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Electronic, vibrational, and configurational relaxation of the $F_H(\mathrm{OH}^-)$ center in KBr

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The relaxation after optical excitation of the $F_H(\mathrm{OH}^-)$ center in KBr is studied with a picosecond pump-probe technique for induced transparency. Three different relaxation components can be distinguished: (i) a nearly temperature-independent component decaying in a few ps; (ii) a component which decays slower than 10 ns at all temperatures; and (iii) a strongly temperature-dependent component with a time constant of the order of 100 ps at 50 K and at least 10 ns below 20 K. We observe essentially no effect on the relaxation time of the components under $\mathrm{OH}^- \rightarrow \mathrm{OD}^-$ substitution. Because of its picosecond time scale, its temperature independence, and the Raman measurements presented in an earlier paper, we identify the first component as a radiationless electronic transition during lattice relaxation, which occurs mainly near the first crossing point reached. This corresponds to the excitation of one quantum of the stretch vibration. Because the other components change from induced transparency to induced absorption under probe-wavelength variation, they are very probably not related to electronic relaxation processes. The nanosecond component is interpreted as vibrational relaxation. It appears in the relaxation scans as a result of the influence of the stretch vibration on the electronic absorption. Effects of the probe power on the relaxation measurements below 30 K, show that also optical conversion between the two KBr:$F_H(\mathrm{OH}^-)$ configurations is involved in the relaxation process. These configurations possess different electronic absorption bands and are essentially different orientations of OH^- with respect to the F center. The third, strongly temperature-dependent component is associated with the recovery of the thermal equilibrium between these configurations. [S0163-1829(96)03434-0]

I. INTRODUCTION

This is the third in a series of three papers, in which the relaxation properties of the $F_H(\mathrm{OH}^-)$ and $F_H(\mathrm{OD}^-)$ center in KBr are studied. In the previous papers (Ref. 1, referred to here as paper I, and Ref. 2, or paper II) the vibrational frequencies and populations of the impurity ion were studied by means of infrared absorption and resonant Raman scattering. In this paper time-resolved measurements on the relaxation processes of the F_H centers are presented.

In most alkali halide hosts, efficient radiative relaxation occurs after optical excitation of the F center.[3] The emission can be quenched by radiationless relaxation processes. In the case of the *crossover* process, the F center returns to the electronic ground state *during* the lattice relaxation in the excited state. The Dexter-Klick-Russel criterion[4,5] states that this occurs near the crossing point between the potential energy curves of the ground and excited electronic states, if the crossing-point energy is lower than the energy reached after optical excitation.[5–8] If the lattice relaxation is fast the crossover process may be avoided, so that the relaxed excited state (RES) is reached. From the RES the second type of radiationless relaxation can occur, *horizontal vibronic tunneling*, occurring *after* the lattice relaxation.[9–11] The two processes can be distinguished by time-resolved measurements of the ground-state recovery, because the crossover process must occur on the time scale of the lattice relaxation (100 fs–10 ps), while the horizontal vibronic tunneling process may be much slower.[11,12]

The F-center luminescence can also be quenched by aggregation of the F center to an impurity with a high-frequency intramolecular vibration, such as OH^-, OD^-, and CN^-. In hosts with the NaCl structure the presence of CN^- impurities does not completely suppress the luminescence,[13] but aggregation of the F center to OH^- and OD^- does.[14–16] Observations of efficient vibrational luminescence of the CN^- ion[13,17] and anti-Stokes resonant Raman scattering (ASRRS) of the OH^- (Refs. 2 and 18) and CN^- ions[19,20] after optical excitation of the F_H-center electron have proven that there is in these cases energy transfer from the F-center electron to the high-frequency internal vibration of the neighboring diatomic impurity [electronic-vibrational (E-V) transfer]. In the case of the $F_H(\mathrm{CN}^-)$, several quanta of the impurity vibration are excited by the energy transfer, accepting most of the available electronic energy.[17] In paper II it was established that in the case of the $F_H(\mathrm{OH}^-)$ center in KBr the excitation of a single quantum is most likely.

As in the case of intrinsic nonradiative F-center relaxation, the question arises whether the nonradiative electronic relaxation in the case of E-V transfer occurs during or after lattice relaxation from the RES. The number of vibrational quanta involved in the E-V transfer process presents a strong indication of the nature of the nonradiative relaxation, for it determines which vibrational levels can be involved. Yet time-resolved measurements are required to determine the nature of the relaxation mechanism. In absence of these measurements, crossover transitions were considered as a possibility to explain the excitation wavelength dependence of the vibrational luminescence for the $\mathrm{F}_H(\mathrm{CN}^-)$ center in CsCl and KCl.[21] Early time-resolved measurements of the electronic relaxation of $F_H(\mathrm{OH}^-)$ centers,[14,22–24] also suggested that a crossover transition might occur. An actual observation of a possible crossover process was presented recently in Ref. 25. A fast relaxation component, with a decay time of about 3 ps, was observed for aggregates of F centers with OD^- and OH^- in KCl and RbCl.

Apart from the nonradiative relaxation processes, the $F_H(OH^-)$ center in KBr has other interesting properties. At low temperatures there is optical bistability between a red-shifted and a blue-shifted absorption band, with peak positions of 587 and 615 nm at 4 K, respectively.[26,27] The different absorption bands have been associated with different orientations of the OH^- ion, which is in a $\langle 200 \rangle$ position with respect to the F center, in units of the interatomic distance.[1,27] This adds a complication to the system, since electronic ground and excited states should be associated with each configuration, as well as vibrational states. At all temperatures, the two configurations are efficiently converted into each other by resonant optical excitation (see paper I and II). Above 10 K the two configurations also convert thermally into one another.[2,26]

The present paper studies the relaxation of the $F_H(OH^-)$ center in KBr by means of a pump-probe technique for optically induced transparency with a higher time resolution than before and with a more systematic temperature and excitation-wavelength variation. In Sec. II the experimental technique is discussed. The induced-transparency data are presented, and a possible interpretation discussed, in Secs. III and IV. We present our conclusions in Sec. V.

