Relaxation of the CN^- Stretching Vibration in Silver Halides: The Role of Accepting Modes

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The vibrational relaxation of CN^- in AgCl and AgBr is found to be 1000 times faster than in the potassium, rubidium, and cesium halides, measured previously. We demonstrate that high-frequency local modes are the source of this difference, which also explains the short times found earlier for CN^- in the sodium halides. An energy gap law fits all of the data, with the highest frequency bulk or localized phonon as the accepting mode. Extrapolating this law down to a single accepting mode, we obtain a subnanosecond lifetime, in agreement with previous measurements of CN^- in aqueous solution.

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The 4.8 μm (2080 cm^{-1}) vibrational stretching mode of CN^- doped in a number of different alkali halides [1], and the isoelectronic molecule CO in the rare gas matrices [2], decay mainly radiatively at low temperatures with a lifetime on the order of 10 ms, in contrast to the ~5 ps nonradiative vibrational relaxation time measured for CN^- in aqueous solution [3]. Although a diatomic has only one normal mode of vibration, thus avoiding the complex issue of rapid energy redistribution among the internal modes of a polyatomic molecule, it is clear that an enormous range in relaxation times can nevertheless occur for the same diatomic molecule in different environments. Here we present the first measurements of the vibrational lifetimes of CN^- in silver halides, finding times intermediate between those in the potassium, rubidium, and cesium halides and those in water. In seeking to understand the origin of the nonradiative decay channel for cyanide in the silver halides, we have discovered the existence of two local modes at 182 (207) cm^{-1} and 299 (317) cm^{-1} for CN^- in AgBr (AgCl). By supposing that the stretching vibration is decaying into an appropriate number of these localized phonon modes, we can rationalize the relaxation rates of CN^- in all of the solids with a single scheme: an energy gap law in which the highest-frequency bulk or localized phonons, as appropriate, constitute the dominant accepting modes. This model predicts that NaCl and NaBr must also have high-frequency local modes, in order to explain their short relaxation times (a few hundred microseconds), and these modes are in fact found. Furthermore, we can explain the picosecond relaxation found for CN^- in water, by assuming that the internal vibrations of the host molecules provide a near-resonant accepting mode. Extrapolating the energy gap law down to a single accepting mode gives a subnanosecond lifetime, in good agreement with the observed lifetime, especially in light of the fact that we have not made any corrections to the coupling parameters in the energy gap law.

The cyanide-doped silver halide samples were prepared by the Bridgman technique in the dark (the samples photodarken at room temperature under exposure to light, due to migration and aggregration of the silver ions in the samples) and small pieces were cut and polished by hand. In order to measure the relaxation time of the cyanide stretching mode, we pump the $0 \rightarrow 2$ overtone (cf. left-hand side of inset diagram in Fig. 1) at ~4115 cm^{-1} using a tunable infrared laser system. The output from a Nd^{3+}:YAG laser is frequency doubled into the green at 532 nm and used to pump a near-infrared dye laser; its output is then difference-frequency mixed with the residual 1.064 μm in a $LiNbO_3$ crystal to generate pulses with 6 ns duration, 0.3 cm^{-1} bandwidth, and 200 μJ energy that are focused onto the samples mounted in a variable-temperature cryostat. The resulting fluorescence

