

Vibrational Relaxation of SH⁻ in Mixed Potassium Halide Crystals at 1.7 K

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Abstract

The vibrational relaxation times of SH⁻ in a KI + 2% KBr and in a 50% KCl + 50% KBr crystal have been measured by incoherent laser saturation at 1.7 K. The times are found to be intermediate between those measured in the corresponding unmixed components. This supports a model in which the primary vibrational decay channel is into local modes of the impurity molecule.

Introduction

The 1→0 vibrational relaxation rates of various diatomic hydride molecules doped at low concentrations in rare gas matrices have previously been measured at liquid-helium temperatures and found to be relatively small—Ne:OH relaxes in 10 μs [1], Ar:NH in 200 μs [2], and HCl in solid Ar, Kr, and Xe decays in 1 ms [3,4]. The deuterated analogs in the same hosts are found to relax between 2.3 and 160 times slower than these hydrides. This unequivocally rules out a multiphonon-relaxation scheme, since the lower frequencies of the deuterated species would have translated into a lower order, and hence faster, decay process. The relaxation has instead postulated to be into rotational modes of the diatomic. In this case, the deuterides couple into modes having higher rotational quantum numbers than the hydrides, because while the vibrational frequency scales inversely with the square root of the reduced mass, the rotational constant is proportional simply to the reciprocal of this mass via the moment of inertia [5].

In contrast to the slow relaxation of the hydrides in rare gas crystals, the fundamental stretching modes of OH⁻ and SH⁻ in the alkali halides relax in ~1 ns [6]. This enormous difference in timescales leads one to suppose that the relaxation mechanism operative in the latter systems must be fundamentally different than the simple rotational coupling postulated above. In order to investigate this possibility, the vibrational relaxation of SH⁻ in mixed alkali halide hosts is studied here. By "alloying" two different salts together, disorder is introduced into the matrix, which may open up new energy decay channels. In fact, however, the results demonstrate that the lifetimes in the mixed hosts are intermediate in value between the relaxation times in the two unmixed components. This indicates that the accepting mode is localized at the impurity itself, supporting a previous hypothesis [6] that the high-frequency librations play the key role in the de-excitation dynamics. Unexplained by this model, however, is the fact that even though the librational modes are increasingly destroyed by the host disorder, the lifetime remains short in a maximally disordered 50% KCl + 50% KBr crystal.

Experimental Techniques

Single crystals of KSH-doped mixed alkali halides were grown by the Czochralski method in an argon atmosphere. After removing a boule from the crystal-growing furnace, it was immediately annealed at ~50 °C below its melting point for ~10 hours in a nitrogen-gas-purged tube furnace to eliminate the thermal stresses which otherwise caused such boules to spontaneously fracture into small pieces. IR absorption spectra of the samples were collected using a Fourier-transform interferometer.

The vibrational lifetimes of the SH⁻ molecules were measured using the technique of incoherent laser saturation. Briefly, the 0→1 transition is optically pumped; the 1→2 and higher order transitions are not excited because the ~100 cm⁻¹ vibrational anharmonicity of the diatomic is much larger than the laser bandwidth. As the laser intensity is increased, a given molecule is excited more and more often.

Ultimately, a point is reached at which the rate of absorption of light by impurities in the ground state exactly balances the rates of spontaneous and stimulated emission by excited molecules. At this point, the system is said to be saturated or bleached, and approximately half of the SH^- centers are in each of the two states. One can think of this as a pump-probe experiment in which the time delay between the pump and probe photons is controlled by the light intensity. Clearly, the intensity, I_s , at which the system begins to saturate is inversely proportional to the absorption cross section, σ , and to the vibrational lifetime, T_1 . Thus, T_1 can be determined from a measurement of I_s if the cross section is known. In the case of SH^- in KCl and KBr, the integrated cross section has been determined from the ratio of the area of the absorption peak to the photometrically determined impurity concentration [7]. We have performed a similar analysis to measure the $\text{KI}:\text{SH}^-$ cross section. The cross sections for the mixed crystals are taken to equal the average of the values for the two components, weighted by their mole fractions in the mixture.