II. EXPERIMENTAL DETAILS

The optically induced transparency technique uses two pulsed laser beams to observe the relaxation of the system.[28,29] First, a small fraction of the centers is excited by a pump pulse. Due to the decrease of the ground-state population, the transmittance of the sample increases, and this is detected by a delayed probe pulse. The pump-pulse induced intensity change of the probe pulse is measured as a function of the delay time between pump and probe pulse. We used two different experimental setups. In the first one a mode-locked Ar^+ laser synchronously pumps one or two Rhodamine-6G dye lasers. If a single dye laser is used for both pump and probe, the time resolution is about 7 ps. When different dyes lasers are used for the pump and probe beam, jitter reduces the resolution to 20–30 ps. The advantage of using two different lasers is that the tuning range of the R6G lasers (575–640 nm) allows us to pump and probe preferentially either of the two configurations of the $F_H(OH^-)$ center. In the second setup a single dye laser is pumped by a pulse-compressed frequency-doubled Nd:YAG-laser, which yields a time resolution of 0.5 ps. Phase-sensitive detection is applied, with a high-frequency modulation of the pump beam (10 MHz) and a low-frequency modulation of the probe beam (560 Hz). Since the phase adjustment of the high-frequency lock-in amplifier depends on the relaxation time, a slow and a fast relaxation channel cannot be detected in phase simultaneously.[29] For a determination of the relative amplitudes of the relaxation components, two scans have to be performed with a phase difference of 90°. One should also take into account the accumulation effect of the excitation, when a component decays slower than the repetition period of the excitation pulses. At a pulse repetition rate of 82 MHz and a pump beam modulation frequency of 10 MHz, the amplitude of slow components can be increased by up to a factor 1.6.[11]

Since one is pumping and probing an electronic absorption band, one expects primarily to observe electronic relaxation processes. But even in the case of the unperturbed F center other processes have to be considered. Each kind of excitation that affects the electronic absorption contributes to the measurements. Because of the strong electron-lattice coupling, the probe beam can only be absorbed again when the lattice is near its equilibrium for the electronic ground state. This means that also lattice relaxation is involved. In the case of a crossover transition, the lattice relaxation is the rate-limiting process, rather than the electronic transition.[29] The $F_H(OH^-)$ center possesses several additional degrees of freedom: (i) The excitation of the stretching mode of the impurity may have an effect on the absorption band of the neighboring F center, as was observed for the $F_H(CN^-)$ in CsCl.[30] Therefore, vibrational relaxation of the stretching mode, which occurs on a time scale of at least several nanoseconds,[2,31] could be visible in our measurements. (ii) The OH^- also has a librational degree of freedom, which may be of importance. (iii) Because this F_H center has two configurations with different absorption bands, one may expect a contribution from the efficient optical conversion between these two configurations. One should realize that the latter three contributions induce a transient shift of the electronic absorption, rather than transient bleaching. This means that depending on the wavelength of the probe beam, they are observed as induced transparency (positive sign) or induced absorption (negative sign). The experimental setup only enables one to determine the *relative* sign of different relaxation components.

The OH^- and OD^- doped KBr samples were grown at the University of Utah, or supplied by the University of Osnabrück. The OH^- doped samples had a concentration slightly below 10^{-3} mole fraction. The crystal with the OD^- doping (8.8×10^{-4} mol) also contained a fraction of OH^- (1.5×10^{-4} mol). The sample preparation and optimal $F\rightarrow F_H$ conversion are discussed in paper II.

III. ELECTRONIC RELAXATION

A. Experimental observations

Figure 1 summarizes the results of the ground-state recovery measurements with 0.5-ps time resolution. In the decay of the $F_H(OH^-)$ and $F_H(OD^-)$ center, there is a fast relaxation component with a time constant between 1.5 and 3 ps and an amplitude which can exceed 50% of the total induced transparency. Within the experimental error, this time constant is independent of temperature and is not affected by isotope substitution. Considering our care to prevent the formation of unwanted aggregate centers and the large amplitude of the fast decay component, we can attribute it only to the $F_H(OH^-)$ center. We also verified that there is no such fast component in undoped KBr, even if a large amount of F-center aggregates is present.

At 5 K, we observe that the decay time of the fast component is about 3 ps when pumping and probing the system at 620 or 600 nm, and about 1.5 ps when probing it at 580 nm. This is true for both the $F_H(OH^-)$ and $F_H(OD^-)$ centers. It indicates a slightly different relaxation behavior of the ‘‘red’’ and ‘‘blue’’ configurations. Because there is optical

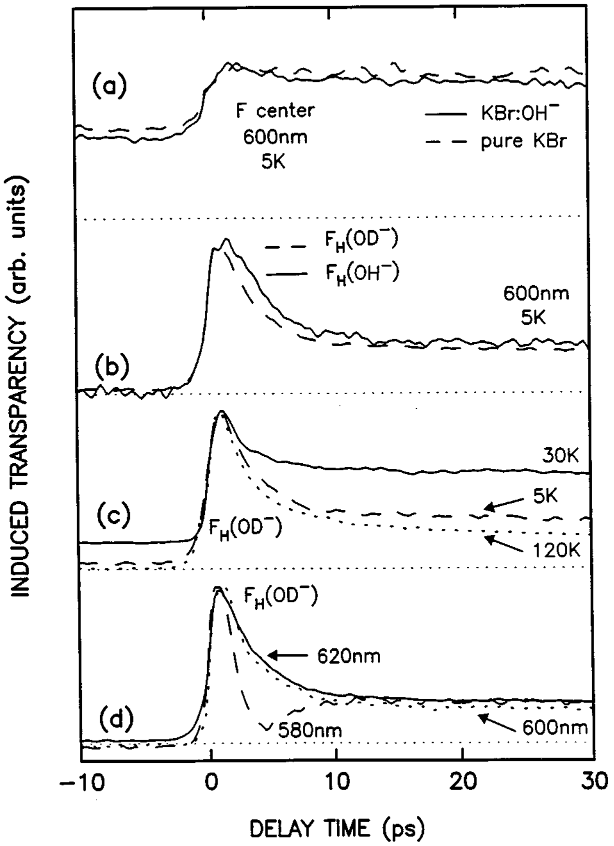

FIG. 1. High-resolution (0.5 ps) induced transparency measurements on $F_H(OH^-)$ and $F_H(OD^-)$ centers in KBr. (a) The relaxation at 5 K of F centers in pure KBr (dashed line) and in KBr:OH^- (full line). The presence of a signal before zero delay time is due to the buildup of a component slower than the repetition time of the laser pulses (12 ns). (b) The relaxation of the $F_H(OH^-)$ center (full line) and the $F_H(OD^-)$ center (dashed line) at 5 K, with an excitation wavelength of 600 nm. (c) Relaxation of the $F_H(OD^-)$ at 5 K (dashed line), 30 K (full line), and 120 K (dotted line), with an excitation wavelength of 600 nm. (d) Relaxation of the $F_H(OD^-)$ center at 5 K, measured at a wavelength of 620 nm (full line), 600 nm (dotted line), and 580 nm (dashed line).

bistability at this temperature, the majority of the F_H centers are expected to be in the blue configuration with the laser at 620 nm, and in the red configuration with the laser at 580 nm. However, the observed signal is the ground-state recovery of a small fraction of excited centers. Because the configuration of a F_H center can be changed in the excited state, we do not know to what mixture of red and blue centers our decay curves correspond.

Apart from the fast electronic relaxation component, we have observed that the relaxation of the $F_H(OD^-)$ center at 5 K, when measured at 580 nm, includes a smaller, fast rise of the induced transparency [Fig. 1(d)]. The rise time of this component is about 1.8 ps.

