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# Transient absorption of vibrationally excited $F_H(\mathrm{CN}^-)$ centers in cesium halides: Insight into the electronic-to-vibrational energy transfer

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Pump-and-probe–type experiments covering a wide time range between tens of picoseconds and milliseconds reveal a transient optical absorption of the $F$ center–$\mathrm{CN}^-$ defect complex in cesium halides. Its pronounced structure is interpreted in terms of electronic-vibrational transitions of the defect with the $\mathrm{CN}^-$ stretching mode highly excited. The detailed analysis shows a substantial change of vibronic energies in the excited electronic state by nonlinear coupling. The measured time for the electron-vibrational energy transfer of about 70 ns in CsBr (and shorter in CsCl) demonstrates that the transfer takes place in the relaxed excited state. We also find that the 10 ms recovery component is due to vibrational relaxation.

In alkali halides, an $F$ center associated to a substitutional $\mathrm{CN}^-$ molecular ion represents a class of defects with interesting properties different from those of the "classical" $F$ aggregates.[1,2] The most striking feature of this so-called $F_H(\mathrm{CN}^-)$ center is the occurrence of strong infrared vibrational luminescence (VL) around 5 $\mu$m ($\approx$250 meV) as well as of anti-Stokes resonant Raman scattering (RRS) both generated by optical excitation in the electronic absorption. It demonstrates the transfer of *electronic* energy into the $\mathrm{CN}^-$ *vibrational* stretching mode ($e$-$v$ transfer) which becomes highly excited. Compared to NaCl-type alkali halides, the energy transfer is especially efficient in cesium halides where the electronic emission is largely quenched. Interestingly enough, in contrast to these findings, no immediate indication in the optical spectrum was found so far for the coupling between the $F$ electron and the $\mathrm{CN}^-$ vibrational mode. While this would manifest itself as a sideband system on the high energy side of the $F_H(\mathrm{CN}^-)$ absorption, one only observes a splitting into bands $F_H(1)$ and $F_H(2)$ due to the reduced symmetry.

Despite extensive experimental work (for details see Refs. 3 and 4) and several theoretical proposals,[5–7] two important questions have not been satisfactorily clarified up to now: (1) What is the nature of the coupling between the $F$ electron and the $\mathrm{CN}^-$ molecule ion and (2) how fast and at which stage during the optical cycle does the $e$-$v$ transfer actually happen?

In principle the energy transfer in the $F_H(\mathrm{CN}^-)$ center may take place in any of four stages that, like in the case of the isolated $F$ center, are (i) excitation into an unrelaxed excited state (URES) by optical absorption, (ii) rearrangement of the surrounding lattice proceeding within femto to picoseconds and leading to a relaxed excited state[8] (RES), (iii) radiative and/or nonradiative decay into an unrelaxed ground state (URGS) in the pico to microsecond regime depending upon radiative lifetime (for the isolated $F$ center in CsBr we measured $\tau_{\mathrm{rad}} \simeq 5$ $\mu$s) and the rates of competitive nonradiative relaxation processes and, finally, (iv) return of the electron-lattice system into the ground state (GS) again. Because of the excitation of the $\mathrm{CN}^-$ stretching mode it seems obvious that in case of the $F_H(\mathrm{CN}^-)$ defect molecular-vibrational relaxation has to be taken into account as an additional step in ground state recovery proceeding on a 10 ms time scale.[2] While in principle the time-delayed appearance of the infrared VL or anti-Stokes RRS could be used to monitor the dynamics of the vibrational population, actual experiments are difficult as they suffer from the lack of fast sensitive detectors or the low Raman efficiency. In this work, we instead measured the transient optical absorption that we discovered for the $F_H(\mathrm{CN}^-)$ center and which we found to be sensitive to the vibrational population. Hav-

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ing none of these shortcomings, in particular this method enabled us to investigate the $e$-$v$ transfer dynamics by using a pump-and-probe–type experimental setup.

For our investigations we used CsBr and CsCl crystals that were grown by the Bridgman method at the University of Paderborn. Doped with 0.1% mole fractions CsCN these were additively colored in potassium vapor to produce $10^{15}$–$10^{16}$ $F$ centers per cm$^3$. The $F$ center–CN$^-$ aggregation was accomplished by $F$ band light irradiation at 165 K from where the samples were rapidly cooled down to the measuring temperature of 6 K. The ratio of the $F_H(2)$ and $F_H(1)$ absorption strengths is found to be always larger than 2:1. This reflects the fact that unaggregated $F$ centers contribute with their absorption to the $F_H(2)$ band.

