

RELAXATION AND IR SPECTROSCOPIC PROPERTIES OF THE CN⁻ STRETCHING MODE IN SILVER HALIDES

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The relaxation times of the CN⁻ stretching mode in AgCl and AgBr at 1.7 K are found to be a few hundred microseconds. These times are shorter by more than two orders of magnitude than those for CN⁻ in most alkali halides. High frequency local modes discovered in the silver halides are suggested to act as fast relaxation channels causing this difference. Reexamination of CN⁻ doped sodium halides also reveals a local mode clearing up the previously found short times in these materials, too. An energy gap law fits all data.

Key words: Silver halides, CN⁻ impurity molecule, vibrational absorption and luminescence, lifetime of CN⁻ stretching mode, vibrational relaxation mechanism.

1 INTRODUCTION

CN⁻ molecular ions substituted at anion sites in alkali halides have been widely used as a model system to explore the effect of an ionic crystal matrix on properties of the impurity molecule. As to the vibrational spectra of the cyanide, the occurrence of infrared luminescence due to deexcitation of the CN⁻ stretching mode¹ allows to determine relaxation times and to investigate the possible relaxation mechanisms which were not cleared up satisfactorily until now. At low temperature, for the majority of the alkali halide crystals the stretching mode is long-lived with lifetimes close to radiative ($\tau_{\text{rad}} \approx 50 \text{ ms}$)² in striking contrast with CN⁻ in the sodium halides. Here the decay times are a few hundred microseconds, i.e. shorter by more than two orders of magnitude.

In seeking to understand this remarkable difference and explore the nature of the nonradiative decay channels we have investigated cyanide doped into the silver halides AgCl and AgBr³. Like alkali halides, these materials are ionic but with a considerable degree of covalent bonding. It originates from the presence of the Ag 4d-electrons which also can be expected to have a marked influence on the impurity-lattice interaction and, hence, vibrational relaxation behaviour.

2 EXPERIMENTAL RESULTS

Like in alkali halides, we observed in AgCl and AgBr vibrational luminescence around the fundamental CN⁻ stretchmode frequency but with relaxation times as short as in NaCl and NaBr^{1,3}. Using tunable infrared laser pulses with 6 ns duration and pumping either the sideband of the fundamental ($\nu = 0 \rightarrow 1$) or the weak overtone-absorption ($\nu = 0 \rightarrow 2$) the time dependence of the $\nu = 1 \rightarrow 0$ and $\nu = 2 \rightarrow 1$ intensities was measured exploiting that the transitions are shifted relative to each other by 26 cm^{-1} due to anharmonicity. For CN⁻ concentrations $\leq 0.5 \text{ mol\%}$, the decay curves were single exponential giving at 1.7 K lifetimes of 150 (370) μs for $\nu = 1 \rightarrow 0$ and 80 (170) μs for $\nu = 2 \rightarrow 1$ in AgCl (AgBr), respectively. These times differ by nearly three orders of magnitude from those found in the potassium, rubidium, and cesium halides¹ where the long times are ascribed to the fact

