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Vibrational relaxation of the F center in NaI and NaBr

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High-resolution Raman measurements have been performed to study the coupling of lattice modes to the F center in NaBr and NaI. In both cases, a prominent line near or in the region of the energy gap between the acoustic and optical phonon bands dominates the Raman spectrum. Its linewidth was measured and extrapolated to 0 K it turned out to be about 3 and 0.5 cm^{-1}, respectively, for NaBr and NaI. These values are related to the lifetime of the local vibrational excitations, showing a relatively fast vibrational relaxation. Calculating the nonradiative transition probability during the vibrational relaxation in the electronic excited state, the efficiency of reaching the relaxed excited state (RES) of the F center is analyzed. The calculations show that, if the experimental value of the vibrational lifetime is used, the model predicts a high probability of reaching the RES in the case of NaBr. In the case of NaI the prediction strongly depends on the choice of the electronic matrix element for the interstate nonradiative transition. By comparison with similar cases of vibronic transition matrix elements reported in the literature, the efficiency of reaching the RES in NaI is expected in the range 0.05 to 1.

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I. INTRODUCTION

The optical properties and the radiationless transitions of the F center in alkali halides (an electron bound to an anion vacancy) are determined to a large extent by the influence of the strong coupling of the electron to several lattice modes whose energy spectrum can be measured by resonant Raman experiments. The optical cycle of the F center is presented in Fig. 1 within the commonly used configurational coordinate scheme. After optical excitation E_0, the system undergoes a vibrational relaxation E_R to a new equilibrium state the relaxed excited state (RES) from which luminescence occurs with a Stokes-shifted energy E_e on a μs timescale. The system undergoes again vibrational relaxation towards the equilibrium configuration of the electronic ground state. This typical optical cycle applies to all rubidium and potassium halides and to NaF and NaCl, while a smaller group of crystals, including NaBr, NaI, and the lithium halides, shows a very small efficiency of luminescence. A general criterion for nonradiative deexcitation formulated by Dexter *et al.*[1] (the DKR rule) suggested the following interpretation for this peculiar feature: whenever the level excited by the absorption transition lies at an energy higher than the crossing point of the potential-energy curves of the ground and the excited states (point X in Fig. 1), a nonradiative electronic transition occurs during the lattice relaxation. It was shown that the occurrence or absence of luminescence could be predicted on the basis of the parameters inferred from optical absorption data.[2]

Several theoretical approaches have been adopted to support theoretically the DKR rule and to give a quantitative prediction of the emission efficiency. Bartram and Stoneham[3,4] have given a description in which they assumed at the crossing of potential-energy curves, a very strong mixing of the two electronic states. As a result the system jumps back and forth rapidly between them until it cools down following either the ground- or the excited-state potential curve. Hence the fluorescence quantum efficiency is determined in their model by the branching ratio, the ratio of the vibrational cooling rate in the two electronic states at the crossing point. Leung and Song[5] have performed a calculation in which the radiationless electronic transitions at all vibrational levels reached after optical excitation were considered, while back transitions from the ground state were neglected. Both these treatments rely on the assumption of a slow vibrational relaxation in comparison with the electronic transition. A different approach, based on the Landau-Zener theory, has been exploited considering the classical trajectory of a vibrational wave packet.[6,7] The validity range of this model is complementary to the former one, requiring the coherent superposition of several accepting modes. A review of the models and of the involved processes can be found in Ref. 8.

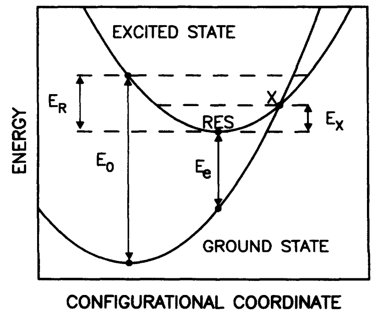

FIG. 1. Configurational coordinate diagram for the ground and excited states of the F center.

