Anomalous Isotope Effect in the Relaxation of the SD and SH Vibrational Stretch Modes in Amorphous As_2S_3

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The vibrational relaxation rate of the SD stretching mode in amorphous As_2S_3 is found to be comparable to that of the SH molecule in the same material. This result is in marked contrast to the behavior expected for multiphonon decay into vibrational quanta of the amorphous host. The lack of an isotope effect in the relaxation rate is shown to be due to an efficient decay channel into a high frequency local vibrational mode of the impurity molecule. Our results demonstrate that local modes cannot only influence but can dominate the decay of molecular impurities in solids. [S0031-9007(96)00827-7]

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Nonradiative processes dominate the relaxation dynamics of most molecules in crystals and glasses, as well as in liquids [1–3], with the exception of a few systems such as CN^- in alkali halides [4], and the observed relaxation rate can be up to 8 orders of magnitude larger than the radiative rate. Because of the ubiquity of nonradiative relaxation processes, extensive experimental and theoretical efforts have been made to clarify the physical principles governing these processes. The experimental progress achieved in recent years is largely a result of the development of powerful tunable ultrafast lasers, necessary to perform nonlinear experiments on vibrational transitions [5]. The simplest theoretical approach explaining nonradiative relaxation assumes a multiphonon process in which the energy of the impurity vibrational state is transferred to several host vibrational quanta [6,7]. However, it has become evident that a number of results cannot be explained in terms of this simple multiphonon decay process. In particular, the vibrational frequency of hydrides such as OH and SH and their isotopes are typically well above the vibrational spectra of the host, and the large relaxation rates that have been found for these molecules in a variety of systems [1,2,8] may originate in the existence of high frequency local modes of the impurity molecules such as librations, bending, or torsional modes, which act as accepting modes in the relaxation process [9].

Our approach to investigating the nonradiative decay mechanism is to measure the effect of isotopic substitution on the relaxation rate (the isotopic effect) by studying the deuterated analogs of diatomic hydride impurities (deuterides) in the same host. In this Letter we present a detailed study of the vibrational relaxation rate of the SD impurity vibrational stretch mode in As_2S_3 and compare the results with previous measurement of its isotope, the SH molecule in the same host [8]. This system has been chosen because the host material is transparent in the region of both the SD and SH vibrations and the stretch mode frequencies of the molecules lie well above the vibrational spectrum of the host. Since the vibrational frequencies of the deuterated molecules are redshifted by approximately $2^{1/2}$ from the hydride values, the multiphonon decay mechanism for the deuteride should than require the excitation of $2^{1/2}$ fewer host vibrational quanta according to the “energy gap law” [7], which states that impurity vibrational modes should relax primarily by the lowest order, and therefore fastest, process available. Assuming a multiphonon decay mechanism, the deuteride impurity stretch mode should decay in a lower order, and thus faster, process than the hydride stretch mode.

Previous measurements, however, have shown fast relaxation rates on the order of 10^{10} $\sec^{-1}$ for SH [8]. In addition, persistent infrared spectral hole burning experiments have shown similar dephasing times for both the SD and SH molecules [10], thus, there have been indications that this system behaves anomalously, providing incentive for detailed study of the decay mechanism of the molecular relaxation.

The samples were prepared by melting optical grade As_2S_3 in an atmosphere of D_2 in a sealed quartz tube. A furnace with a rocking mechanism was used to melt the sample to ensure a homogeneous distribution of impurity throughout the sample. A deuterium atom forms a covalent bond with a bulk sulfur atom at a broken-bond defect in the bulk to form an SD impurity. After several hours the samples were removed from the oven and rapidly quenched. The finished samples were polished into 6 mm diameter, 2–3 mm thick disks.