The laser system used for the saturation measurements consisted of a frequency-doubled- $\text{Nd}^{3+}:\text{YAG}$ -pumped dye laser having a 10 Hz repetition rate; the output of the dye and the residual 1.064 μm fundamental from the YAG were difference-frequency mixed in a LiNbO_3 crystal to generate mid-infrared pump pulses. The center frequency of the output beam was precisely tuned to a SH^- peak of interest by monitoring the low-power transmission through a sample. The IR pulses had a spectral bandwidth of 0.27 cm^{-1} and a temporal FWHM of 6 ns. The beam was focused onto a cleaved sample suspended in a superfluid-liquid-helium immersion cryostat; a pinhole could be translated vertically into the sample position to ensure coincidence of the focus and the center of the sample. The FWHM diameter of the focal spot was independently measured using a scanning razor blade. The spectral, temporal, and spatial beam profiles are assumed to be Gaussian on average. The transmitted and incident signals were measured using room-temperature PbSe detectors mounted on integrating spheres. The sample transmission was computed and recorded as a function of the incident peak intensity; the latter was stepped using a variable attenuator. Reflection losses at the cryostat windows and at the front surface of the sample were corrected for, to give the internal values of the incident intensity and transmission.

Experimental Results

INFRARED SPECTROSCOPY

In Fig. 1, the IR absorption spectra at 1.7 K of nominally $\text{KI} + 2 \text{ mol}\% \text{ KBr} + 0.02 \text{ mol}\% \text{ KSH}$, 50 mol% $\text{KCl} + 50 \text{ mol}\% \text{ KBr} + 0.5 \text{ mol}\% \text{ KSH}$, and for comparison $\text{KCl} + 0.01 \text{ mol}\% \text{ KSH}$ are presented. Beginning with the latter, three peaks having an instrumentally deconvolved FWHM of 0.085 cm^{-1} are observed; their relative frequencies and intensities support the labeled assignments according to the natural abundances of the sulfur isotopes.

The middle panel in Fig. 1 shows how this simple isotopic spectrum is altered when 2% of the host anions, which are next nearest neighbors (*nnn*) to the SH^- impurities, are substituted for. In addition to the fact that the dominant $^{32}\text{SH}^-$ peak is broadened and asymmetric, and that a weak, broad line has appeared at high frequencies, the most obvious new feature is the peak which lies between the two isotopic modes. These latter two modes are identified as $^{34}\text{SH}^-$ and $^{32}\text{SH}^-$ centers which have only 1-*nnn*, by comparison with the spectrum of an unmixed $\text{KI}:\text{SH}^-$ crystal; for convenience, such molecules will be referred to as being "single-neighbored." The new peak is then assigned to $^{32}\text{SH}^-$ molecules which have exactly one Br-*nnn*; they shall be termed "mixed-neighbored." Such a mode would be expected to have a slightly lower frequency than that of a single-neighbored $^{32}\text{SH}^-$ center because the smaller radius of a bromine ion compared to that of iodine results in a slightly enlarged substitutional cavity size. This assignment is supported by a measurement of the ratio of the integrated strengths of two peaks, which is found to be ~20%, in rough agreement with the expected value of $12(0.02)/0.98 = 24\%$ assuming a random distribution of Br- atoms. Upon warming the sample, the single-neighbored peak is found to broaden faster than does the mixed-neighbored mode. This indicates that the respective

phonon couplings are different; a similar effect has been seen previously for KBr:CN^- perturbed by neighboring Na^+ impurities and is thought to arise from a hindering of the diatomic reorientations by these impurities [8].

Finally, the bottom panel in Fig. 1 shows a spectrum in a host for which the mixing ratio is as large as it can be. Now all that is visible is a single, smooth Gaussian profile with a width of 6 cm^{-1} and a peak frequency of 2577.3 cm^{-1} . Interestingly enough, this frequency is much lower than what is predicted by Vegard's law [9], namely 2583.6 cm^{-1} , which is the average of the unmixed $\text{KCl:}^{32}\text{SH}^-$ and $\text{KBr:}^{32}\text{SH}^-$ frequencies. One possible explanation is that the impurity molecules preferentially occupy sites in which more of its neighbors are bromine rather than chlorine atoms. However, the spectral width and peak position measured here are unchanged when the dopant concentration is reduced by a factor of 10, which suggests that the occupation of available sites by the SH^- molecules is completely random. An alternative explanation is that the impurity molecules are on average displaced off center in the mixed compared to the unmixed host, in such a manner that the stretching mode is pushed down slightly in frequency.