A later investigation[9] confirmed the presence of a very weak F-center luminescence in NaBr and NaI. Although the small quantum efficiency agrees with the prediction of the DKR model, the authors argued on the basis of the temperature dependence of the $F \rightarrow F'$ conversion efficiency, that the system reaches the relaxed excited state (RES) before horizontal vibronic tunneling to the ground state occurs.[9,10] The ground-state recovery of the F center in NaBr and NaI has been studied recently with picosecond optical pulses.[11–13] It has been shown to be consistent with a model of radiationless transitions from a thermalized state, i.e., *after* the configurational relaxation.[14]

However, the same measurements do not explicitly contradict the DKR model and could also be interpreted in terms of transitions *during* the configurational relaxation. The tens-of-ns ground-state recovery at low temperature in NaBr and NaI should be associated with the vibrational cooling in this case. Such large values are in contrast with a recent calculation of ionic relaxation around defect centers in the ballistic regime[15] and with measurements of optical phonon lifetimes[16] and configurational relaxation in the excited state of color centers.[17,18] All reported vibrational relaxations occur on a picosecond timescale or even less.[19] In qualitative agreement with the DKR model, however, resonant Raman measurements[20] in NaI and NaBr revealed that mainly one narrow mode coupled to the F-band transition, the width of which has not yet been resolved. As a consequence, the configurational relaxation of the F center in these host crystals could be exceptionally slow. High-resolution linewidth measurements of the narrow Raman-active modes yield information on the timescale of the vibrational relaxation and may decide whether or not the ground-state recovery measurements are associated with the crossover process.

After briefly illustrating in Sec. II the details concerning the experimental setup and the samples, the Raman measurements will be presented in Sec. III. In Sec. III A, the attention will be focused on the narrow spectral lines near the phonon gap, which dominate the Raman spectrum in colored NaI and NaBr. The temperature dependence of their linewidths will be analyzed in Sec. III C and it will be argued that the extrapolated value at zero temperature is related to the relaxation of the local vibrational excitation. The consequences of the reported measurements on the description of the relaxation processes in the excited electronic state will be discussed in Sec. IV. Also, the theoretical treatments of the electronic transition during the vibrational relaxation in the excited electronic state will be reanalyzed.

II. EXPERIMENT

Pure NaBr samples (from the Crystal Growth Laboratory of the University of Utah and from Harshaw Chemical Co.) and NaI crystals (from Fairlight) were stored and always handled under dry N_2 atmosphere. Several techniques have been proven to produce sufficient coloration in NaBr samples.[9] Additive coloration and x-ray irradiation yielded low F-center concentrations ($\sim 10^{16}$ cm^{-3}). Higher concentrations of F centers can be obtained with a hydrogenation procedure by which a very high ($\geq 10^{19}$ cm^{-3}) concentration of U centers (substitutional H^- ions) are created in the crystal. Subsequently, $U \rightarrow F$ conversion can be achieved by a short x-ray irradiation at room temperature (Siemens tungsten x-ray tube, operating at 50 kV and 30 mA). In this way, F-center concentrations of 10^{17} cm^{-3} can easily be reached. Due to the poor penetration of the substitutional hydrogen in the samples, only a thin layer ($\sim$0.5 mm) at the surfaces could be colored.[21]

In NaI samples, the hydrogenation procedure is the only efficient way to create appreciable F-center concentrations.[9] Due to the lower melting point of NaI, lower hydrogenation temperatures are required. This fact reduces the maximum U-center concentration obtainable with the procedure. Nevertheless, sufficient F-center concentrations (up to $\sim 10^{17}$ cm^{-3}) were easily reached. In contrast to the case of NaBr, the obtained hydrogen distribution was homogeneous over a thickness of several millimeters in this crystal.[9]

