



Novel temperature dependence of the vibrational relaxation of SH^- in a two-state hopping system

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Abstract

Vibrational saturation measurements of the SH^- molecule doped in KBr are performed from 1.7 to 78 K. If a single relaxation time is fit to the saturation curves, it is found to increase with increasing temperature, in contrast to theoretical expectations. However, $\text{KBr}:\text{SH}^-$ has recently been shown to possess two distinct elastic configurations between which interconfigurational hopping has been identified. If the vibrational lifetimes are different in these two states, an increasing effective decay time for the system as a whole can be obtained even when the two individual times remain constant or even decrease with rising temperature.

1. Introduction

There continues to be great interest by the chemical physics community in studies of vibrational relaxation (in the electronic ground state) of molecules doped in solids because of the insights such experiments shed upon lattice dynamics and atomic interactions [1–7]. A set of empirical laws, whose theoretical bases are not fully developed in all cases, has arisen to explain the observed phenomena: an energy gap law for decay into an appropriate number of phonons [8,9] or rotational modes [10,11], and the dominant coupling to internal vibrational or local modes in systems which possess such lower frequency modes [12]. Due to the onset of thermally stimulated processes, the vibrational relaxation rate, $1/T_1$, is theoretically found to increase with increas-

ing temperature for temperatures greater than about $h\nu_{\text{acc}}/k$, where ν_{acc} is the frequency of the accepting mode, be it a typical phonon, rotational, or local mode.

In this Letter, we report on incoherent vibrational saturation measurements of SH^- in KBr which indicate an unusual temperature dependence for the vibrational lifetime. Specifically, the results establish that the overall value of T_1 increases with temperature, almost doubling between 1.7 and 78 K, in striking contrast with expectations. A recently developed jump-rotational-diffusion model can account for our measured results, wherein the defect-lattice system possesses two distinct elastic configurations: a low-temperature state in which the SH^- molecules librate, and a second configuration, populated at higher temperatures, in which low-frequency Debye

rotations of the ions are supported [13]. We expect that similar hopping models will find application to other systems besides $\text{KBr}:\text{SH}^-$.

2. Experiment

Single crystals of KBr substitutionally doped with either 100 or 5000 ppm (by mole fraction) of KSH were grown by the Czochralski method at Cornell University's Materials Science Center. The more highly doped sample serves to characterize the weak librational mode at low temperatures, as well as the broad high-temperature vibrational spectrum. The lower doping concentration is used to resolve and saturate the sharp low-temperature vibrational modes in absorption spectroscopy — at 1.7 K, 0.085 cm^{-1} wide peaks are observed at 2573.71, 2574.77, and 2575.88 cm^{-1} , whose relative frequencies and intensities agree with calculations for the stretching modes of $^{34}\text{SH}^-$, $^{33}\text{SH}^-$, and $^{32}\text{SH}^-$ according to the natural abundances of the sulfur isotopes. Of these, the last dominates, having a relative abundance of 95.0%, and saturation experiments were typically performed on this mode; an independent measurement of the lowest frequency $^{34}\text{SH}^-$ peak in a long sample was performed which verified that the lifetime is isotope independent. The vibrational anharmonicity, $2x_e\nu_e$, is found to be 101.2 cm^{-1} , which ensures that only the $0 \rightarrow 1$ transition is pumped by the laser.

The laser system used for the incoherent saturation measurements consists of a 10-Hz-repetition-rate doubled- $\text{Nd}^{3+}:\text{YAG}$ -pumped dye laser (using Exciton dye LDS 867); the output of the dye and the residual $1.064\text{ }\mu\text{m}$ fundamental from the YAG are then difference-frequency mixed in a LiNbO_3 crystal and filtered to generate mid-infrared pump pulses. The center frequency of the output beam is tuned exactly to the SH^- peak frequency, ν_{vib} , at each temperature by monitoring the low-power transmission through the sample. The IR pulses are measured to have a spectral bandwidth of 0.27 cm^{-1} , a temporal FWHM of 6 ns, and energies of up to $\sim 150\text{ }\mu\text{J}$. The beam is focused onto a cleaved, 1.4-mm-long 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. Independently,