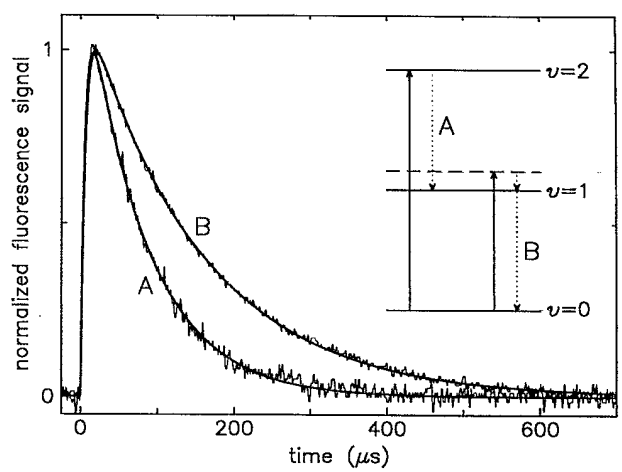

FIG. 1. *Main plot*—Curve *A*: $2 \rightarrow 1$ fluorescence signal due to overtone pumping of AgCl + 0.1 mol% AgCN at 1.7 K, fitted by a single exponential with a decay time of 80 μs. Curve *B*: $1 \rightarrow 0$ fluorescence signal from pumping the +317 cm^{-1} sideband of AgCl + 0.5 mol% AgCN at 1.7 K, with a fitted 150 μs exponential decay. The peak fluorescence intensities have been normalized to unity and the origins have been fixed at the onset of the signals. *Inset*—The two experimental schemes corresponding to fluorescence curves *A* and *B*: the solid (dashed) horizontal lines denote the vibrational (sideband) levels and the solid (dotted) vertical lines depict the pumping (relaxation) pathways.

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is collected by an InSb detector in a 90° geometry and a long-wavelength-pass filter is used to eliminate the scattered pump signal.

Curve *A* of Fig. 1 shows the resulting fluorescence signal from a sample of AgCl + 0.1 mol % CN^- at 1.7 K. The data are well described by a single exponential, $\exp(-t/\tau)$, with $\tau = 80$ μs. Similarly, a value of 170 μs is found for CN^- in AgBr. Surprisingly, these relaxation times are about a factor of 1000 smaller than the corresponding decay times of CN^- in the potassium, rubidium, and cesium halides at low temperatures and concentrations [1]. In comparison to the host-independent radiative lifetime of 50 ms [4], it is clear that the decay is mainly nonradiative. This implies that the observed fluorescence is almost entirely due to $2 \rightarrow 1$ transitions, because any emitted $1 \rightarrow 0$ photons will quickly get reabsorbed with the subsequent $1 \rightarrow 0$ decays being most likely nonradiative. (The $2 \rightarrow 1$ photons, in contrast, do not get reabsorbed because of a 26 cm^{-1} vibrational anharmonicity for CN^- in AgCl and AgBr, very similar to the anharmonicity measured previously for CN^- in the alkali halides [5].)

To account for the much faster relaxation of CN^- in the silver halides, we have measured the stretching mode sideband spectra with a Fourier-transform infrared interferometer. Figure 2(a) shows this region for nominally AgBr + 1 mol % AgCN at three temperatures. The main line at 2071 cm^{-1} corresponds to the stretching mode of $^{12}C^{14}N^-$ and the two sharp peaks at lower frequencies are due to other less-abundant CN^- isotopes. Various weak phonon sideband modes (due to the combined excitation of the stretching mode and lattice quanta) can be seen, extending out to the longitudinal optic (LO) peak [6]. Figure 2(b) shows the sideband region of nominally AgCl + 0.5 mol % AgCN; the CN^- stretching frequencies are remarkably similar to those of AgBr:CN^- (cf. Table I). The phonon sidebands, extending out to +196 cm^{-1} (plus signs are used throughout this Letter to designate frequency shifts relative to the $^{12}C^{14}N^-$ stretching mode), are much weaker than they are in the AgBr spectra, owing to the lower cyanide concentration in the AgCl sample (actually almost a factor of 4 less, not merely 2 as would be estimated from the nominal doping concentrations). The ~20 cm^{-1} wide lines at about +40 cm^{-1} in Figs. 2(a) and 2(b) are identified as cyanide librational modes, by analogy to the corresponding modes in the alkali halides [5]. In particular, in NaCl:CN^- [7] the librational sideband has a very similar width, peak frequency, and temperature dependence to the +40 cm^{-1} sidebands seen here. No evidence for rotations of the cyanide ion is found up to 300 K. After accounting for all of these features in the spectra, there remain two ~5 cm^{-1} wide lines at +182 (207) and +299 (317) cm^{-1} in AgBr (AgCl), above the LO frequencies.