The experiments were specifically designed to cover a wide spectral range and nearly ten orders of magnitude in time. The setup for the *picosecond* to 3 ns range was described previously.[9] The pump source here was a Nd:YAG (yttrium aluminum garnet) laser pumped dye laser providing 60 ps pulses (energy≈150 $\mu$J) that determined the time resolution. The same laser was employed in the *nanosecond* range (up to several thousands of ns). The absorption changes in this time regime were probed by a weak pulse cut out of a cw dye laser by means of a Pockels cell (pulse width 175 $\mu$s). Using Pyridine 1, DCM, and Rhodamine 6G as dyes, this laser could be tuned between 1.67 and 2.17 eV. The probe beam was detected by a photomultiplier (Hamamatsu R955) the signal of which was sampled by an ultrafast single shot digital storage oscilloscope (LeCroy 9361). The overall time resolution of this setup was several ns. We stress that in these experiments the repetition rate of consecutive excitations was kept low (5 Hz). This was found crucial in order to avoid any repumping of centers which, due to the long CN$^-$ vibrational lifetime (≈10 ms), otherwise would not have been completely relaxed.

Finally, to study the slower processes in the *micro* and *millisecond* time range, a chopped Ar$^+$ laser pumped cw dye laser was used for excitation (laser power: 70 mW; chopper period: 138 ms), while a cw tungsten quartz lamp delivered the probe beam. The detection of the probe signal was realized by a silicon photodiode the current of which was amplified and sampled by a high speed analog-to-digital converter (IOtech ADC 488 16 bit, 100 kHz). The time resolution in this case was limited to about 10 $\mu$s.

For reasons of stray light suppression, the probe beam was sent through a 0.25 m double monochromator except for the ps investigations that were performed with a single monochromator. With two reflection gratings (600 and 1200 grooves/mm) the broad spectral range between 1.10 and 2.90 eV could be covered.

Supposing that the $e$-$v$ transfer would proceed extremely fast, we started investigations in the picosecond range that we already reported in a previous paper.[9] In these experiments it was possible to bleach the $F_H(\mathrm{CN}^-)$ absorption to about 50% of its original strength by pumping with a 60 ps laser pulse. Following the bleaching, however, only a surprisingly small portion (≈10–15 %) recovered on the picosecond scale while the main part remained bleached even after 3 ns. This demonstrated that the $e$-$v$ transfer must be much slower. We therefore extended the time scale by several decades into the ns range and measured in detail the absorption change as a function of time at various detection energies $E_D$ in a broad spectral range around the $F_H(\mathrm{CN}^-)$ absorption.

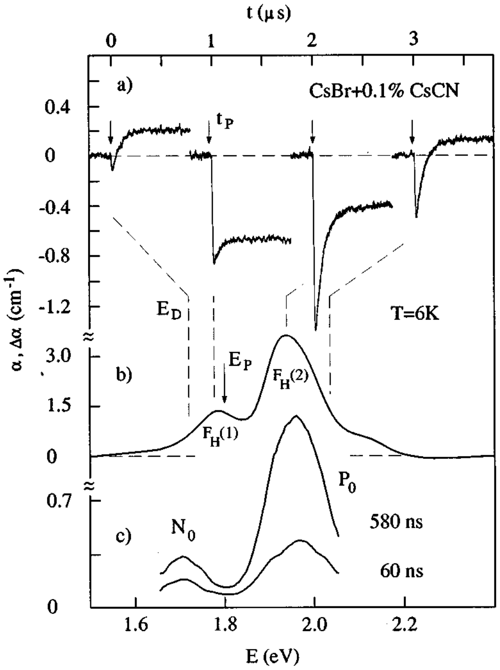

FIG. 1. Pump-probe experiments in CsBr+0.1% CsCN with ns resolution: (a) Time dependence of absorption change $\Delta\alpha(t)$ under $F_H(1)$ pump light ($E_P = 1.806$ eV) probed at different detection photon energies ($E_D$) across the $F_H(\mathrm{CN}^-)$ band as indicated. The curves are not corrected for the system response. For clarity they are shifted along the time axis; the arrows mark the time positions ($t_P$) of the pump pulse in each case. (b) $F_H(\mathrm{CN}^-)$ absorption spectrum $\alpha(E)$. (c) Spectral dependence of the ns component measured at 60 ns and 580 ns after the pump pulse. For explanation of bands $N_0, P_0$ see text.