B. Crossover relaxation and E-V transfer

The time scale of the fastest component is in the range of the lattice relaxation, which follows an electronic transition of F centers and other color centers.[32,33] After optical excitation lattice relaxation occurs in the excited state. In principle, this process can be observed and can give rise to (negative) signals in induced-transparency measurements, if the absorption from the excited state overcompensates the reduced absorption from the ground state. This is unlikely, since we observe the fast component when pumping and probing near the maximum of the F_H band, and the oscillator strength associated with this band is fairly high ($f=0.75$).[3] For the undisturbed F center, it is known that the excited-state absorption is found in the near infrared, far away from our probing light.[34]

The lattice relaxation can also be observed in the ground-state recovery measurements, if the electronic relaxation is faster than the lattice relaxation. This is the case when the electronic relaxation occurs near the crossing point between the potential curves of the ground and the excited electronic state, during the lattice relaxation in the excited state.[6] A 10-ps relaxation component observed in the induced-transparency measurements on the F center in NaI was interpreted as a contribution due to this crossover process.[35] For the isolated F center in KBr this process cannot occur, since the crossing point lies above the energy reached after optical excitation. When energy transfer to the stretching mode of OH^- or OD^- occurs, additional potential energy curves have to be considered, which are shifted upwards by a multiple of the vibrational frequency (Fig. 2), as has been tried also for CN^-.[21] They represent an electronic state of the F center with an excitation of the stretch vibration. The additional curves introduce new crossing points with the excited electronic state, which lie considerably lower than the ones of the unperturbed F center.

The parameters for the potential curves were derived from optical-absorption data for the (unperturbed) F center in KBr.[10] Thus, they represent the $1s$- and $2p$-like state, which are most relevant in the case of the crossover process. Some of the aspects that have been neglected are the following: (i) The electronic energies for the pure F center are modified by the presence of the impurity, as is obvious from absorption spectra. (ii) Also, we should include two types of F_H centers with different features, at least for the electronic ground state. (iii) Due to the electric dipole of the molecule the $2p$ states of the F_H center may be split. (iv) It is not known whether the two F_H center configurations remain stable in the excited electronic state. Therefore, it should be stressed that the diagrams of Fig. 2 may only be used to have a rough idea of the relevant energies in the problem.

Because of the high vibrational frequency of OH^- and OD^-, even the crossing point corresponding to one excited vibrational quantum in the ground state is well below the level reached by optical excitation. In principle, any of the new crossing points could cause the fast electronic relaxation that we observe. The efficiency of the transition at a crossing point is determined by the competition between the lattice relaxation rate on the one hand, and the rate of the simultaneous electronic transition of the F center and vibrational transition of the OH^- on the other hand. The lattice relaxation rate is lower near the RES of the F_H center, which is favorable for the crossing points with higher vibrational levels of the OH^- ion. But if the crossover process at earlier crossing points is highly efficient, only a negligible fraction of the excited centers will reach the lower lying crossings.

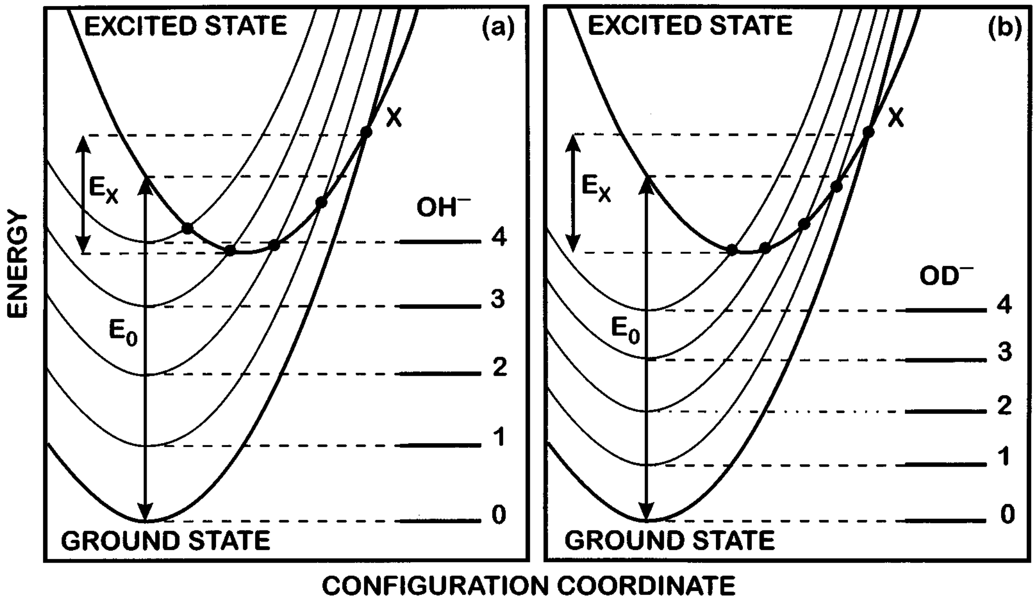

FIG. 2. Configuration-coordinate diagram for the $F_H(\mathrm{OH}^-)$ and $F_H(\mathrm{OD}^-)$ centers in KBr, incorporating the vibrational energy levels of the impurity. The validity and applicability of these diagrams are discussed in the text.

Resonant Raman measurements (see paper II) show that the primary E-V transfer for the $F_H(\mathrm{OH}^-)$ center only excites the vibrational level for the red configuration, while for the blue configuration the transfer efficiency to the level $v=2$ was estimated to be 10% of the transfer to $v=1$. That mainly one quantum is excited in the E-V transfer suggests that the system most often branches to the ground state at the first crossing point. Since for OD⁻ the first crossing point lies higher in energy than that for OH⁻, the lattice relaxation rate is higher and one expects a less efficient population of the first vibrational level of OD⁻ than of OH⁻. Indeed, for the blue configuration of the $F_H(\mathrm{OD}^-)$ a higher probability to populate the second and third vibrational levels was found than for the $F_H(\mathrm{OH}^-)$ center. For the red configuration no difference was observed. In addition, no population of the $v>3$ levels was observed under primary-transfer conditions, although these vibrational levels can be observed under strong repumping, especially for OD⁻. This indicates that the crossover at $v=1$ and $v=2$ is indeed highly efficient. We expect that only a very small fraction of the excited F_H centers reaches the RES.

This model for the relaxation process is also consistent with the very similar relaxation rate observed for OH⁻ and OD⁻, in spite of the completely different energy-level scheme of the vibrational excitations with regard to the electronic transitions: For a crossover transition the rate-limiting process is the lattice relaxation, which is essentially the same in the two cases. The observed temperature independence is also in agreement with the assumption of a crossover process. Conversely, if the RES would be reached in the optical cycle of the $F_H(\mathrm{OH}^-)$ and $F_H(\mathrm{OD}^-)$ centers, different energy barriers would be observed for vibronic tunneling to the ground electronic state and simultaneous excitation of one vibrational quantum of the stretching mode, because of the different crossing-point energies for $F_H(\mathrm{OH}^-)$ and for $F_H(\mathrm{OD}^-)$. The exponential dependence on the energy barrier[11] then implies a very strong isotope effect on the electronic transition rate, in contrast to the observations. And because the energy barrier is also the thermal activation energy for the tunneling process from the RES, it is also implied that the relaxation would be temperature dependent. Of course the presence of crossing points near the RES could cause the relaxation of this state to be so fast, that the rate-determining process for the ground-state relaxation is again the lattice relaxation. However, in this case the excitation of higher vibrational levels of the impurity ion would be more likely. In particular, the crossing points for transfer of two OH⁻ quanta and three OD⁻ quanta nearly coincide with the RES in Fig. 2. The excitation of these levels in the primary E-V transfer is very small (see paper II).