LASER SATURATION

In Fig. 2, saturation data averaged over ~ 200 laser shots per data point are plotted as the filled circles for two different modes of the $\text{KI} + 2\% \text{ KBr} + 0.02\% \text{ KSH}$ sample. Curve *A* corresponds to saturation of the single-neighbored $^{32}\text{SH}^-$ center (cf. Fig. 1), while curve *B* gives the results for mixed-neighbored $^{32}\text{SH}^-:\text{Br}^-$. The difference in the low-power transmissions for the two cases simply reflects their different peak absorption coefficients. More interestingly, the knees in the two curves, which correspond to the saturation intensities, I_s , occur at roughly the same intensity. In detail, these data can be fitted to a numerical integration of the appropriate rate equations [10]. This gives the continuous curves in the figure; the two modes are found to have an identical lifetime, $T_1 = 700 \text{ ps}$.

Saturation of the $50\% \text{ KCl} + 50\% \text{ KBr} + 0.5\% \text{ KSH}$ sample was complicated by the fact that the laser pulses produce persistent spectral holes. Systematic measurements of the burn-time dependence of the hydrosulfide ions at the absorption peak for various incident pulse energies lead to the following interpretation. The hole burning quantum efficiency is 0.0036 , the saturation intensity is $\sim 20 \text{ MW/cm}^2$ as computed in the limit of strong inhomogeneous broadening, $\sim 30\%$ of the centers resonant with the laser can be hole burned, and the exponential lifetime of the spectral holes in the dark is 14 s . This

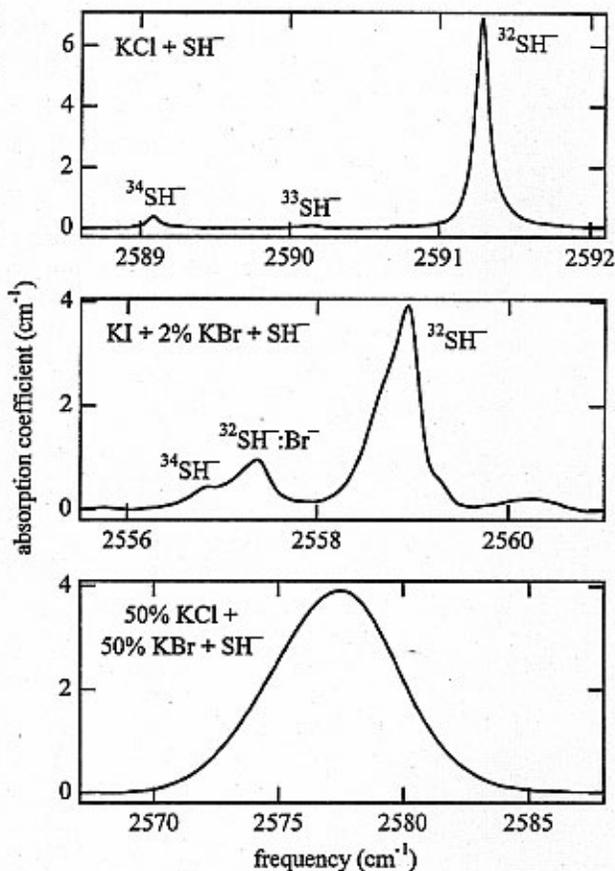


Figure 1. Absorption spectra at resolutions of 0.04 , 0.1 , and 1 cm^{-1} from top to bottom.

quantum efficiency is about an order of magnitude larger than that of SH^- in $\text{KI} + 2\% \text{KBr}$ (which does not burn in the current saturation setup), which is reasonable given that the ability to persistently hole burn originates in the strain gradients induced by the atomic disorder; furthermore, this hole decay time is comparable to that measured in other SH^- mixed crystals [11]. The fact that not all of the centers burn may be a consequence of the relatively broad linewidth of the laser compared to typical hole-antihole frequency separations observed in this previous study.

