^{-1}$; samples with <r> = 2.4 are shown with open symbols, those with <r> = 2.6 have solid symbols.

If there was a correlation with the chemical composition, which influences the vibrational density of states, the same symbols (filled and open) should be grouped together for similar molar content. Remarkably, such a correlation is not observed. Further, it is known experimentally that an increase in the Ge- content of such glasses increases the upper limit of the vibrational density of states[15] and hence, this component would be expected to produce an increased relaxation rate, which is not seen in Figure 4.

Our conclusion from this investigation of the molecular nonradiative relaxation time in the chalcogenide glass series is that the vibrational lifetime of the guest molecule depends not only on the local hydrogen bonding but also on the topological environment in the glassy matrix as parameterized by the mean coordination number.

## ACKNOWLEDGMENT

This work is supported in part by NSF-DMR-931238, ARO-DAAH04-96-1-0029, ONR-NOOO14-94-1-1023 and the MRL central facilities. G. S. and B. U. thank the Alexander von Humboldt Foundation for partial financial support.

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