Several observations can be made which shed light on the identity of these high-frequency modes. First, they are too broad to be attributable to vibrations of isolated impurity molecules. Furthermore, they are also observed directly in the far infrared (FIR) with the same frequencies and widths as in the sidebands, which proves that they cannot be combination modes of CN^- with other defects. Thus they must be localized translations of the

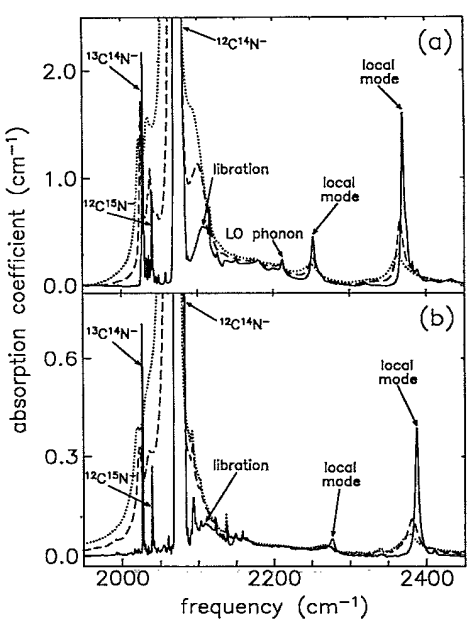

FIG. 2. Absorption coefficient in the vibrational sideband region of (a) nominally AgBr + 1 mol % AgCN, and (b) nominally AgCl + 0.5 mol % AgCN, at 1 cm^{-1} resolution. The vibrational lines due to the various CN^- isotopes are indicated, along with the librational, bulk phonon, and local mode sidebands of the $^{12}C^{14}N^-$ stretching mode. The sample temperatures are as follows: solid line, 1.7 K; dashed line, 85 K; and dotted line, 150 K.

TABLE I. Absorption features labeled in Fig. 2. The peak frequencies are tabulated, along with the spectral shifts from the stretching mode in the case of the $^{12}C^{14}N^-$ sidebands.

Sample	Feature	Frequency (cm^{-1})	Shift (cm^{-1})
AgBr	$^{13}C^{14}N^-$ stretch	2028	
	$^{12}C^{15}N^-$ stretch	2040	
	$^{12}C^{14}N^-$ stretch	2071	
	Libration	2107	+36
	LO phonon	2212	+141
	Local mode	2253	+182
	Local mode	2370	+299
AgCl	$^{13}C^{14}N^-$ stretch	2027	
	$^{12}C^{15}N^-$ stretch	2039	
	$^{12}C^{14}N^-$ stretch	2070	
	Libration	2109	+39
	Local mode	2277	+207
	Local mode	2387	+317

entire cyanide molecule. In fact, the strengths of the FIR lines relative to the sidebands (roughly 15) and the rapid temperature broadening of the lines (cf. Fig. 2) are consistent with their being local modes of the impurity.

The low-temperature nonradiative relaxation, characterized by a time τ_{nonrad}, of a vibration with frequency ν_{vib} into N accepting modes (to within a lattice phonon which takes up any energy difference) of frequency ν_{acc} is described by an energy gap law [8]

$$\tau_{\text{nonrad}} = \tau_0 e^{BN}, \tag{1}$$

where $N = \nu_{\text{vib}}/\nu_{\text{acc}}$ for energy conservation, and τ_0 and B are two parameters which depend on the coupling constants between the vibration and the accepting modes. In the present case, since the localized phonon modes are higher in frequency than the bulk lattice phonons, fewer of them are required to match the energy of a cyanide vibration. If the coupling strengths to the two sorts of phonon modes are comparable, the relaxation into local modes will be exponentially faster than relaxation into bulk phonons. This could explain the factor of 1000 faster decay times measured for CN^- in the silver halides compared to in the potassium, rubidium, and cesium halides, because no local modes occur in these latter hosts [9], presumably due to a softening of the interatomic potential in the neighborhood of the impurity.