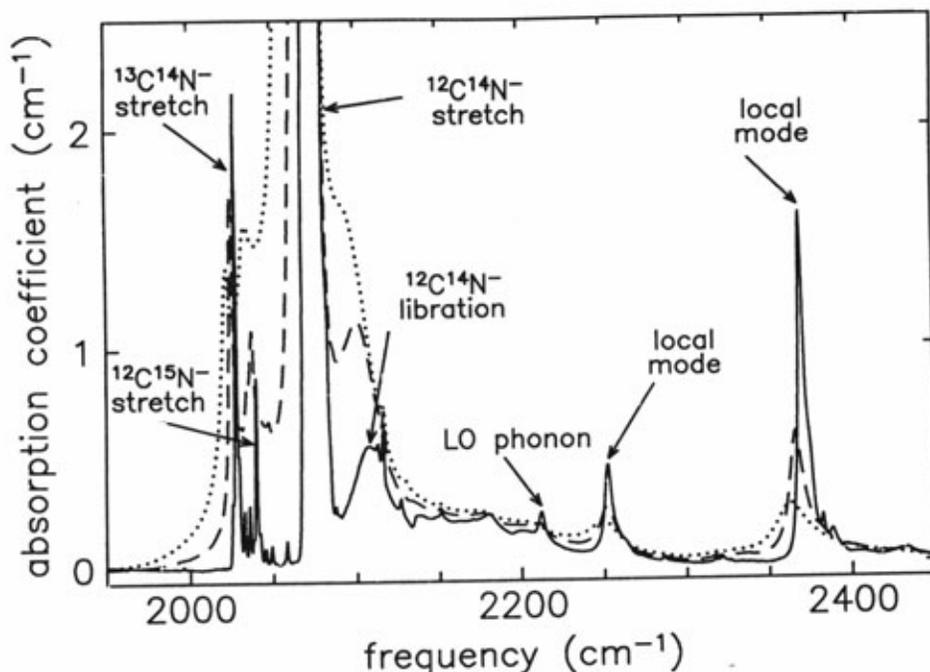


FIGURE 1 Infrared absorption of AgBr + 1 mol% AgCN (nominally) at 1.7 K (solid line), 85 K (dashed) and 150 K (dotted) showing the CN^- stretch mode and coupled sideband spectra.

that the nonradiative processes, which can be fast compared with the radiative decay, would require a large number of phonons to match the vibrational energy and thus are unlikely.

In order to explain the short times found for the silver halides and reveal the type of coupling modes we measured the vibrational sideband spectra of the main $^{12}\text{C}^{14}\text{N}^-$ line (at 2070 and 2071 cm^{-1} in AgCl and AgBr; Figure 1) employing Fourier-transform spectroscopy. Most important, besides the interaction with librational modes (at $\approx 40 \text{ cm}^{-1}$) and the lattice phonons, we discovered two unusual intense modes at 207 (182) cm^{-1} and 317 (299) cm^{-1} for CN^- in AgCl (AgBr). These modes also absorb directly in the far-infrared suggesting dipole transitions as origin. The excitation spectra of the CN^- vibrational luminescence measured by tuning the laser across each of the sidebands (Figure 2) nicely reproduce the absorption. It indicates that they are localized excitations of the cyanide, which transfer their energy into the pure stretching mode excitations. Additional support for this interpretation comes from the isotope shift of the sidebands in $^{13}\text{C}^{15}\text{N}^-$ doped AgBr (at 176 and 290 cm^{-1}) which is in agreement with the prediction by the simple oscillator model. In the silver halides, these localized modes obviously represent an efficient nonradiative decay channel for the cyanide vibration, of lower order than the phonons. Acting as accepting modes they are the reason for the reduced relaxation times that we find.