a scanning razor blade is used to measure the $95\text{ }\mu\text{m}$ FWHM diameter of the focal spot. The spectral, temporal, and spatial profiles are assumed to be Gaussian on average. The laser polarization is along a [100] axis of the crystal, while the SH^- dipoles are known to be $\langle 111 \rangle$ oriented [14]; the saturation analysis accounts for this difference in orientations, as well as for the mismatch in the laser and absorption spectral widths at low temperatures. The transmitted and incident signals are monitored using room-temperature PbSe detectors mounted on integrating spheres and electronically amplified, filtered, and averaged. The sample transmission is computed and recorded as a function of the incident peak intensity; the latter is stepped using a variable attenuator under computer control. Reflection losses at the cryostat windows and at the front surface of the sample are corrected for, to give the internal values of the incident intensity and transmission.

3. Results

In Fig. 1, the averaged saturation data are plotted by the filled circles and squares for four different temperatures. It should be noted that these temperatures are actually those of the copper sample holder; at high incident intensities, the pumped volume of the sample undergoes a significant transient rise in temperature, because the relaxation is nonradiative and a large amount of heat gets dumped into a small

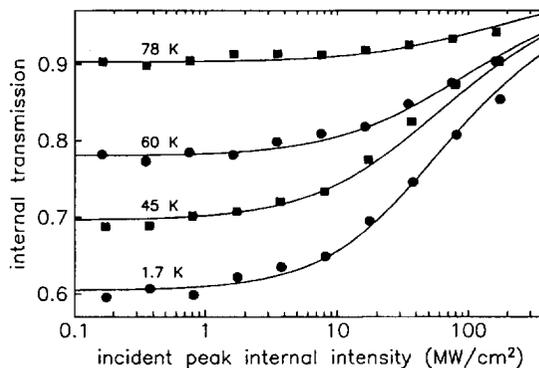


Fig. 1. Vibrational saturation data (symbols) at the indicated bath temperatures of nominally $\text{KBr} + 100\text{ ppm KSH}$. The continuous curves are fits to a rate-equation analysis, giving $T_{1A} = 450\text{ ps}$ and $T_{1B} = 1\text{ ns}$.

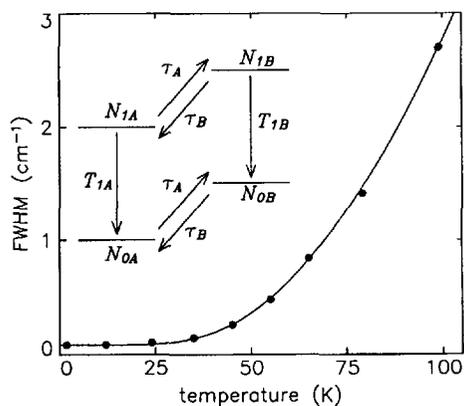


Fig. 2. Temperature dependence of the KBr: $^{32}\text{SH}^-$ vibrational linewidth (\bullet). The continuous curve is a fit to Eq. (1) which describes inhomogeneous and phonon-dephasing broadening. Inset diagram: schematic energy-level diagram for the states relevant to the optical pumping and relaxation of the $0 \rightarrow 1$ vibrational transition of KBr: SH^- .

volume in a very short time. Assuming a cylindrical focal volume, a transient temperature rise of 30 K is calculated for the highest energy pulses from the known T^3 heat capacity of KBr for an initial sample temperature of 1.7 K. (Note that the repetition rate of the laser is sufficiently low that the sample has time between shots to relax back to the bath temperature.) Fortunately, the homogeneous width remains small at 32 K (cf. discussion of Fig. 2 below), so that this effect only introduces a minor correction into the saturation analysis; furthermore, the temperature rise is negligible for lower energy pulses or for higher initial temperatures.

