

RELAXATION OF THE STRETCHING MODE OF SH⁻ IN POTASSIUM HALIDES AT LOW TEMPERATURES

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The energy relaxation times at 1.5 K of the SH⁻ stretching vibration in three different potassium halide hosts are measured by incoherent laser saturation and found to vary from 85 to 340 ps. These times are a factor of 10⁸ smaller than those previously found for the stretching mode of CN⁻ in the same hosts. This is surprising in light of the fact that the vibration-to-phonon coupling strengths of SH⁻ and CN⁻ are comparable.

Introduction

The discovery of infrared vibrational fluorescence from diatomic molecules in solids, first for CO in noble gas matrices¹ and later for CN⁻ in alkali halide hosts² showed that at low temperatures radiative dominates over nonradiative relaxation. Here, we describe experiments on SH⁻ in alkali halides which show that for this diatomic the opposite is true, that is to say, it decays nonradiatively on a 100 picosecond timescale. In contrast, the fundamental stretching mode of CN⁻ ($\nu_1 = 2080 \text{ cm}^{-1}$) relaxes at low temperatures in a time on the order of tens of milliseconds,³ comparable to the calculated radiative lifetime τ_{rad} . This accords with the fact that nonradiative multiphonon relaxation processes are very unlikely because of the large number of Debye phonons required to match the energy of the molecular vibration (between 16 and 27, depending on the host). We find that the defect-lattice couplings for SH⁻ and CN⁻ are similar, as measured by the strengths of their vibrational phonon sidebands, and thus strong vibrational fluorescence would also be expected for excited SH⁻ defects in alkali halides, especially since the multiphonon decay channel should be even weaker for SH⁻ due to the larger energy of its stretching mode ($\nu_1 = 2550 \text{ cm}^{-1}$) and hence to the higher order process required. However, incoherent laser saturation measurements, as described here, demonstrate that SH⁻ has very short lifetimes in potassium halides.

Experimental Results

The sideband spectra in the phonon region (0-139 cm⁻¹) on the anti-Stokes side of the zero-phonon vibrational lines for samples of nominally 0.15 mol % CN⁻ and 0.2 mol % SH⁻ in KI were measured at 1.5 K and 0.04 cm⁻¹ resolution. These spectra were normalized⁴ by dividing them by the product of the absolute frequency and the chemically-determined concentration and multiplying the result by 10¹⁸ times the cube of the frequency

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shift from the zero-phonon line in order to put the sideband strengths in a form such that their integrated sideband areas give a concentration- and frequency-independent measure of the vibrational coupling to phonons. The integrals from 0 to 165 cm^{-1} are 12 cm^{-1} for CN^- and 14 cm^{-1} for SH^- . Thus, SH^- is about as strongly coupled to phonons as is CN^- .

In light of this result, one might expect SH^- to decay mainly radiatively, just as CN^- does. An attempt was thus made to look for vibrational fluorescence. We resonantly pumped the first overtone ($\nu = 0 \rightarrow 2$ transition) of the SH^- molecule in a nominally KI + 0.2 mol % KSH crystal at 1.5 K using the nanosecond infrared laser described below (with a pulse energy of 3 mJ). An InSb detector was used to look for fluorescence emitted by the $2 \rightarrow 1$ and $1 \rightarrow 0$ transitions, with an InAs filter to block the scattered pump light. No radiation was detected. Using the noise of the detector as a limit on the signal, we find an upper limit for the nonradiative relaxation time: $\tau_{\text{nr}} < 5\text{ ns}$. In comparison to the calculated radiative lifetime, $\tau_{\text{rad}} = 110\text{ ms}$, nonradiative decay channels clearly dominate the relaxation dynamics of the SH^- stretching mode.