Some caution should be applied in interpreting the time constant of the fast component as the ground-state recovery time. For a simpler system, such as the pure F center in NaI, one can assume that the lattice relaxation is the rate-determining process for the ground-state recovery, and identify the measured time constant with this lattice relaxation.[11,12] The $F_H(\mathrm{OH}^-)$ center is a more complicated system, because each configuration of the F_H center possesses its own set of electronic levels, coupled to the vibrational levels of the impurity. If one solves the set of rate equations of a model for this center, such as those presented in Fig. 3, one finds solutions which depend on combinations of the different relaxation rates of the system. The quantitative interpretation of the observed relaxation times depends on the relaxation scheme presumed for the F_H center.

In addition, there is the small, fast rise of the induced transparency observed in Fig. 1(d), that is yet unidentified. It can be assumed that this component could also appear with a positive amplitude, in which case can probably not be distinguished from the electronic relaxation itself. This might be partially responsible for the observed wavelength dependence of the relaxation rate.

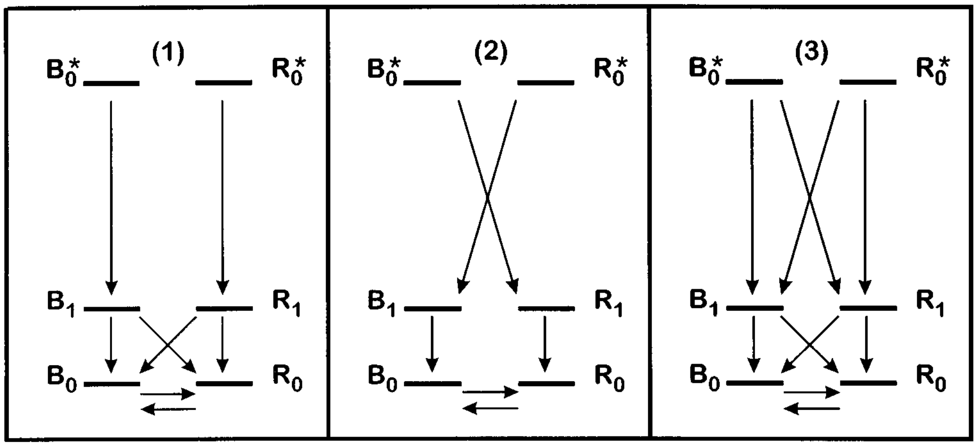

FIG. 3. Some possible models for the $F_H(\mathrm{OH}^-)$ center, illustrating electronic and vibrational relaxation. The levels of the red configuration are labeled R, those of the blue B. The subscripts indicate the vibrational state, the superscript * the electronic excited state.

IV. SLOW RELAXATION COMPONENTS

A. Experimental observations

Besides the fast component discussed in the previous section, there are slow components visible in Fig. 1. To study these, we present measurements with a lower time resolution ($\approx$30 ps) but a longer delay range (1600 ps). Figures 4(a) and 5 show a set of ground-state recovery curves observed at 50 K. The data were recorded with the pump laser at 580 and 620 nm, resonant primarily with the blue and red configurations, respectively. The probe wavelength was varied over the tuning range of the R6G dye laser. Similar measurements were performed for several temperatures between 5 and 90 K. Both the pump and the probe beam have an average laser power of about 10 mW, typically. The phase adjustment of the high-frequency lock-in amplifier is performed at the the end of the scan, so that the slowest component is in phase. The amplitude of the fast component is reduced by this procedure and by the low time resolution. The corresponding scans 90° out of phase were also recorded to account for the phase error. Since we are arguing here mainly on the time scale of the relaxation, we displayed only the in-phase measurements.

In the case of anisotropy in the sample, the relaxation measurements can depend on the polarization of the pump and probe pulses. Anisotropy may be due to the nature of the sample itself, or can be caused by the incident light. Induced transparency measurements were recorded with parallelly polarized and with perpendicularly polarized pump and probe beams, and did not yield a polarization dependence in samples of good quality.

Three different time scales are observed in the decay of the induced transparency. Of course, one cannot separate components slower than the limited time delay range (1600 ps) of the experimental setup or faster than the 20-ps resolution. There is a very slow contribution, decaying on a time scale of nanoseconds or even tens of nanoseconds. Its amplitude is positive or negative, depending on the probe wavelength. The sign of a second component with a time constant of a few hundreds of picoseconds at 50 K also changes, when varying the wavelength of the probe beam. Finally, the fast electronic relaxation can be seen in some scans, e.g., the one recorded with the pump beam at 580 nm and the probe beam at 620 nm.

In Sec. III it was argued that the fast 3-ps component, associated to electronic relaxation and the associated lattice relaxation, corresponds to induced transparency (positive signal). In the decay scans with 30-ps time resolution this component is observed as a small unresolved peak at probe wavelengths between 610 and 630 nm. We assigned a positive sign to the small transient peak and then determined the sign of the other scans by requiring a gradual change of the amplitudes with probe wavelength. A negative contribution does not necessarily imply that the total signal becomes negative at a particular time delay. Rather, there is a rise time for induced transparency associated with it instead of a decay time.

The slowest and the intermediate relaxation component are the dominant contributions visible on Figs. 4 and 5, due to the limited time resolution in this case. With higher resolution (Fig. 1) it is clear that their actual contribution is only 50% or less, at least under the excitation conditions used. The observed amplitude of the slow components in Figs. 4 and 5 is exaggerated by the phase adjustment and by the the accumulation effect of several excitation pulses at a modulation frequency of 10 MHz.

The ''intermediate'' component with a time constant of the order of 100 ps at 50 K, as visible on Figs. 4 and 5, is always positive when the pump laser is at 620 nm. With the pump laser at 580 nm, its amplitude becomes negative at wavelengths above 615 nm. The amplitude of the slowest relaxation component, with a time constant of the order of nanoseconds or tens of nanoseconds, is positive if the probe is on the red side of the F_H bands and negative if the probe is on the blue side.