In Fig. 1(a) we show the transient absorption change $\Delta\alpha(t)$ probed at four representative photon energies when the $F_H(1)$ band is pumped. It is clearly obvious from the curves that the $F_H(\mathrm{CN}^-)$ band [shown in Fig. 1(b)] is rapidly bleached in proportion to the original absorption strength ($\Delta\alpha<0$). Subsequently, within 200 ns, the absorption approaches a stationary value, the observed positive and negative absorption changes ($\pm\Delta\alpha$) indicating that the bleaching effect must be superimposed by the growth of a new absorption. Its spectral dependence is obtained by plotting the amplitude of the nanosecond component as a function of $E_D$. In Fig. 1(c) it is displayed at two different times after the pump pulse, extracted from a set of measured time curves densely covering the whole spectral range. We emphasize that the bleaching of the initial $F_H(\mathrm{CN}^-)$ absorption is eliminated from these spectra since $\Delta\alpha(E)$ is evaluated by taking the maximum bleaching as reference level. Clearly the transient spectra are significantly different from the original $F_H(\mathrm{CN}^-)$ absorption [compare Figs. 1(b) and 1(c)]. This unambiguously demonstrates that the ns absorption component is not correlated with the simple electronic ground state recovery of the $F_H(\mathrm{CN}^-)$ center, but rather represents the rise of a transient absorption system.

In order to follow its complete temporal behavior we had to extend our measurements by another six decades into the

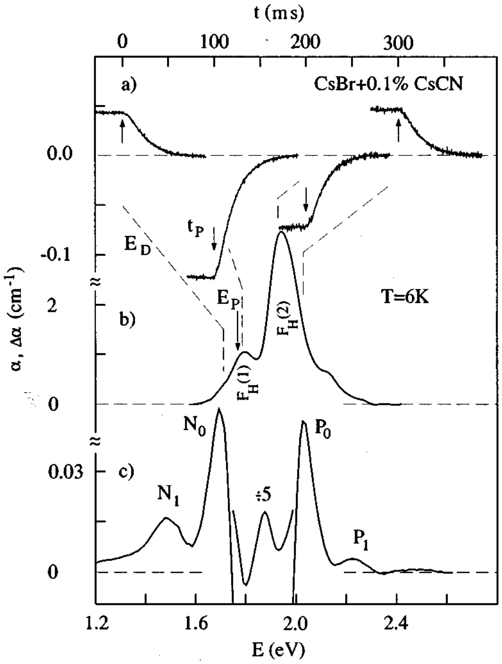

FIG. 2. Pump-probe experiments in CsBr+0.1% CsCN with $\mu$s resolution: (a) Time dependence of absorption change $\Delta\alpha(t)$ observed with chopped laser pumping in the $F_H(1)$ band ($E_P = 1.770$ eV). Plots as in Fig. 1; the arrows denote the laser cutoff after a stationary absorption change was reached. (b) $F_H(\mathrm{CN}^-)$ absorption spectrum $\alpha(E)$. (c) Spectral dependence of the (stationary) absorption change occurring with the pump laser turned on and off. Negative values $\Delta\alpha(E)$ are divided by a factor of 5 and shifted upwards. For explanation of $N_0$, etc., see text.

micro and millisecond range (Fig. 2). Due to the chopped operation of the dye laser pump in the setup, during the excitation period a quasistationary absorption is reached (with $\Delta\alpha$ positive or negative) which slowly recovers again after switching the laser off. Figure 2(a) shows the absorption change $\Delta\alpha\,(t)$, again for $F_H(1)$ band pumping, recorded at the indicated energies. It is evident that during the cw laser excitation a similar situation is met as in the nanosecond experiment in Fig. 1(a) when the stationary absorption was reached. Turning the laser off [arrows in Fig. 2(a)] the final recovery actually occurs within about 50 ms. On a very long time scale (seconds) another weak absorption could be detected which presumably is related to $F'$-type centers.

The spectral dependence of the millisecond component in Fig. 2(c) derived from a set of time curves, as before, contains four induced absorption bands ($N_0$,$N_1$,$P_0$,$P_1$) at the low and high energy side of the original $F_H(\mathrm{CN}^-)$ absorption. The strong bands $N_0$ and $P_0$ correspond to those in Fig. 1(c), however, they are slightly altered by the superimposed bleaching of the $F_H(1)$ and $F_H(2)$ bands. The spectrum nicely demonstrates that the $F_H(\mathrm{CN}^-)$ electronic ground state population is reduced with the missing absorption turning up again nearly quantitatively in form of the additional structured absorption. We also find that the bleaching is reversible and the original $F_H(\mathrm{CN}^-)$ spectrum is restored even after many pumping cycles. The results with pumping the $F_H(2)$ band are similar aside from the effect of the underlying $F$ absorption.