Two things should be noted about the temperature dependence of the data in Fig. 1. First, and most obviously, the low-power transmission increases with temperature. This arises because the unsaturated absorption coefficient decreases as the width of the vibrational peak increases. (Note that the integrated strength of the vibrational spectrum is independently found to be conserved to better than 10% between 1.7 and 300 K.) This can be seen from the main plot in Fig. 2 — the filled circles give the absorption linewidths measured using a FTIR interferometer, where the instrumental linewidth has been deconvolved in quadrature from the data. But in addition to this, careful inspection of Fig. 1 indicates that the knee in the curves, which approximately defines the saturation intensity I_s , moves to higher intensities

with increasing temperatures. The saturation intensity is inversely proportional both to the vibrational lifetime, T_1 , and to the peak absorption cross section, σ_{peak} . Even though the overall value of T_1 increases with temperature, as shall be shown below, the peak cross section decreases sufficiently more rapidly that the saturation intensity ends up by increasing in magnitude. In fact, I_s quickly exceeds our maximum intensity of $\sim 200 \text{ MW/cm}^2$ for temperatures above that of liquid nitrogen.

4. Analysis

The incoherent saturation data of Fig. 1 can be analyzed using rate equations. However, standard approximate solutions for these equations cannot be used here because the laser bandwidth is not in all cases narrower than the homogeneous absorption width, the vibrational peaks are not clearly homogeneously or strongly inhomogeneously broadened at low temperatures, and the lifetimes are not very different from the laser pulse temporal width. In consequence, the rate equations are instead numerically integrated over the spectral, temporal, radial, and longitudinal coordinates, as well as over the individual homogeneous lines lying within the laser bandwidth. The analysis requires a knowledge of the absorption cross section as a function of frequency. In general, this cross section has a Lorentzian lineshape whose area is equal to the integrated cross section, σ_{int} , and whose width is equal to the homogeneous linewidth, γ_{homo} . The former parameter is calculated to be $2.3 \times 10^{-18} \text{ cm}$ from measurements of the absorption strength for KBr: SH^- samples whose concentrations have been determined independently [15]. The homogeneous linewidth is given by $1/\pi T_2$, where T_2 is the total dephasing time, which in turn is equal to $(0.5/T_1 + 1/T_2^*)^{-1}$. Here T_2^* is the pure dephasing time; its value can be determined from the measured absorption linewidths, γ_{abs} , in Fig. 2. For this purpose, the continuous curve in the main part of this figure is a fit to two-phonon elastic scattering processes, as described by [16]

$$\gamma_{\text{abs}}(T) = \gamma_{\text{abs}}(0) + \beta \left(\frac{T}{\theta_c} \right)^7 \int_0^{\theta_c/T} \frac{x^6 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where θ_c is a cutoff on the order of the Debye temperature, θ_D , and β is an empirical constant. The fit values are $\gamma_{\text{abs}}(0) = 0.085 \text{ cm}^{-1}$, the absorption width at 1.7 K; $\beta = 120 \text{ cm}^{-1}$; and $\theta_c = 250 \text{ K}$, to be compared with the Debye temperature of KBr, $\theta_D = 173 \text{ K}$. This fit predicts a Lorentzian lineshape with a width of 31.6 cm^{-1} at RT, in reasonable agreement with the experimental value of 30 cm^{-1} after subtracting off the phonon sidebands. Neglecting the lifetime contribution to the broadening, which is largest at 1.7 K where it equals merely 0.012 cm^{-1} (cf. fitted overall values of T_1 below), $\gamma_{\text{abs}}(0)$ gives the inhomogeneous width while the second term on the right-hand side of Eq. (1) gives $1/\pi T_2^*$. Hence the only remaining unknown is T_1 , which is thus obtained by fitting the numerically integrated solutions of the rate equations to the data in Fig. 1.

When this analysis is performed, T_1 is found to be 450 ps at 1.7 K, accounting for a few small corrections neglected in Refs. [17,18]. This is much smaller than the radiative lifetime, which can be calculated from σ_{int} to be 35 ms. Indeed, a careful attempt to measure laser-induced vibrational fluorescence from SH^- doped crystals by pumping the first overtone gave a null result. Unexpectedly, however, the fitted values of the lifetimes are found to increase with increasing temperature, almost doubling to $\sim 800 \text{ ps}$ at 78 K. The uncertainties in these fitted values of the relaxation times are $\pm 20\%$, as judged by varying T_1 and plotting the resulting saturation curves. The observed decrease in the relaxation rate is found to be approximately proportional to the vanishing of the absorption strength of the librational mode with increasing temperature. In contrast, all existing theoretical models (e.g. Refs. [8,11]), to the best of our knowledge, deduce relaxation times which decrease with rising temperature.