For a correct analysis of the wavelength dependence in Figs. 4 and 5, one should consider the following. The average concentrations of red and blue centers, as seen by the pump and probe beam in the time-resolved measurements, are determined by the balance between optical and thermal reorientation. At each wavelength and power setting of the probe pulses the average concentration of red and blue cen-

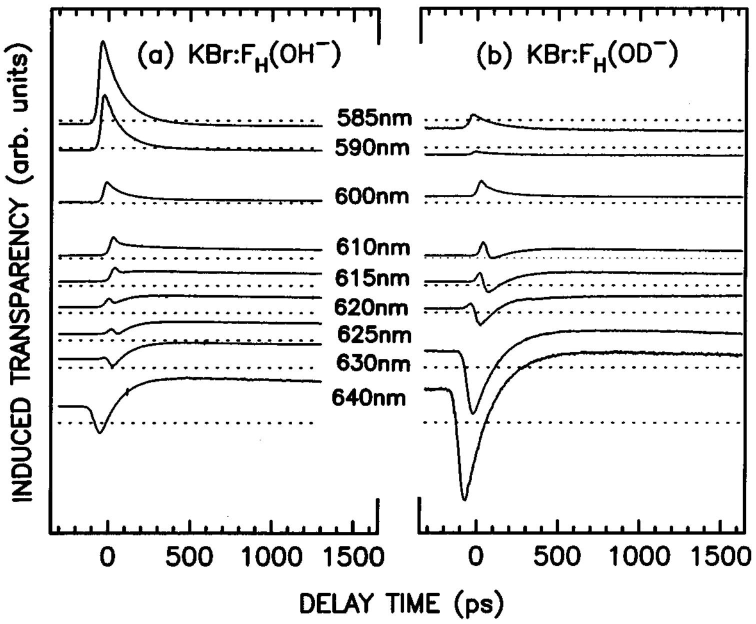

FIG. 4. Induced transparency measurements on (a) the $F_H(\mathrm{OH}^-)$ center and (b) the $F_H(\mathrm{OD}^-)$ center in KBr, at 50 K. Because of the use of different lasers as source for the pump and probe pulses, the resolution is about 30 ps. The pump pulse is at 580 nm, the probe pulse is varied as indicated with the scans.

ters is different. Therefore, the induced transparency signal at a fixed time delay as a function of probe wavelength cannot be interpreted directly as the change of the absorption spectrum induced by the pump beam. This remark is only relevant as long as optical conversion is not negligible with respect to thermal conversion. Resonant Raman measurements show that thermal conversion dominates above 25 K (see paper II).

Figure 6 presents the temperature dependence of the induced-transparency scans with both the pump and probe wavelength at 600 nm. At low temperatures, this wavelength is almost equally resonant with the blue and red configuration of the F_H center. At higher temperatures the bands shift towards the red, and the laser is primarily resonant with the blue center. The experimental data thus show a combination of temperature and wavelength dependence, which should be taken into account. At 5 and 10 K, the presence of the 3-ps component is visible, but it is not seen at higher temperatures. A comparison with Fig. 1(c) shows that the relative amplitude of the fast component is indeed much lower at 30 than at 5 K. The decrease of its relative amplitude is probably linked to the increasing effect of thermal reorientation. The two other components are both very slow below 20 K and are indistinguishable. One of them, which we will call the intermediate component, becomes faster than the maximum optical delay with increasing temperature. Above 50 K we can easily separate it from the slowest contribution. At 40 K, it is about 700 ps; at 50 K this decreases to 300 ps and at 60 K to 80 ps. Above 70 K, the experimental resolution determines the shape of this component.

We also measured the ground-state recovery of the the $F_H(\mathrm{OD}^-)$ center [Fig. 4(b)]. The results are very similar to those for $F_H(\mathrm{OH}^-)$. There is some isotope effect on the amplitude and sign of the two slower components, but the decay times do not change significantly. Raman measurements revealed that there is an important difference between the $F_H(\mathrm{OH}^-)$ and $F_H(\mathrm{OD}^-)$ centers: Either the vibrational lifetime of the OD^- is considerably longer than that of the OH^-, or the transfer efficiency is higher (See paper II). For $F_H(\mathrm{OD}^-)$ this results in a repumping of the electron before the OD^- has relaxed vibrationally from previous E-V transfer events, even at low laser powers. In the delay measurements the total average laser power incident on the sample is about 20 mW, which is large enough to cause some repumping. Although the Raman measurements were performed with a cw laser beam, the result remains relevant, since the

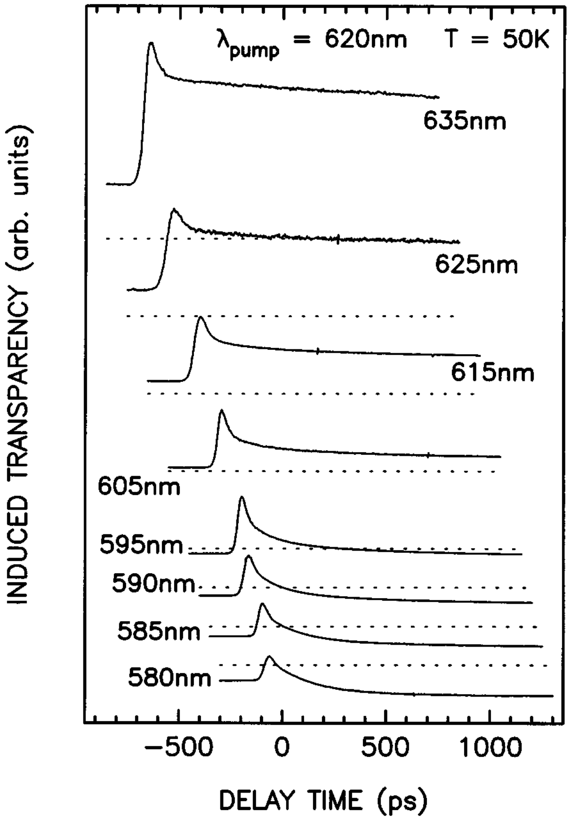

FIG. 5. Induced transparency measurements on the $F_H(\mathrm{OH}^-)$ center, complementary to those of Fig. 4(a). The pump pulse is now at 620 nm.

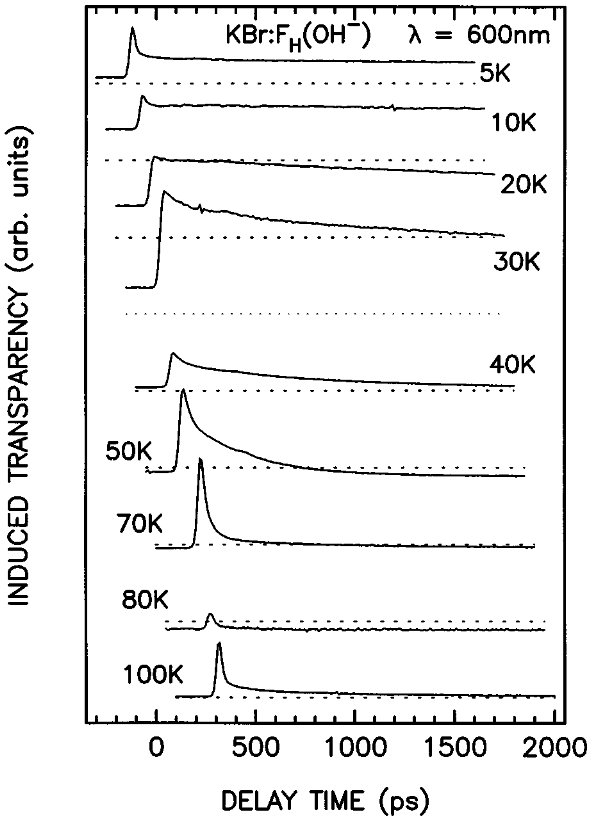

FIG. 6. Temperature dependence of the ground-state recovery of the $F_H(\mathrm{OH}^-)$ in KBr, recorded with both pump and probe at 600 nm and with a resolution of about 30 ps.