The absorption spectra of As_2S_3 were measured using a Bruker IFS66V FTIR Spectrometer. The SD stretch mode in As_2S_3 shows a broad (50 cm^{-1} FWHM) absorption centered at 1807 cm^{-1}, shown as the solid line in Fig. 1(a). Because of amorphous nature of the As_2S_3 host, a distribution of SD molecular impurity sites results in an inhomogeneously broadened stretch mode absorption line [8]

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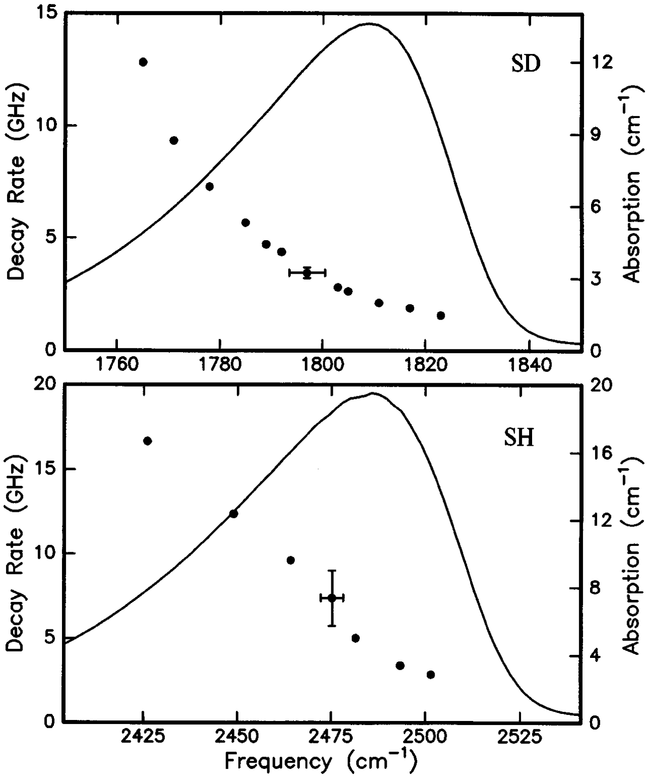

FIG. 1. Absorption spectra (solid lines) and relaxation rates Γ (circles) of the first excited state of the stretch modes of SD (a) and SH (b) (reproduced from Ref. [8]) in As_2S_3 at 80 K. The frequency axis in (b) has been scaled by the ratio of the SD and SH peak frequencies in order to demonstrate the equivalent of the absorption line parameters.

due to differing hydrogen bonding strengths and geometries between the deuterium and the nonbonding electrons of a neighboring sulfur [11].

Shown in Fig. 1(b) is the corresponding absorption line of the SH molecule in As_2S_3. The frequency axis is compressed by the ratio of the center frequencies of the SH and SD absorption line in order to demonstrate the similarity of the absorption lines. This indicates that the two molecules are identical with respect to the coupling to the host, occupation of sites in the amorphous hosts, and the host structure itself. Thus any influence on the relaxation rate by sample-specific parameters can be ruled out, allowing a comparison of the relaxation dynamics based on the different impurity stretch mode frequencies only.

The measurements of the relaxation rate of SD in As_2S_3 were done using a free electron laser (FEL) at the Stanford Picosecond FEL Center [12], using a pump-probe technique wherein a weak pulse, resonant with the transition to the first excited impurity vibrational state, probes the bleaching of the absorption caused by a strong pump pulse of the same frequency. The FEL is tunable over a wide range in the midinfrared, for these experiments, 7 cm^{-1} FWHM micropulses of approximately 150 nJ to the sample. Saturation levels on the order of 1% were typical. In the small-saturation limit, the relation between the probe signal $I(\Delta t)$ and the delay time Δt can be written as $I(\Delta t) \propto \exp(-\Gamma\,\Delta t)$, where Γ is the relaxation rate of the excited state. Note that simultaneous resonant excitation of higher transitions is disallowed by the anharmonicity of the stretch mode. Figure 2 shows a sample pump-probe transmission signal as a function of delay time between the pump and probe pulses, where the solid line represents a single exponential fit to the data.

The relaxation rate of the SD stretch mode as a function of frequency was measured by tuning the FEL across the broad SD stretch mode absorption line. The circles in Fig. 1(a) show the results at 80 K. The relaxation rates exhibit nearly an order of magnitude variation across the absorption line, ranging from 12.5 GHz at 1765 cm^{-1} to 1.6 GHz at 1823 cm^{-1}. The typical errors shown are due to the linewidth of the laser and the error associated with the least-squares exponential fit of the decay. These results exhibit a frequency dependence very similar to that of the SH impurity stretch mode relaxation rates in the same host shown (circles) in Fig. 1(b), reproduced from Ref. [8]. The strong variation of the relaxation rate across the absorption line has been attributed to changes in the hydrogen bond strength [8] which affects the coupling between the stretch mode and the decay products. The similarities in the absorption spectra and the relaxation rate data demonstrate the similarity in the site-specific molecule-host coupling of the two impurities.