5. Discussion

This apparent contradiction between experiment and theory can be resolved once it is realized that the impurity–lattice system can hop between two distinct elastic configurations (labeled A and B) with increasing temperature. In the B configuration, which lies 175 K in energy above the A configuration, the vibrational relaxation is slower owing to the absence

of the high-frequency librational accepting modes. The rate-equation analysis can be modified to account for these two configurations by reference to the inset diagram in Fig. 2. This shows the ground-state (0) and first-excited (1) vibrational levels of SH^- in the two configurations, having populations N_{0A} through N_{1B} ; the lifetimes in the two configurations, T_{1A} and T_{1B} ; and the temperature-dependent hopping rates from one configurational ground state to the other, τ_A and τ_B . (For simplicity the hopping rates in the excited vibrational states are assumed to be the same as in the ground states.) The vibrational frequencies and absorption cross sections are taken to be essentially identical in the two configurations; if this were not so, one would see two peaks upon warming the sample or a temperature-dependent absorption strength, respectively. Expressions for the ground-state hopping rates have been previously determined [13] by fitting the temperature dependence of the librational absorption strength and are given by $\tau_A = (44 \text{ fs}) \exp[(800 \text{ K})/T]$ and $\tau_B = (710 \text{ fs}) \exp[(625 \text{ K})/T]$. Relaxation from N_{1A} directly to N_{0B} , or from N_{1B} to N_{0A} , is assumed not to occur; this assumption is supported by the observation that isolated SH^- molecules in the alkali halides do not persistently hole burn [19]. Immediately prior to the onset of each laser pulse, the ground-state vibrational levels are in thermal equilibrium with each other for temperatures of 45 K and above, which implies that $N_{0A}/\tau_A = N_{0B}/\tau_B$; this is true because the hopping times are at most $2.3 \mu\text{s}$, much faster than the shot-to-shot delay times of 0.1 s. The pump pulse subsequently excites molecules in both configurations to the excited levels, which either decay nonradiatively to their respective ground states or hop into the excited level of the other configuration; note that the latter process is slower than the former at all temperatures investigated here, so that thermal equilibrium between the two excited levels is not maintained and a simple population-weighted average of T_{1A} and T_{1B} would *not* accurately represent the relaxational dynamics.

At 1.7 K, on the other hand, only the A configuration is populated, so that the single-configuration model is valid and hence $T_1(0) = T_{1A}(0) = 450 \text{ ps}$, as plotted by the continuous curve in Fig. 1. Given [8] that the relaxation rate for vibrational decay into $N = \nu_{\text{vib}}/\nu_{\text{acc}}$ accepting modes is approximately pro-

portional to $[1 - \exp(-h\nu_{\text{acc}}/kT)]^{-N}$, a lower limit on the magnitude of ν_{acc} can be computed from the requirement that the lifetime broadening must be much smaller at RT than the dephasing contribution to the absorption linewidth given by Eq. (1). This implies that ν_{acc} must be larger than 200 cm^{-1} ; since the LO frequency of KBr is only 165 cm^{-1} , this rules out multiphonon decay processes.

For the A configuration, the only mode observed in a complete IR survey of the low-temperature absorption spectrum which has a frequency between the LO and vibrational modes is the 332 cm^{-1} libron, strongly corroborating an earlier suggestion that reorientational relaxation provides the dominant decay channel [18]. This librational frequency corresponds to a temperature of 478 K, which is sufficiently larger than the highest temperature of interest here, namely 78 K, that the temperature dependence of T_{1A} can be neglected and its value fixed at 450 ps.

In the B configuration, the rotational modes are of much lower frequency and the decay must be into an as-yet unidentified high-frequency local mode, perhaps a vibrational mode which appears because of the off-center position of the impurity and/or its nearest neighbors. For simplicity we will assume that T_{1B} is likewise temperature independent, although reasonable fits can also be obtained if its value is allowed to decrease with increasing temperature, provided that it remains larger than 450 ps by 78 K so that the overall lifetime of the system increases. There is thus only one free parameter to fit the three high-temperature saturation runs in Fig. 1. The best-fit value was found to be $T_{1B} = 1 \text{ ns}$, giving the continuous curves in this figure.