repetition period of the pulses used here is shorter than the estimated vibrational lifetime of OD^-. Apparently, the repumping present for OD^- has no significant effect on the time constants, but could be responsible for the somewhat different amplitudes. The difference in vibrational relaxation times also has an effect on the phase adjustment of the lock-in amplifiers, so that the observed relative amplitudes of slow and fast components are different.

B. Elimination of slow electronic contributions

We have to consider possible weak effects arising from small amounts of unwanted centers, which might explain the presence of the slow components. The luminescence quenching and the absorption spectra indicate that the large majority of the F centers are aggregated to an OH^- or OD^- impurity. However, these are not sufficient to exclude ''loose pairs,'' i.e., stable combinations of F centers and OH^- impurities at a distance which is larger than in the $F_H(\mathrm{OH}^-)$ center. The luminescence of the F center is quenched by the OH^- even before an F_H aggregate center is created.[14,16] Indeed, the anti-Stokes Raman spectra in paper II show that there is E-V transfer from F centers to impurities, whose frequency is not affected by the nearby presence of an F center. Time-resolved measurements of the decay of F centers in doped samples *before* aggregation,[16,22] show a wide range of relaxation components. The luminescence of the F center will of course be quenched by any relaxation process on a time scale sufficiently faster than the *radiative* relaxation time of the F_H center, which can be of the order of microseconds. The $F \rightarrow F_H$ conversion process will produce mainly the stablest pairs, which can be expected to have a small F-OH^- distance and thus a relatively fast radiationless relaxation. The measurements presented in paper II show that for at least a fraction of the ''loose pairs'' there is an energy transfer to the OH^- ion of similar nature as for the F_H center, because mainly the first and second vibrational levels are populated by the primary transfer. This suggests that the radiationless relaxation of these centers could be similar, i.e., a crossover process, which would imply a very fast (≤ 10 ps) relaxation component for these loose aggregates. But there is no conclusive evidence in this direction, nor is there any evidence that such an E-V transfer occurs in *all* remaining loose F-OH^- pairs. A comparison between the relaxation processes in partially and completely aggregated samples provides no evidence for an additional relaxation component in partially aggregated samples. At least we know that the contribution from the electronic relaxation of these unaggregated F centers is not expected to have a negative sign. Thus it cannot provide a complete explanation for the observed slow or intermediate components, although it could contribute to the observed amplitude of these components.

The small amount of F_2 centers present in the sample can be excited by their absorption band underlying the F_H-center band. However, for the F_2 concentrations in our samples the absorption strength is $\leq 3\%$ of that of the F_H-center band, and so will be its contribution to the induced-transparency measurements. A slow, negative component has been observed in undoped KCl containing F centers and a large concentration of F-center aggregates.[36] It was tentatively attributed to electronic energy transfer from the F center to F_2 centers, creating the triplet F_2 center, that has absorption bands underlying the F band. We performed ground-state recovery measurements in the F-center band of an undoped KBr crystal containing a much larger amount of F_2 centers and other F-center aggregates than was present for the measurement of Figs. 4 and 5. Effects as observed for KCl, were not present for KBr, neither were they present in doped KBr crystals before $F \rightarrow F_H$ conversion. For the F_H center the electronic relaxation is much faster than that of the unperturbed F center, strongly reducing the probability of energy transfer to F_2 centers after $F \rightarrow F_H$ conversion.

Measurements on the intrinsic luminescence quenching of the F center in NaBr revealed a relaxation component, attributed to the conversion of F centers to F^- centers and recapture of conduction electrons.[12] Even in undoped KBr, maximally 10% of the F centers can be converted to F^- centers below 90 K at low F-center concentrations.[37] The presence of OH^- impurities reduces the ionization efficiency, even before optical aggregation.[14,16] Therefore, we can exclude that electron tunneling from the excited F center to a neighboring F center, which occurs at high F-center concentrations, causes a high ionization efficiency in our case. It has been observed that electron transfer can occur between the F center and the OH^-, but only for some F-OH^- pairs, which have to be at a relatively large distance from each other.[38]

On the basis of the time scale of the 3-ps component and the distribution over the vibrational levels due to the E-V transfer, it was concluded that crossover processes are probably observed. One may consider the case that the probability of avoiding the crossing points is nonzero. Additional relaxation components on a time scale slower than the lattice relaxation can then occur due to electronic nonradiative relaxation from the RES. Such a simultaneous observation of a crossover process and a transition from the the RES was, e.g., proposed for the intrinsic nonradiative relaxation of the F center in NaI.[35] However, since both the intermediate and slow component have a negative sign somewhere in the wavelength range between 595 and 620 nm, they are probably not related to electronic relaxation: It was argued in Sec. III that excited-state absorption, associated with the negative sign of electronic relaxation, is not likely to be observed so close to the F_H-band maximum. In the same section it was explained that a large isotope effect would be expected for transitions from the RES on a time scale longer than lattice relaxation, because different tunneling barriers result from the energy-level scheme. For the intermediate relaxation component only a small difference is observed.

C. Vibration, libration, and reorientation of the impurity

Since none of the slower components can be associated with electronic relaxation, we have to consider the vibrational and rotational excitations of the impurity molecule that could modify the ground-state absorption properties of the F_H center. Librations of the OH^-might accept part of the energy released by the nonradiative relaxation of the electron. But it is not very likely that the librational mode, with an energy of about two optical phonons, would have a lifetime as large as $\sim$100 ps or longer. The linewidth of the undisturbed OH^- librator in KBr is of the order of 10 cm^{-1} at very low temperatures and is associated in Ref. 39 with lifetime broadening. This would imply a lifetime of the order of 1 ps. One could speculate that the libration is responsible for the small, fast component with a negative sign, apparent in Fig. 1(d) (Sec. III). But it cannot be responsible for the slower components.

The strong temperature dependence and the subnanosecond time scale of the intermediate relaxation component above 50 K are in contrast with the known features of the vibrational relaxation of the stretching vibration.[2,31] The stretching vibration of the impurity ion, with a lifetime of at least several nanoseconds, may be the cause of the slowest relaxation component. All estimated lifetimes for this vibration are well above the length of the delay stage (see paper II).