The F-center concentration was monitored with a spectrophotometer (Varian CARY05). The distribution of F centers in the crystals has been checked by means of Raman measurements at several depths under the surface. The measurements on NaBr were performed with a Spex double monochromator under 514-nm excitation (1-cm^{-1} resolution). The measurements on NaI were performed by means of a DILOR 800-mm Triple Monochromator with CCD (charge coupled device) detection. The multichannel detection permitted high-quality measurements at low incident power. In this way the influence of the local heating produced by the exciting laser beam could be avoided, as discussed in Sec. III B. With multichannel detection the apparatus has a spectral resolution of 0.5 cm^{-1} at 632.8-nm HeNe laser excitation. Excitation at 514 nm from an Ar$^+$ laser, at 568 nm from a Kr$^+$ laser, at 580 nm from an R6G dye laser, and at the 632.8 nm from a HeNe laser were used for the resonant Raman measurements. The first two wavelengths approximately coincide with the F-band maxima in NaBr and NaI, respectively, while the last one falls in the low-energy tail of the F band in NaI (see Fig. 2).

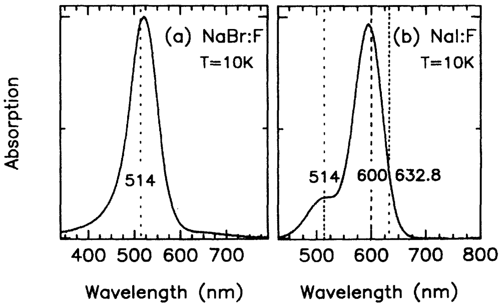

FIG. 2. (a) Absorption spectrum of the F center in NaBr at 10 K; (b) absorption spectrum of the F (max. at 595 nm) and F' (max. at 510 nm) centers in NaI at 10 K. The excitation wavelengths employed in the Raman measurements are also indicated.

III. LINEWIDTH MEASUREMENTS

A. Experimental results

The resonant Raman spectrum under 568-nm excitation is presented in Fig. 3 for NaBr at 15 K. Due to the pronounced mass difference between the anion and the cation, an energy gap separates the acoustic and the optical mode parts of the phonon spectra (105–126 cm^{-1}).[22] A narrow double-peaked band (main peak at 138 cm^{-1}, second peak at about 150 cm^{-1}) is present just above the gap region. It has been argued in Ref. 22 that such a narrow resonance is the result of the perturbation introduced by the defects on the short-range longitudinal force constants. Using a simple model for the lattice dynamics of the defect in which only nearest-neighbor interactions are assumed and in which only the nearest-neighbor force constants are modified by the presence of the defect, the nearest-neighbor projected density of states of Γ_1 symmetry has been calculated as a function of the change of the force constant. The frequency and the relative intensity of the narrow resonance in the calculated Raman spectrum show a good correlation with the experimental polarized first-order Raman spectrum for a force-constant weakening of 55%.[22]

The Raman spectra under three different excitation wavelengths are reported in Fig. 4 for NaI. A gap between the acoustic and the optic phonon bands is present also in NaI (78 cm^{-1}–116 cm^{-1}).[23,24] The spectrum under 514-nm excitation shows two narrow lines near the upper edge of the phonon gap. The lower-energy peak (114 cm^{-1}) has been related to the *F* center, while the second one at 120 cm^{-1} has been attributed to the *F'* center.[25] This attribution is confirmed by the spectra at lower excitation energies (580 and 632.8 nm). These wavelengths are not far from the peak of the *F* absorption band but they are out of resonance for the *F'* band which is known to possess in NaI the unusual feature of a relatively narrow absorption band on the high-energy tail of the *F* band. Therefore, only the line at 114 cm^{-1} is visible in these spectra. Also, the relative amplitude of the 120-cm^{-1} line appears clearly correlated to the *F*-center concentration, in agreement with the well-known dependence of the *F'*-center formation on the total concentration of defects. Buisson *et al.*[23] interpreted the polarized Raman spectra assuming a decrease of 67% in the longitudinal force constant between the *F* center and its nearest neighbors and of 20% in that between the nearest and the fourth neighbors.