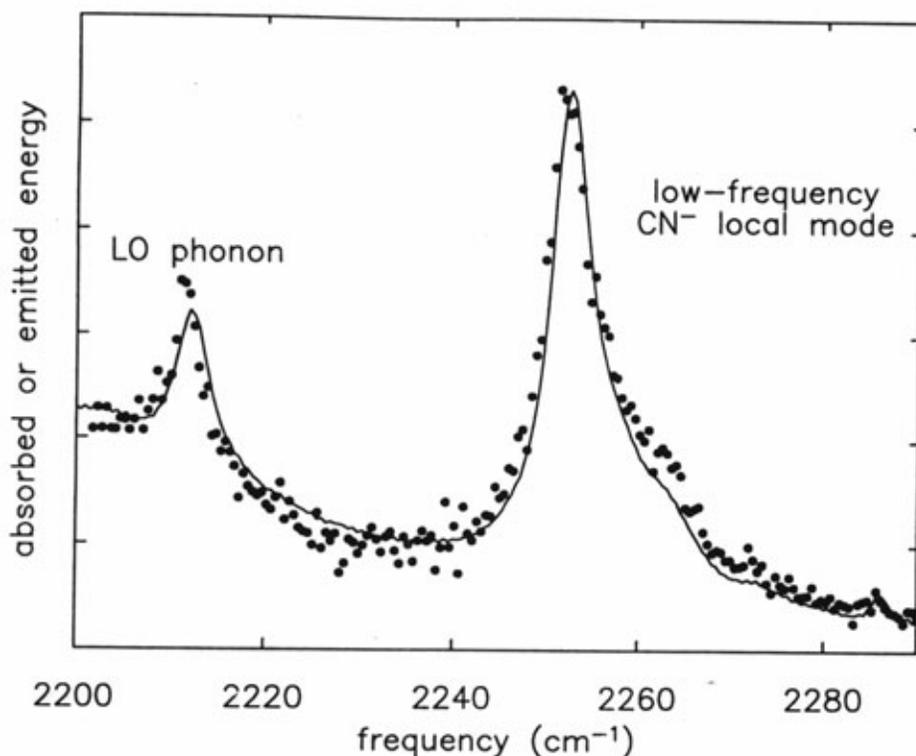


FIGURE 2 Excitation spectrum of the CN⁻ stretchmode luminescence at 1.7 K (points) measured across part of the CN⁻ sideband in Figure 1. Solid line: absorption.

3 CONCLUSIONS

Supposing that the CN⁻ stretchmode in the silver and alkali halides each decays into the highest-frequency (localized or lattice phonon) mode available, an energy gap law⁴ can be fitted to all decay times as function of the number N of accepting modes (Figure 3). This scheme suggests the existence of cyanide local modes also for NaCl and NaBr to account for their short CN⁻ relaxation times, and in fact we found these modes. Physically, the local modes are caused by a sufficiently strong interatomic potential in the neighborhood of the impurity. Obviously, in the sodium halides the potential must be qualitatively different from that in the other halide crystals as reflected by the $\langle 100 \rangle$ orientation of the cyanide in NaCl and NaBr in contrast to the usual $\langle 111 \rangle$ orientation in the other fcc alkali halides. It is worthwhile noting that a $\langle 100 \rangle$ orientation has been conjectured as most likely in the silver halides, too.⁵ In that case the $2\sigma_z$ - and $2\pi_{xy}$ -orbitals of the cyanide would strongly overlap with the d-electron wavefunctions of the surrounding host lattice silver ions presumably being the origin of the strong high energy local modes.

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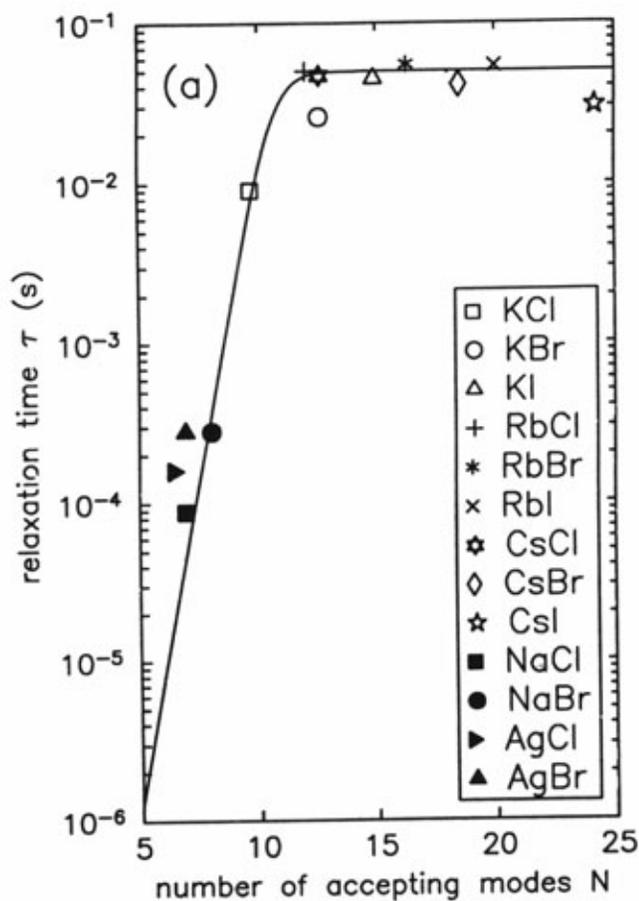


FIGURE 3 $\text{CN}^-(\nu = 1 \rightarrow 0)$ stretchmode relaxation times at 1.7 K vs. number of accepting modes in various host crystals as shown. The alkali halide data are taken from Ref. 1; the solid line is a fit by an energy gap law and using $\tau_{\text{rad}} = 50 \text{ ms}$ (for details see Ref. 3).

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