The vibrational relaxation can play a role in the ground-state recovery in several ways. (i) The excitation itself of the stretching mode of the OH^- can cause changes in the ground-state absorption. A similar effect has been experimentally observed for the $F_H(CN^-)$ center.[30] (ii) The relaxation of the stretching vibration creates librational modes. Even if the vibration itself does not modify the ground-state absorption, the librational or rotational excitation created by vibrational relaxation may do so. This would result in a slow component, because the vibrational relaxation of the stretching mode is the rate-determining process. However, the population of the librational modes is expected to be negligible, because of its short lifetime. (iii) The decay of the stretching mode can cause reorientation of the OH^-, with the associated change in absorption. About 3600 cm^{-1} of energy is dissipated into rotational degrees of freedom, and the rotational barrier for the OH^- is assumed to be less than 1000 cm^{-1}. Reorientation of the molecule is a likely consequence. Similar as in the previous case the effect would be small, if the thermal reorientation is faster than the vibrational relaxation.

This brings us to the important question of how and when the optical reorientation of the OH^- ion takes place. The infrared-absorption measurements of paper I have shown that this a very efficient process, with quantum efficiencies $\eta_{b\rightarrow r}$ and $\eta_{r\rightarrow b}$ of the order of 0.6 and 0.3, respectively. For clarity, we will enumerate the possibilities. We illustrate them in Fig. 3.

(1) The optical excitation and subsequent nonradiative relaxation of the $F_H(OH^-)$ center excites the stretching vibration of the ion, but does not directly induce reorientation nor excitation of the librational mode. The slow component is then associated with the vibrational excitation. On a nanosecond time scale, it is converted into librations or rotations, causing reorientation of the OH^- ion. If thermal reorientation is relatively slow, a relaxation component related to it could then be present after vibrational relaxation.

(2) The reorientation of the OH^- occurs during the rapid electronic excitation and deexcitation cycle. It could be, e.g., a consequence of the dissipation into phonons of most of the electronic energy. In this case, thermal reorientation can be experimentally observed immediately after electronic relaxation, because the thermal equilibrium between the two configurations has been disturbed.

(3) A combination of the previous possibilities may occur: The optical excitation and subsequent nonradiative relaxation as well as the vibrational relaxation initiate a reorientation.

D. Dependence of the ground-state recovery on laser power

Contributions of optical reorientation processes may be identified by their effect on the relative concentrations of the red and blue configurations of the F_H center. The higher the laser power, the larger this effect will be. The dependence of the ground-state recovery signal on probe power is presented in Fig. 7 for temperatures of 5 and 65 K. For easy comparison, the induced-transparency signal was divided by the pump and probe power. At 65 K the induced-transparency measurements are apparently proportional to the probe power. Since electronic saturation effects are avoided by the use of low excitation power, this is expected if the concentration of the centers is essentially independent of power. At 5 K, however, the amplitudes of the very fast relaxation component and of the slower components (which are indistinguishable at this temperature) are not proportional to the laser power. Even the sign of the slow contributions can change under probe-power variation. At 600 nm there is induced transparency with a 6-mW probe, and induced absorption with a 1-mW probe. At 590 nm the sign effect is opposite to the one observed with a 600-nm probe. At 610 nm

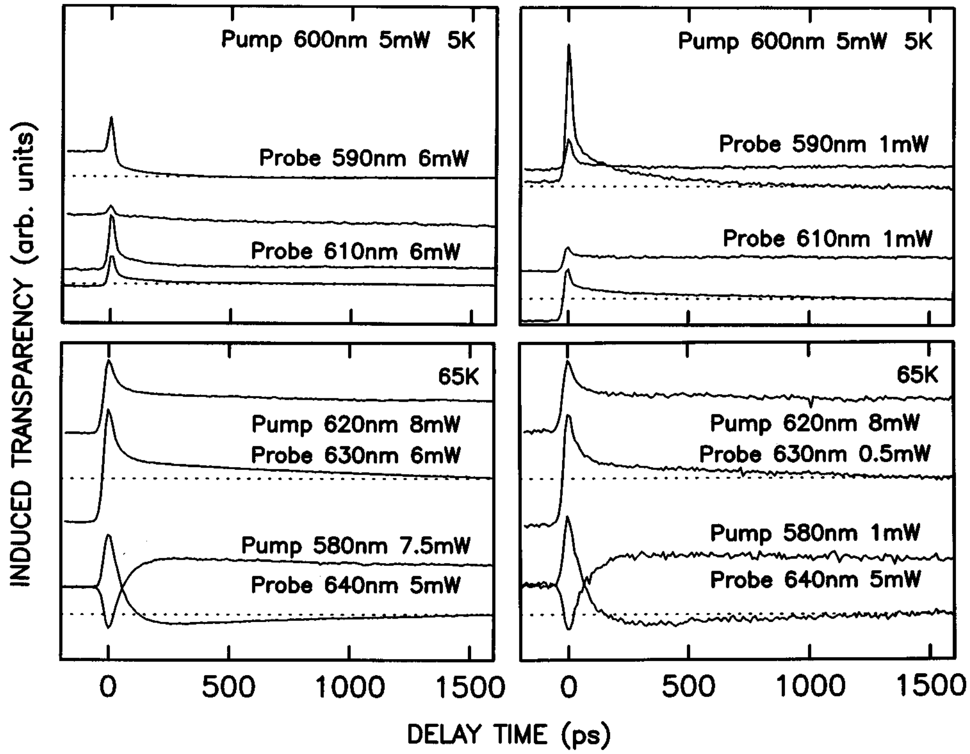

FIG. 7. Dependence on probe laser power of the ground-state recovery measurement, at temperatures of 5 and 65 K. The intensity is normalized by dividing it by the probe power.

there is induced transparency for both probe powers. A similar series of measurements at 20 K shows that the probe-power effect increases when the difference between pump and probe wavelength increases. The effect decreases with increasing temperature and from 30 K on it is essentially absent. It is observed for both OD^- and OH^- doped samples.

The effect at low temperatures shows that the concentration of centers is modified by changing the probe power. The repumping of F_H centers before vibrational relaxation could provide an explanation. A power increase changes the population of the levels of the stretch vibration (see paper II). Since an F_H center with an oscillating impurity molecule may have different electronic relaxation properties than an F_H center with the molecule at rest, a power dependence can be understood in this way. But although there is still a slight repumping observed in the ASRRS measurements on KBr:$F_H(OD^-)$ at the powers used for the induced-transparency measurements, it is absent in the case of KBr:$F_H(OH^-)$. Since the probe-power effect is observed for both isotopes, the repumping possibility is ruled out.