A reasonable definition of the overall effective decay time, T_1 , of the system for any given temperature is the relaxation time, τ , measured in a pump-probe experiment. If N_1 is defined to be equal to the total excited-state population $N_{1A} + N_{1B}$, then τ can be defined as $-N_1/\dot{N}_1$. If the relaxation were described by a single exponential, then τ would be a constant; however, since the two excited levels N_{1A} and N_{1B} do not remain in thermal equilibrium during the relaxation, τ is not a constant — the A configuration relaxes faster than the B configuration, so that τ tends to increase in value with the passing of time. This is made clear in Fig. 3: the dashed curve graphs

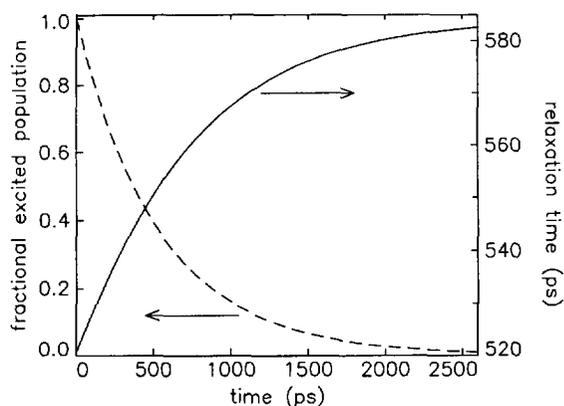


Fig. 3. Vibrational relaxation of KBr:SH⁻ at 45 K after excitation by a delta-function optical pulse at $t=0$. The dashed curve (corresponding to the left-hand axis) describes the time dependence of the total excited-state population, N_1 , normalized to its value immediately after excitation. The solid curve (associated with the right-hand axis) gives the corresponding relaxation time, τ , defined as $-N_1/\dot{N}_1$.

N_1 , while the solid curve plots τ , as functions of time after pumping the system at $t=0$ with a delta-function pulse at 45 K. The relaxation time can be seen to increase from about 520 to 580 ps over the course of the decay; the best-fit single exponential to $N_1(t)$ gives a decay time of 540 ps, which we take as the definition of T_1 . The deviation from this single-exponential fit is at most $\sim 1\%$; however, numerical simulations indicate that the decay would become pronouncedly bi-exponential if the hopping times were longer. At higher temperatures the deviations from single exponentials are even smaller as the hopping times decrease; T_1 is found to be 610 ps at 60 K and 690 ps at 78 K.

Independent confirmation of the model proposed here could come from direct pump-probe measurements of this increase in T_1 from 450 to 690 ps when the sample is warmed up from liquid-helium to liquid-nitrogen temperatures. Unfortunately, currently existing infrared picosecond laser systems have spectral bandwidths which are impracticably large compared to the low-temperature absorption linewidths, while at higher temperatures the saturation intensities needed to bleach the hydrosulfide centers become comparable to the damage threshold of the sample.

6. Conclusion

In conclusion, incoherent saturation measurements of the fundamental vibrational mode of SH^- in KBr have been performed from 1.7 to 78 K. If a single value of T_1 is fit to these data, it is found to increase with temperature, in contrast with existing theoretical models for relaxation processes. However, $\text{KBr}:\text{SH}^-$ possesses two distinct elastic configurations. If the vibrational lifetime is larger in the higher energy B configuration than in the lower energy A configuration, then the overall value of T_1 for the system as a whole is found to increase with temperature, even though T_{1A} and T_{1B} are individually taken to be temperature independent due to the large frequency of their accepting modes. This result continues to hold true even if T_{1A} and/or T_{1B} are permitted to decrease with temperature, and hence our model may apply generally to any system which supports multiple configurations of an impurity and its neighbors. An alternative model, proposed for the anomalous vibrational relaxation of the CO stretching mode of tungsten hexacarbonyl in several different glasses and liquids [20,21], postulates that the guest–host coupling strength decreases with rising temperature due to a decrease in the density of the system. This model cannot explain the present results because the change in the density of KBr is small compared to that of the relevant thermal occupation factors over the temperature range investigated.

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