Comparing the SD relaxation rates shown in Fig. 1(a) with the SH relaxation rates shown in Fig. 1(b) for a given site, as determined with respect to the shift from the line center, the SD lifetimes are nearly a factor of 2 longer than the corresponding SH lifetimes. This result is incompatible with a multiphonon decay process. Since the SD stretch mode is of lower frequency than the SH stretch mode, it must decay in a lower order, faster

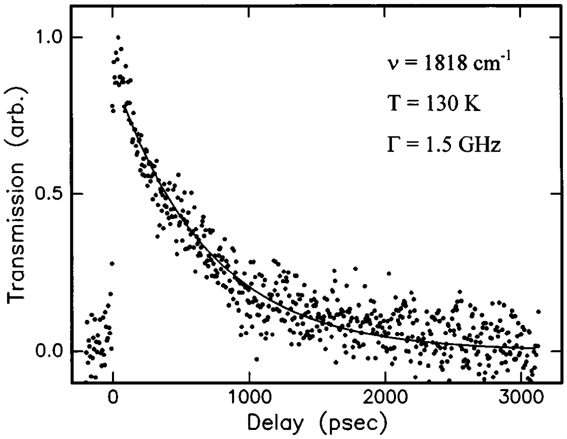

FIG. 2. Typical pump-probe transmission signal as a function of delay between pump and probe pulses.

process if the decay is into host vibrational quanta [6,7], in marked contrast to our observations.

The fact that the relaxation rates of the isotopically shifted SH and SD vibrational stretch modes are very similar can be interpreted as evidence of the existence of decay processes of similar order for both impurities. This implies that the frequency of the decay products must scale with the respective stretch mode frequencies. The SH and SD molecules are covalently bonded to an arsenic atom of the host, thus the As-S-D bending mode is a candidate for a decay product. Its frequency scales with about the same $\mu^{-1/2}$ as the stretch mode, where μ is the effective mass of the oscillator, since the effective mass in both the stretch and the bend modes is close to the mass of the H and D atom, respectively.

To verify the existence of the bending modes we measured the stretching mode sideband spectra, shown in Fig. 3. Weak features in the sideband spectra are due to simultaneous excitation of the stretch mode and another local or host vibrational mode. All absorption peaks identified as sidebands scale linearly with the impurity density and have linewidths larger than those of the fundamental absorption line. The two sidebands at $+165$ and $+350\ \mathrm{cm}^{-1}$ (labeled H_2 and H_1) are associated with the broad host vibrational modes of the As_2S_3 [13] since they are present in the sideband spectra of both impurities. The $+545\ \mathrm{cm}^{-1}$ sideband of SD shown in Fig. 3(a) and the $+738\ \mathrm{cm}^{-1}$ sideband of SH shown in Fig. 3(b) (labeled L_1) scale in frequency as the stretch mode frequencies; thus we identify these modes as the As-S-X (X = H or D) bending mode sidebands of these impurities. The $+190\ \mathrm{cm}^{-1}$ sideband of SD and $+260\ \mathrm{cm}^{-1}$ sideband of SH (labeled L_2) also scale with the stretch mode frequency; in this case we attribute the sideband to As-S-X torsion modes. The absence of an isotope effect in the relaxation rate and the presence of high frequency bending modes demonstrates that the relaxation dynamics of the SD and SH impurity molecules is not governed by a multiphonon process into host quanta, but in fact is dominated by a decay into local modes. To further confirm this result, we investigated the temperature dependence of the relaxation rate, which is determined by the frequencies and number of decay products. Thermal population of the decay products leads to an increased relaxation rate by simulated emission, as modeled by the relation [7]

$$\Gamma(T) = \Gamma_0 \frac{e^{h\nu/kT} - 1}{(e^{h\nu_L/kT} - 1)^L (e^{h\nu_H/kT} - 1)^H}, \qquad (1)$$

where the SD stretch of frequency ν decays in L local mode vibrational quanta of frequency ν_L and H host mode vibrational quanta of frequency ν_H, and $\nu = L\nu_L + H\nu_H$ by energy conservation, $\Gamma(T)$ is the decay rate, and Γ_0 is the low temperature decay rate.