As an essential feature, the final absorption recovery step very well matches the time scale of the relaxation of the CN$^-$ stretching mode. Using the relaxation times of the different vibrational states ($v=0,\ldots,5$) known from infrared VL measurements,[4] a numerical fit correlating the absorption recovery and the vibrational relaxation cascade gives excellent agreement. This demonstrates that during the final recovery step the electron is already in its ground state while the adjacent vibrationally excited CN$^-$ molecule is relaxing thereby affecting tremendously the absorption of the $F$ center.

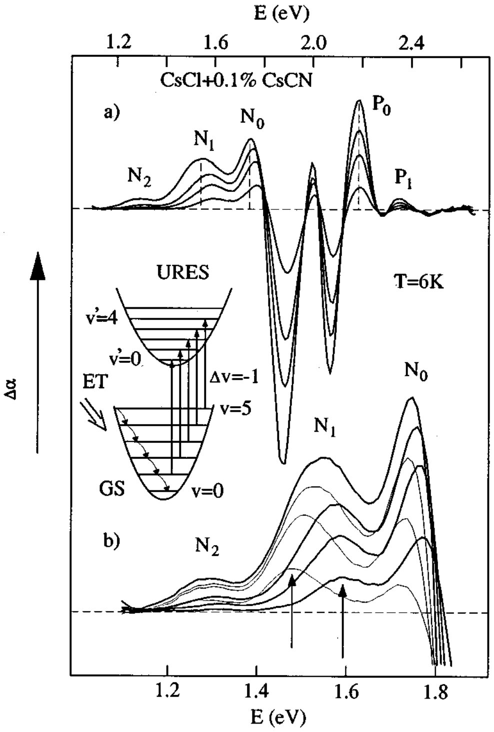

FIG. 3. Pump-probe experiments in CsCl+0.1% CsCN with $\mu$s resolution using a chopped laser as pump source: (a) Spectral dependence of the absorption change $\Delta\alpha(E)$ at different times after laser pumping in the $F_H(1)$ band at $E_P = 1.845$ eV. Strongest signal: stationary absorption change; signal with decreasing amplitudes measured at 4.0, 8.0, and 16.0 ms after laser cutoff. (b) Low energy part of the spectrum above enlarged in scale. Thin lines: spectra measured at 1.6, 5.6, and 11.6 ms after the laser was switched on. Other curves as in spectrum (a). The two arrows mark the total high energy shift of the $N_1$ peak with time. Inset: Potential energy of the $F_H(\mathrm{CN}^-)$ center GS and URES vs the internuclear distance of the CN$^-$ molecule. The $e$-$v$ transfer (ET), vibrational relaxation in the electronic GS and possible $\Delta v = -1$ absorption processes into the URES are indicated.

Focusing on the more detailed origin of the induced absorption structure, in Fig. 3 we reproduce $\mu$s time-resolved measurements in CsCl as host material. Figure 3(a) displays the absorption changes $\Delta\alpha(E)$ under $F_H(1)$ pump light measured at different times during the dark period of the chopped excitation with the strongest signal representing the quasistationary state attained during excitation [see corresponding spectrum for CsBr in Fig. 2(c)]. Apart from the occurrence of an extra peak ($N_2$) facilitating the determination of the peak energy separations, the experiments in CsCl, in comparison with the CsBr results, provide two more pieces of important information.

(i) Despite the very different $F_H(1)$-$F_H(2)$ splittings in CsBr and CsCl (160 and 270 meV, respectively), the transient absorption spectra in the two host materials exhibit a largely identical structure suggesting the same origin. On the low energy side successive maxima have separations ($E_{N2}-E_{N1}\approx 250$ meV in CsCl; $E_{N1}-E_{N0}\approx 230$ meV in CsBr) very close to the $\mathrm{CN}^-$ stretching mode energy of about 250 meV. In particular, no indication is found here that would reflect the $F_H(1)$-$F_H(2)$ splitting. In contrast, the $N_0$ and $P_0$ bands obviously are correlated with the $F_H(1)$ and $F_H(2)$ band positions, respectively, as suggested by the distinctly different $N_0$-$P_0$ energy separations in the two hosts.