The upshot of this analysis is that for intensities of 1 MW/cm^2 or more, 30% of the centers burn away within a few seconds. As

long as the laser pulse train continues to illuminate the sample thereafter, no further centers burn away, even at higher intensities. Thus, provided that this initial transient in the transmission signal is ignored and the intensity is maintained above this threshold level, the persistent hole burning can be ignored. Figure 3 presents the resulting saturation data for two different incident laser polarizations. By using different polarizations it is possible to determine the defect orientations [12], assuming that the absorption cross section does not vary significantly with orientation. First suppose that the SH^- centers in this highly disordered crystal are randomly oriented. In that case the sample appears isotropic to the laser and the angle of polarization in the rate-equation analysis can be integrated out. This gives the dashed curves in Fig. 3, where the lifetime was arbitrarily chosen to fit the data in panel (a). Evidently the result fails to describe the experimental data in panel (b), which rules out the hypothesis of a random distribution of SH^- orientations.

At the other extreme of possibilities, all of the SH^- centers might be $\langle 111 \rangle$ oriented, just as they are in unmixed KCl and KBr [13]. If this is true, it is easy to see that the defects should saturate more easily under $[110]$ than under $[100]$ laser polarization. An exact analysis gives the solid curves in Fig. 3, which now fits the data in both panels simultaneously. Hence, the dipole orientations are $\langle 111 \rangle$ and the vibrational lifetime is found to be 350 ps.

Discussion

The measured vibrational lifetimes of SH^- in the two mixed crystals studied here are summarized in Table 1, together with the corresponding results in the unmixed potassium halides. It can be seen that the relaxation times in the mixed hosts are intermediate between those in the corresponding unmixed crystals. This same result is found to hold true for SH^- in a sample for which the cationic sublattice of the alkali ions is disordered, rather than the anionic sublattice as in the present cases, as well as for SH^- in a cesium halide mixed sample, which has a different crystal structure. Previous measurements of the vibrational relaxation of NH , ND , and CD_3F in mixed Ar-Kr matrices showed a similar effect for these systems as well [14,15]. One concludes from this observation that the relaxation is not affected by the presence or absence of long-range order in the host and that the delocalized lattice modes do not

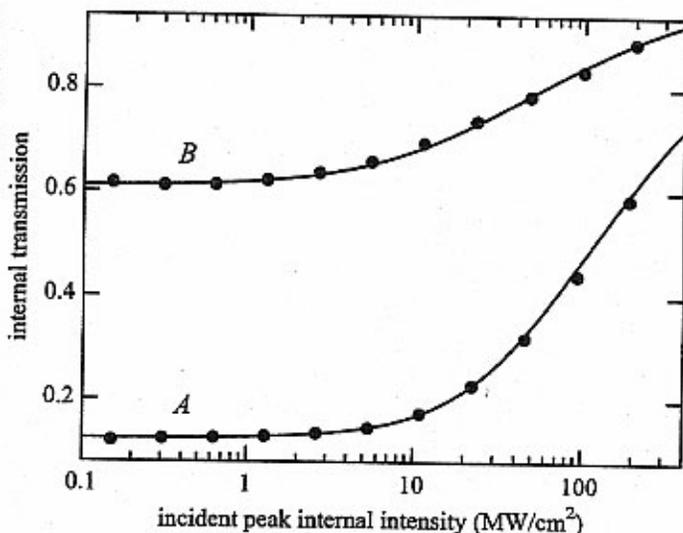


Figure 2. Saturation data for two different peaks of SH^- in a $\text{KI} + 2\% \text{KBr}$ sample at 1.7 K.

constitute the primary accepting channel for the vibrational energy. On the contrary, the accepting modes are localized at the impurity and the vibrational coupling to these modes is driven by a short-range interaction between the molecule and its immediate neighbors.

A cascading energy decay through the high-energy rotational and low-energy librational modes of SH^- composes the lowest order decay process which we have thus far been able to construct. If this is in fact the dominant relaxation scheme, the following picture emerges. The vibrationally excited molecule in its ground librational state relaxes into a near-resonant rotational level in the vibrational ground state. This V-R coupling must be mediated by the lattice, in order to relax the requirement of angular momentum conservation. Theoretical models have ascribed the coupling to repulsive forces (and presumably in the present case Coulombic forces, as well) between the vibrating ends of the diatomic and the neighboring host atoms [16-18]. Alloying the crystal alters

the nature of and the distance to these neighbors; on average, one might thus expect the coupling in the mixed host to be intermediate between that in the two unmixed component crystals, just as is observed.