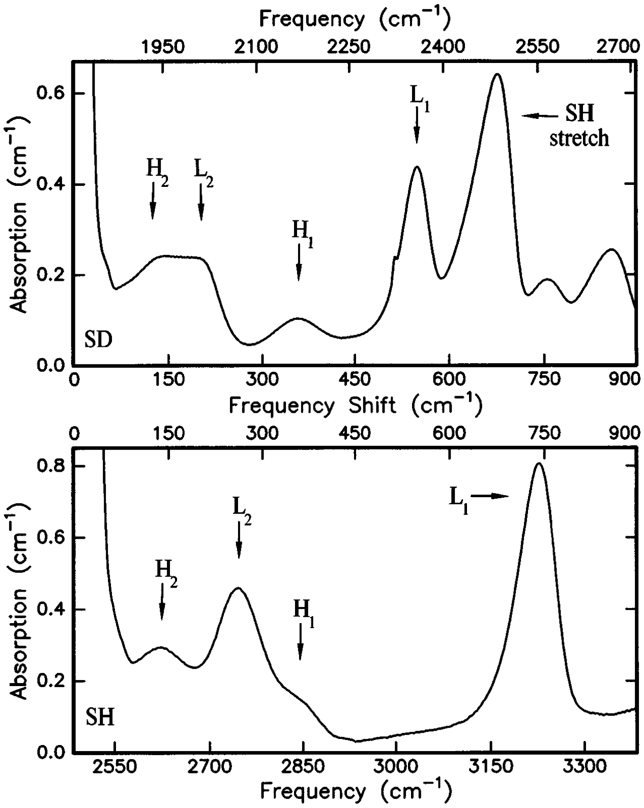

FIG. 3. Magnified sideband region of the stretch mode fundamental absorptions of SD (a) and SH (b). Middle axes indicate frequency shift from stretch mode peak. Peak L_1 is the impurity bending mode sideband, peak L_2 is the impurity torsional mode sideband, and peaks H_1 and H_2 are host mode sidebands.

Temperature dependence measurements of the SD stretch mode relaxation rate were made at 1786 and $1818\ \mathrm{cm}^{-1}$. Figure 4(a) presents the results for the decay rate Γ at $1818\ \mathrm{cm}^{-1}$ (circles). At both frequencies the decay rates show an increase of approximately a factor of 3 between 80 and 375 K. The lowest order process for the decay of the stretch modes into the highest frequency local modes for these systems allows at most the excitation of three bending quanta in each case. The remainder of the energy of the stretch mode is then taken up by host vibrational quanta.

The solid line in Fig. 4(a) shows the temperature dependence of the SD stretch mode relaxation rate at $1818\ \mathrm{cm}^{-1}$ predicted by Eq. (1) for decay into three bending modes quanta and one $183\ \mathrm{cm}^{-1}$ host vibrational. This prediction shows excellent agreement with the experimental data. Other combinations involving fewer bends and more host quanta overestimate the increase in relaxation rate with temperature markedly. Similarly, Fig. 4(b) shows the experimental data for SH reproduced from Ref. [8] (circles) and the predicted temperature dependence for decay into three SH bending quanta plus two $140\ \mathrm{cm}^{-1}$ host quanta (solid line). The agreement between the experimental and the predicted temperature dependencies for both molecules further confirms the dominance of the high frequency local modes in the decay process.