In order to test the idea that the local modes are integrally involved in the relaxation dynamics of the CN^- vibration, we tune our laser system into resonance with the localized sideband modes (right-hand side of the inset diagram in Fig. 1). After filtering out the pump frequency, we observe fluorescence from the $1 \rightarrow 0$ vibrational decay. In Fig. 1, curve B, the $+317\ \text{cm}^{-1}$ sideband of AgCl:CN^- is pumped. Notice that there is no resolvable rise time on the signal (this remained true when we decreased the amplifier time constant to 100 ns), consistent with the expected ultrafast decay of the local mode portion of the excitation into two phonons—the $5\ \text{cm}^{-1}$ width of the local mode corresponds to a decay time of merely 1 ps, assuming it is lifetime broadened. The fluorescence signal can be fitted by a single exponential, with a $1 \rightarrow 0$ relaxation time of 150 μs. The same time is found if the lower-frequency $+207\ \text{cm}^{-1}$ sideband is pumped instead. Similarly, a fluorescence relaxation time of 370 μs is found if the AgBr $+299\ \text{cm}^{-1}$ local mode, $+182\ \text{cm}^{-1}$ local mode, or $+141\ \text{cm}^{-1}$ LO phonon sideband is pumped. These values are roughly double the $2 \rightarrow 1$ decay times of 80 (170) μs observed for AgCl (AgBr), which is expected if the coupling between the vibration and the local-phonon accepting mode is linear [8]. Furthermore, tuning the laser to the weaker features near 2385, 2390, and $2430\ \text{cm}^{-1}$ in Fig. 2(a) and $2410\ \text{cm}^{-1}$ in Fig. 2(b) also results in vibrational fluorescence, indicating that they too must be modes coupled to the cyanide vibration.

This explanation for the rapid vibrational decay of the cyanide via coupling into local modes clears up a 10-year-old puzzle regarding the relaxation of CN^- in the sodium halides. In these hosts, it was found that the low-temperature decay times are only a few hundred microseconds [1], in striking contrast to what was found for CN^- in other alkali halides, but very similar to what we have found in the silver halides. Our measurements of the sideband spectra of samples of 0.5 mol% CN^- in NaCl and NaBr show a line at $+304$ ($+262$) cm^{-1} in NaCl (NaBr), which has the same width and temperature dependence as the local mode sidebands found in AgCl and AgBr. Thus, it is reasonable to also identify the sodium halide line as a local mode [10].

In Fig. 3(a) the low-temperature relaxation times τ have been plotted versus the number of accepting modes N. For the alkali halides, these times were obtained by extrapolating the plateau in Lüty's data [1] at around 100 K down to zero temperature. This corrects for the low-temperature rise in his observed decay times, which we attribute to reabsorption of the $1 \rightarrow 0$ photons with a consequent bottleneck in the propagation of light out of the samples. (By about 100 K, this is no longer a problem because the $0 \rightarrow 1$ absorption is substantially weakened and the relaxation becomes increasingly nonradiative.) The highest-frequency accepting mode possible has been