One important aspect of the problem is not explained by this picture, however. Systematic measurements of the $\sim 300 \text{ cm}^{-1}$ SH^- librational mode in alloyed crystals with varying mixing ratios indicate that the integrated strength of this mode vanishes with increasing lattice disorder [19]. This can be explained by assuming that the disorder creates multiple elastic configurations of the impurity-neighbor system, not all of which support librational motion. But in those configurations in which the high-frequency librational accepting modes are absent, longer vibrational relaxation times would be expected, assuming that the librations are not replaced by some other local accepting mode of comparable frequency. Then, the lifetime averaged over all the molecules in the sample would be expected to increase, in contradistinction to the observations in Table 1. Further investigations will be

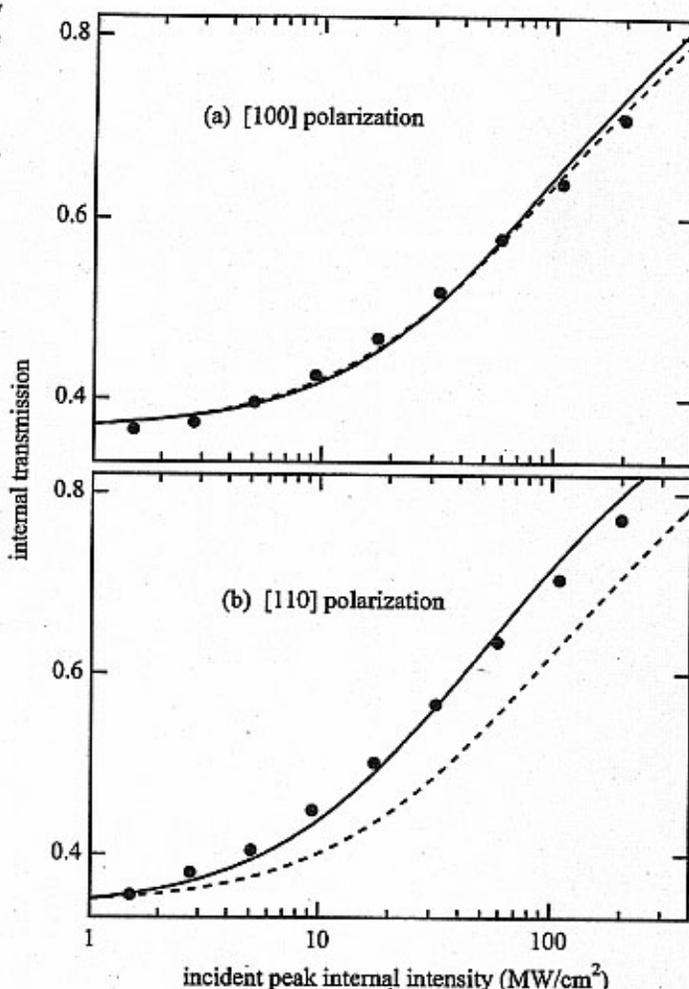


Figure 3. Saturation data for the 50/50 mixed crystal at 1.7 K with the predictions for two different defect orientations.

necessary to determine which of the above assumptions are erroneous.

Summary

Samples of KI + 2% KBr and of 50% KCl + 50% KBr substitutionally doped with KSH have been characterized by IR absorption spectroscopy. The SH⁻ stretching modes have then been saturated by incoherent laser pumping at 1.7 K. The vibrational relaxation times are found to be intermediate between those measured in the corresponding unmixed hosts. This can be explained by a model in which the primary vibrational decay channel is into reorientational modes of the impurity molecule, except that the lifetime is not found to decrease with increasing atomic disorder, even though the strength of the librational mode does.

Table 1. Vibrational lifetimes of SH⁻ at 1.7 K.

Host Crystal	Lifetime (ps)
KCl	280
KBr	400
KI	1000
KI + 2% KBr	700
50% KCl + 50% KBr	350

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