(ii) During the millisecond recovery step some of the positions of the induced absorption peaks turn out to be strongly time dependent indicating that various transitions participate. For illustration we display in Fig. 3(b) the enlarged low energy part of the spectrum in which all bands are seen to gradually shift to higher energies during the light and dark period of the chopper. For $N_1$, e.g., this shift amounts to more than 100 meV in total (see arrows).

Combining all observations, one has to attribute the discovered transient absorption band system to an electronic-vibrational transition progression of the $F$ center–$\mathrm{CN}^-$ complex that is characterized by strong nonlinear coupling. The $F_H(1)$ and $F_H(2)$ bands are assigned to $\Delta v=0$ transitions starting from $v=0$. Different from these, transitions $v=0\rightarrow v'\geqslant 1$ [which anyhow would partly overlap with the high energy region of the $F_H(\mathrm{CN}^-)$ absorption] do not give rise to measurable vibronic sidebands, implying that the linear coupling is weak. A preliminary analysis gives a linear coupling strength of $S<0.1$. Optical pumping populates higher vibronic levels shifting part of the absorption to energies where it does not overlap with the original $F_H(\mathrm{CN}^-)$ absorption. We attribute the bands $N_0$ and $P_0$ [connected with $F_H(1)$ and $F_H(2)$, respectively] also to $\Delta v=0$ transitions which, however, start from $v\geqslant 1$. Correspondingly, the $N_1$ and $N_2$ bands are $\Delta v=-1$ and $\Delta v=-2$ transitions belonging to the $F_H(1)$ component as seen from their energy separations relative to $N_0$. As the sideband structure here essentially is caused by the $F_H(1)$ transition, it implies a relatively stronger electron-vibrational coupling for $F_H(1)$ than $F_H(2)$ qualitatively consistent with earlier suggestions (see, e.g., Ref. 4). The $P_1$ band is caused by a $\Delta v>0$ transition, its detailed assignment being difficult because of the superposition of several bands in this part of the spectrum.

As the known anharmonicity shift of the GS vibration [$\approx$3 meV (Ref. 2)] is far too small to account for the large (low and high) energy shift of $N_0$ and $P_0$ relative to $F_H(1)$ and $F_H(2)$, respectively, one is forced to assume a nonlinear $F$ center–$\mathrm{CN}^-$ coupling. It obviously leads to a quite substantial change of vibrational frequency in the excited electronic state, different for $F_H(1)$ and $F_H(2)$. From analyzing the data, this change is as large as 15 to 25 meV, a result which is in quantitative agreement with the temporal shift of the transient absorption maxima. It is well known from infrared VL that the $e$-$v$ transfer in cesium halides preferentially populates the $v=3$ and 4 levels.[4] After pulsed excitation, cascading into lower vibrational states takes place which are the initial states for the absorption process. Because transitions with equal $\Delta v$ occur at different energies (see inset of Fig. 3) the relaxation leads to the observed shift. This gives direct experimental evidence of the strong interaction between the electronic states of the excited $F$ center and the $\mathrm{CN}^-$ molecule in the URES even though the linear coupling is small.

Addressing finally the time scale of the energy transfer, it is clear that the builtup time of the induced absorption directly reflects the dynamics of the vibronic state population and, hence, the $e$-$v$ transfer time. For CsBr [cf. Fig. 1(a)] the quantitative analysis gives $\tau_{e\text{-}v}=73\pm 5$ ns. Somewhat shorter times were recently estimated for the $F_H(\mathrm{CN}^-)$ center in CsCl.[10] We also find the $e$-$v$ transfer time in this host material shorter than in CsBr but below our time resolution of several nanoseconds in these experiments.

As the $e$-$v$ transfer times are several orders of magnitudes longer than typical lattice relaxation times, it is reasonable to assume that the $e$-$v$ transfer occurs after configurational relaxation in the RES. Regarding the energy transfer mechanism, we believe that nonlinear interaction is important. While the association of the $F$ center to the $\mathrm{CN}^-$ ion only leads to a 0.4% change in $\mathrm{CN}^-$ oscillator frequency[2,4] the nonlinear coupling results in an order of magnitude larger (6–10 %) change in the URES with an even more dramatic effect to be expected in the RES due to the larger spread of the electronic wave function towards the $\mathrm{CN}^-$ molecule. We propose that this effect of the excited $F$ electron is crucial in modeling the $e$-$v$ transfer. In particular, our results support the idea that the $F$ center–$\mathrm{CN}^-$ pair must be considered an entity or "supermolecule,"[5,6] but with a significant variation of coupling strength in the course of the optical cycle.

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