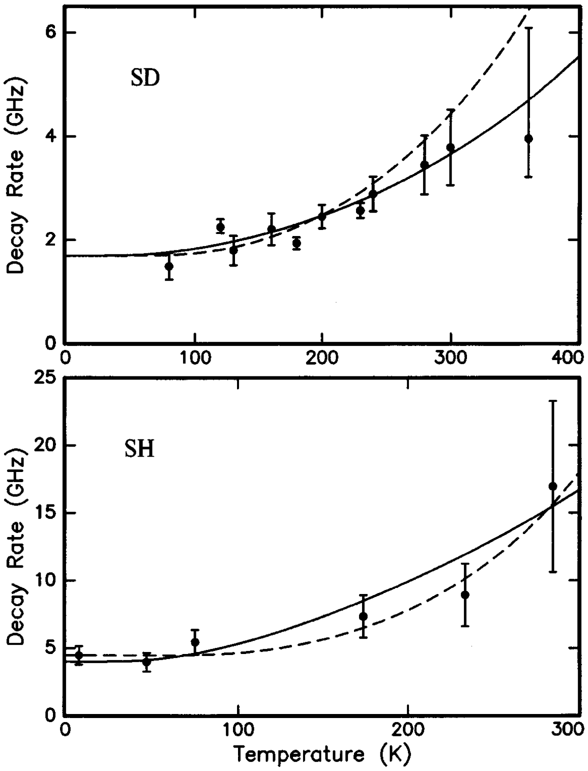

FIG. 4. Temperature dependence of the SD (a) and SH (b) (reproduced from Ref. [8]) stretch mode decay rates Γ (circles) at 1818 and 2494 cm^{-1}, respectively. For the SD molecule (a) the solid line shows the theoretical dependence for the decay into three 545 cm^{-1} bending modes plus one 183 cm^{-1} host quantum. For the SH molecule (b) the solid line represents a decay into three 738 cm^{-1} bending modes and two 140 cm^{-1} host quanta. The dashed lines show the predicted temperature dependence for decay into five and seven 360 cm^{-1} host quanta, respectively.

In a previous paper, the decay of the SH stretch mode in $\mathrm{As}_2\mathrm{S}_3$ has been assigned to a 7th order multiphonon process into the largest $\mathrm{As}_2\mathrm{S}_3$ host vibrational quanta based on measurements of the temperature dependence of the decay rate [8]. The dashed line in Fig. 4(b) was generated using Eq. (1) for decay into seven equal 360 cm^{-1} host quanta. Note that this curve fits the experimental data well, although the lack of the isotope effect in the relaxation rate rules out this process. We point out that the temperature dependences of a relaxation process alone is not sufficient to identify a decay process, although it can be used to confirm it. As an example, the energy gap law and the multiphonon relaxation assumption would imply that the SD stretch mode should decay into five of the same host quanta since the SD stretch mode frequency is reduced by roughly a factor of 5/7 from the SH frequency. The dashed line in Fig. 4(a) shows the temperature dependent decay rate expected for this fifth order process using Eq. (1) for decay into 360 cm^{-1} host quanta which poorly agrees with the data, overestimating the decay rate at high temperature.

In conclusion, the importance of local modes in the decay dynamics of the SH and SD vibrational stretch mode in $\mathrm{As}_2\mathrm{S}_3$ has been demonstrated. Investigating the isotope effect on the relaxation rate, we conclusively rule out a multiphonon decay into host vibrational quanta, but show instead that the relaxation process is dominated by the decay into high frequency bending modes of the molecules. Our results indicate that the relaxation into high frequency local modes must be taken into account when the relaxation of diatomic molecules in crystals, glasses, and on surfaces is studied.

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[1] E. J. Heilweil, Chem. Phys. Lett. **129**, 48 (1986).
[2] E. J. Heilweil, M. P. Casassa, R. R. Cavanaugh, and J. C. Stephenson, Chem. Phys. Lett. **117**, 185 (1985).
[3] D. D. Dlott and M. D. Fayer, IEEE J. Quantum Electron. **27**, 2697 (1991).
[4] F. Lüty, Cryst. Lattice Defects Amorphous Mater. **12**, 343 (1985).
[5] *Ultrafast Phenomena*, edited by G. R. Fleming and A. E. Siegman (Springer, Berlin, 1986), Vol. 5, and references therein.
[6] A. Nitzan, S. Mukamel, and J. Jortner, J. Chem. Phys. **60**, 3929 (1974).
[7] S. A. Egorov and J. L. Skinner, J. Chem. Phys. **103**, 1533 (1995).
[8] U. Happek, J. R. Engholm, and A. J. Sievers, Chem. Phys. Lett. **221**, 279 (1994).
[9] U. Happek, C. E. Mungan, W. von der Osten, and A. J. Sievers, Phys. Rev. Lett. **72**, 3903 (1994).
[10] S. P. Love and A. J. Sieves, Chem. Phys. Lett. **153**, 379 (1988).
[11] D. Hadzi and S. Bratos, in *The Hydrogen Bond*, edited by P. Schuster, G. Zundel, and C. Sandorfy (North-Holland, Amsterdam, 1976), Vol. 2, p. 565.
[12] T. I. Smith, H. A. Schwettman, K. W. Berryman, and R. L. Swent, Proc. SPIE Int. Soc. Opt. Eng. **1854**, 23 (1993).
[13] G. Lucovsky, Phys. Rev. B **6**, 1480 (1972).