To determine the relaxation time below this upper limit, we use incoherent saturation techniques. Tunable infrared laser pulses (6 ns pulse length, 0.27 cm^{-1} laser bandwidth, 10 Hz repetition rate, and up to $400\text{ }\mu\text{J}$ pulse energy) were generated at around 2550 cm^{-1} by difference frequency mixing of YAG and tunable dye laser radiation in a LiNbO_3 crystal. After passing through variable attenuators, the laser pulses were focused onto each of the SH^- doped samples (dopant concentrations of 60 - 100 ppm) at 1.5 K. The incident and transmitted intensities were measured using PbSe detectors.

After tuning the frequency of the laser to the peak of the SH^- absorption line, transmission measurements were made as the incident laser intensity was varied. Typical saturation results are shown in Fig. 1 for SH^- in KBr. The experimental points were obtained by measuring the transmission for several hundred laser pulses with different intensities, dividing the intensity axis into bins, and averaging together the data points within each bin. Saturation of the vibrational transition is evident, with an onset at an incident intensity of about 20 MW/cm^2 . The saturation could not be followed to intensities above about 200 MW/cm^2 due to resulting crystal damage.

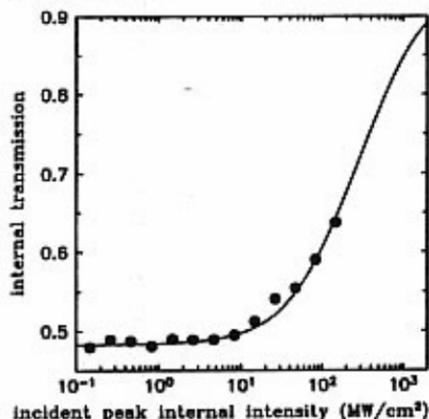


Figure 1. Transmission of $\text{KBr}:\text{SH}^-$ as a function of the incident laser intensity.

Analysis of the Saturation Data

Owing to the large anharmonic shift⁵ of 100 cm^{-1} in the vibrational ladder of SH^- , the incident radiation is only resonant with the $\nu = 0 \rightarrow 1$ transition, so that the molecule can be treated as a two-level system. We have applied a rate equation analysis⁶ to compute the transmission as a function of the peak incident intensity, numerically integrating over the transverse (assuming a Gaussian radial profile at the focus) and longitudinal coordinates,

over the temporal and frequency distributions of the laser (both assumed to be Gaussian), and over the homogeneous components (assumed to be Lorentzians with width determined by T_1) composing the absorption spectrum of the sample as the laser pulse propagates through the crystal. The final result depends upon the integrated absorption cross section of SH^- . This value was determined by performing a chemical analysis⁵ to find the actual SH^- concentration in a crystal and dividing this into its measured absorption strength. The value of the energy relaxation time T_1 for each host was then varied until a best fit to the experimental data was found; for example, the fitted saturation curve for $\text{KBr}:\text{SH}^-$ is presented in Fig. 1 as a solid line.

The results of the fits for SH^- are presented in Table 1 for three different hosts, together with the corresponding lifetimes for CN^- (at 12 K) from Ref. 3. The fitted value for T_1 for $\text{KI}:\text{SH}^-$ agrees, to within errors, with the value found from persistent spectral hole-burning,⁷ assuming that energy relaxation dominates over pure dephasing. We thus find a difference in the relaxation times of seemingly similar molecules, SH^- and CN^- , of eight orders of magnitude.

Table 1. Energy relaxation times for SH^- at 1.5 K and for CN^- at 12 K (from Ref. 3) doped in the indicated host crystals at low concentrations.

host crystal	T_1 for SH^-	T_1 for CN^-
KCl	85 ps	8 ms
KBr	200	33
KI	340	35

Conclusions

In conclusion, we have performed incoherent saturation experiments on the fundamental stretching vibration of SH^- molecules in potassium halide hosts. We find that the energy relaxation times are about 8 orders of magnitude shorter than the corresponding times for CN^- , a result that cannot be explained by nonradiative decay into phonons.

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