The two different configurations of the F_H center can be optically converted into each other, but also relax to a thermal equilibrium distribution above 10 K. On this system we focus two series of laser pulses at different wavelengths, one with a low-frequency modulation and one with a high-frequency modulation. This will cause a complicated behavior. For simplicity, consider the situation at very low temperature, where thermal relaxation is absent. Let, e.g., the probe pulse be resonant primarily with the blue configuration, and the pump pulse primarily with the red configuration. With increasing probe-beam power the concentration of the red configuration will be higher. A higher number of centers will thus be excited by the pump beam and a different fraction of the excited centers will be converted to the other configuration. At temperatures above the bistability range, the probe and pump pulses not only compete with each other but also with the thermal relaxation. If the thermal reorientation at elevated temperatures is faster than the optical reorientation caused by the probe, the signal is no longer dependent on the power of the probe pulses.

The interpretation of the power effect as a consequence of optical and thermal reorientation of the F_H center is supported by the following arguments: (i) The equilibrium concentrations under a weak probe beam and a stronger pump beam are expected to be different than those in the case of comparable power for the two beams. (ii) The effect is expected to be largest if the equilibrium imposed by the probe beam alone is as different as possible from the one imposed by the pump beam alone. This is the case when the probe beam is resonant with a different F_H-center configuration as the pump beam. This agrees with the increased probe-power effect with increasing difference between pump and probe wavelength. (iii) The effect disappears from 30 K on, where the thermal reorientation rate is increased. This agrees with the conclusion from the Raman-scattering measurements that with similar excitation powers the thermal reorientation dominates the optical conversion above 25 K (cf. paper II).

After having established that the optical reorientation of the molecular impurity indeed affects the induced-transparency measurements, we should still assign it to one of the relaxation components observed at higher temperatures. By an argument of elimination, one would conclude that the intermediate component, with a time constant of the order of 100 ps at 50 K, is related to the thermal reorientation: Vibrational relaxation can only be associated with the slower component, which decays at all temperatures in at least several nanoseconds (see paper II). The intermediate relaxation component exhibits an essential feature of the thermal reorientation of the impurity molecule. Since the probe-power effect on the induced-transparency measurements disappears at temperatures of about 30 K, one expects that the reorientation rate is strongly temperature dependent there. This is true for the intermediate component and its time scale drops below the nanosecond time scale (Fig. 6).

One may wonder whether a thermal reorientation time of the OH^- molecule of the order of 100 ps at 50 K can be expected. The reorientation of the free OH^- depends strongly on the host lattice. For KBr:OH^- it occurs on a time scale of 10 μs at 1.3 K, but in KCl at the same temperature the time is 10 ns. This suggests that the reorientation rate is very sensitive to perturbations, such as the presence of an F center. The OH^- tunneling can therefore be quite different for the F_H center than for the free OH^-. One should realize that the value we observe here is the reorientation rate for the *vibrationally excited* OH^- ion, which might also be different. The reorientation rate of the free OH^- also exhibits a strong temperature dependence.[40] Below 5 it is proportional to T, with a similar dependence in various hosts. Between 5 and 15 K it was found to be proportional to T^4 in RbBr. If we extrapolate this to higher temperatures, we find a reorientation rate 10^3 faster at 50 K than at 10 K. Reorientation rates of the order of magnitude of 100 ps at 50 K are thus not unrealistic. The vibration of the K^+ ion between the F center and the OH^- might also have an important role in the conversion of the two configurations into another, because its average position is different in either of them. Little is known about this vibration, but it is assumed to be soft, so that it would be easily excited at higher temperatures.[27]

The relaxation time of the intermediate component, which we associated with the reorientation rate, is very similar for OH^- and OD^-. One may expect that the different librational frequencies and masses of the OH^- and OD^- result in different reorientation rates. However, the lattice distortion around the ion, that is thought to be of critical importance for its reorientation rate,[40] is expected to be very similar for the two isotopes.

It is an important observation that the thermal reorientation component that we have identified occurs *immediately after* the fast electronic relaxation (Fig. 4). This proves that at least part of the reorientation of the impurity ion is done during the fast electronic relaxation, of course without excluding that the decay of the OH^- stretch vibration induces additional reorientation. In Sec. III we have mentioned that the observed decay time of the fast component at 4 K depends on the excitation wavelength. This indicates that the optical reorientation process is not random, i.e., the mix of configurations that returns to the ground state does depend on the relative presence of the configurations before excitation. This implies that the fitted 1.5 and 3 ps relaxation times, which result from a fitting of the decay curve to a single exponential, actually represent different superpositions of at least two different relaxation components.

V. CONCLUSIONS

To explain the isotope effect and the temperature, excitation-wavelength, and power dependence of the time-resolved induced-transparency measurements, we propose the following picture of the relaxation of the $F_H(OH^-)$ center. After optical excitation, the F_H center relaxes within a few picoseconds to the electronic ground state by an electronic relaxation during the lattice relaxation. At the same time the OH^- stretch vibration is excited, mainly to the level $v=1$, which corresponds to the first crossing point reached during lattice relaxation. Still, one should be able to show that the electronic transition rate near the first crossing point is large enough to be competitive with the very fast lattice relaxation so closely after optical excitation, in particular in the case of $F_H(OD^-)$. Host-crystal variation may have important effects on the E-V transfer and the mechanism of the electronic relaxation, since the position of the crossing point with respect to the energy reached after optical excitation is varied.

Closely after the electronic relaxation, some of the OH^- impurities appear to be reoriented. The efficiency of this fast optical reorientation is unclear as yet, as well as the way it occurs. It might occur during the lattice relaxation within the electronic excited state. Lattice relaxation implies an outward shift of the nearest neighbors of the F center. In particular the motion of the K^+ cation between the F center and the OH^- might stimulate the reorientation of the OH^-, since the position of this ion is closely related to the orientation of the OH^-.[27] It is also possible that the reorientation is related to the electronic transition itself: the libration of the OH^- might accept some of the energy that is dissipated by this process, or even act as a promoting mode for the transition.[14]

Below 30 K, the OH^- remains in its new orientation for at least several nanoseconds, whereas at 50 K thermal reorientation occurs on a time scale of the order of 100 ps. Our interpretation of this relaxation component could be confirmed by comparing time-resolved measurements on $F_H(OH^-)$ in different host lattices. Strong differences are expected between host lattices in which the $F_H(OH^-)$ center possesses only one configuration on the one hand (KCl), and hosts in which it possesses two configurations on the other hand (KBr, RbBr, and KI).

The third component is associated with the relaxation of the stretch vibration, which is excited by E–V transfer. Since the stretch vibration probably decays into librations and rotations,[31,41,42] one can expect reorientation of OH^- after vibrational relaxation. The short time scale we are looking at does not allow us to confirm this. Neither is it possible to determine whether the reorientation due to the decay of the stretching mode, or the one connected to the electronic transition is responsible for the large quantum efficiency of the optical conversion between the two configurations of the $F_H(OH^-)$ center. Measurements on a longer time scale than possible with our technique would allow a better comparison of the time constant of this relaxation component with the measured[31] and estimated[2] values of the vibrational lifetime of OD^- and OH^-. In particular it would be interesting to observe whether OH^- has a much shorter vibrational lifetime than OD^- in the F_H center. This was one of the possible explanations for the much weaker anti-Stokes resonant Raman spectrum for OH^-.

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