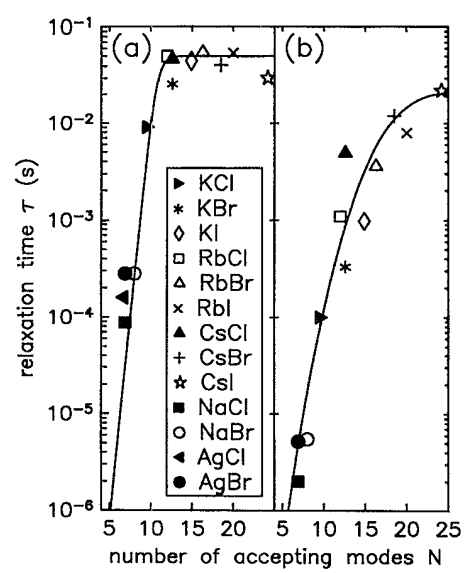

FIG. 3. Relaxation times for the $1 \rightarrow 0$ vibrational decay of CN^- in the indicated hosts at (a) 1.7 K, and (b) 300 K. The times for the alkali halides were estimated from Fig. 2 of Ref. [1], correcting for the reabsorption bottleneck at low temperatures. The lifetimes of the silver halides were obtained by sideband pumping and/or by doubling the times found by overtone pumping. The accepting mode was chosen to be the LO phonon [6] for the potassium, rubidium, and cesium halides, and the highest-frequency local mode for the sodium and silver halides. The curves are fits to Eq. (2) with two parameters, $\tau_0 = 50$ ps and $B = 1.93$.

used for each host in the figure, i.e., the LO phonon frequency [6] in the case of the potassium, rubidium, and cesium halides and the highest-frequency local mode in the case of the sodium and silver halides. The overall relaxation time τ is predicted to be

$$\tau = (1/\tau_{\rm rad} + 1/\tau_{\rm nonrad})^{-1}, \qquad (2)$$

where the radiative lifetime is $\tau_{\rm rad} = 50$ ms [4] and the nonradiative lifetime $\tau_{\rm nonrad}$ is given by Eq. (1) at low temperatures. At high temperatures, it is necessary to modify Eq. (1) to include the temperature dependence expected for N accepting modes [8]:

$$\tau_{\rm nonrad}(T) = \tau_0 e^{BN} \frac{(e^{h\nu_{\rm acc}/kT} - 1)^N}{e^{h\nu_{\rm vib}/kT} - 1}. \qquad (3)$$

The fraction is equal to unity in the limit as $T \to 0$, so that this equation correctly reproduces Eq. (1) at low temperatures. The curves in Figs. 3(a)–3(b) are plots of Eq. (2) after substituting Eq. (3), both fitted with the values $\tau_0 = 50$ ps and $B = 1.93$. Considering that B only depends logarithmically on the coupling constant and on N [8], any variations of B from host to host are expected to be small enough to justify fitting the data, within experimental error, with a constant value of B. At 300 K, where the relaxation is largely nonradiative, the same value of B fits both bulk and localized phonon accepting modes, indicating that the logarithms of their vibrational couplings to CN^- must be similar. However, for a different impurity, such as OH^- [11], the coupling parameters would in general be different.

If we extrapolate the curve in Fig. 3(b) down to a single accepting mode, we obtain a relaxation time of a few hundred picoseconds, 9 orders of magnitude smaller than the radiative lifetime of CN^-. Interestingly enough, this is not too different from the relaxation time measured for CN^- in water [3], particularly if one makes allowance for the fact that the cyanide coupling constant in water would be expected to be somewhat changed from that in salt crystals. This suggests that a CN^- stretching mode is exchanging energy with a single nearly resonant internal vibration of the water molecules.

In conclusion, the $2 \to 1$ vibrational relaxation times of CN^- in AgCl and AgBr have been measured by overtone pumping and have been found to be 80 and 170 μs, respectively, at 1.7 K. This is roughly 1000 times faster than the times measured for CN^- in the potassium, rubidium, and cesium halides. Two local modes for the cyanide-doped silver halide systems have been discovered and shown to be coupled to the CN^- stretching mode by sideband pumping; the higher-frequency one at about 310 cm^{-1}, well above the host LO phonon frequencies, gives rise to an enhanced relaxation rate according to an energy gap law. This model correctly predicts that NaCl and NaBr also have cyanide-impurity local modes, since their relaxation times are comparable to those of the silver halides. By choosing the highest-available-frequency lattice or localized phonon to be the accepting mode, a temperature-dependent energy gap law successfully rationalizes the data for cyanide in all of the solids. The fitted law, furthermore, explains why the relaxation of CN^- in aqueous solution occurs on a subnanosecond timescale—the internal vibrations of the water molecules constitute a nearly-resonant accepting mode.

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