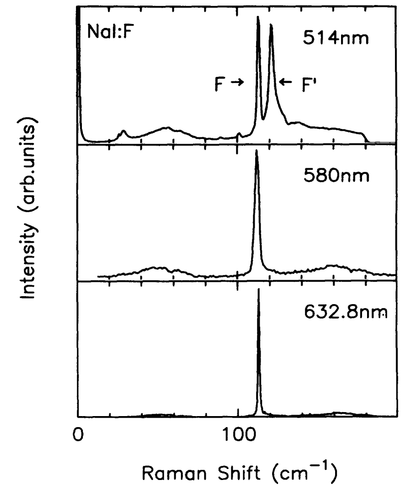

FIG. 4. Resonant Raman spectra of colored NaI at 15 K for different laser excitations. The spectra have been recorded with different spectral resolutions.

Figures 5 and 6 present the high-resolution Raman measurements of the 137-cm^{-1} resonance and the 114-cm^{-1} gapmode of the *F* center in NaBr and NaI, respectively. Comparison with the resolution curve of the experiment shows that the linewidth can be resolved for both samples. The spectra were successfully fitted to the convolution of a Lorentzian and the experimental resolution curve. The results of these fittings are also shown in Figs. 5 and 6. Convolution with a Gaussian line shape led to doubtful or no convergence.

The linewidth derived from the fittings is plotted in Figs. 7 and 8 as a function of the temperature for NaI and NaBr, respectively. In the case of NaI also the linewidth of the first overtone is shown, which turns out to be exactly two times as broad as the fundamental gapmode. The FWHM of the latter one is strongly temperature dependent and, extrapolated to 0 K, it is 0.5 cm^{-1}. The

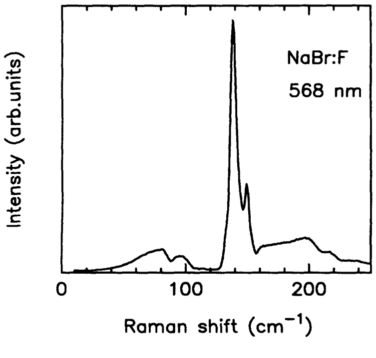

FIG. 3. Resonant Raman spectrum of the *F* center in NaBr at 15 K excited at 568 nm.

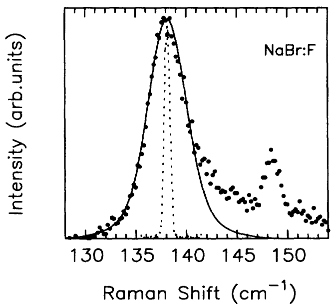

FIG. 5. Comparison of the narrow mode (•) and the resolution curve (···) in NaBr at 15 K. The fit of the spectrum to a Lorentzian line shape convoluted with the resolution curve (——) is also shown.

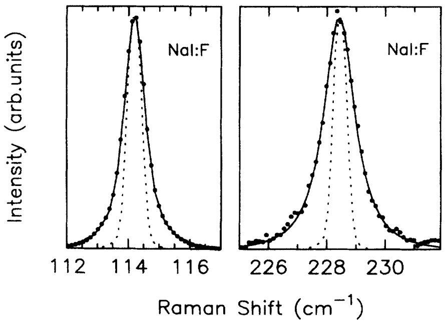

FIG. 6. The gapmode at 114 cm^{-1} and the first overtone at 228 cm^{-1} (•) in NaI are compared with the resolution curve (···). The temperature is $T = 5$ K. The fits of the spectra to a Lorentzian line shape convoluted with the resolution curve (———) are also shown.

linewidth changes by a factor 6 by lowering the temperature from 100 K to 5 K. This result shows that the 114-cm^{-1} mode of the F center in NaI possesses the features of a localized vibrational excitation, as could be expected also from its position within the phonon gap.[23] In contrast, the width of the resonant mode in NaBr is nearly temperature independent and is equal to 3 cm^{-1} at zero temperature.

B. Local heating

Due to the resonant excitation and the nonradiative relaxation, a large amount of energy is transferred from the light beam to the sample. As a result, the temperature of the sample can be locally enhanced and it can sensibly differ from the average temperature of the crystal, depending on the incident laser power and on the density of the absorbing centers. The effective local temperature of the sample can be monitored by means of a comparison of the intensities of the Stokes and anti-Stokes scattering.

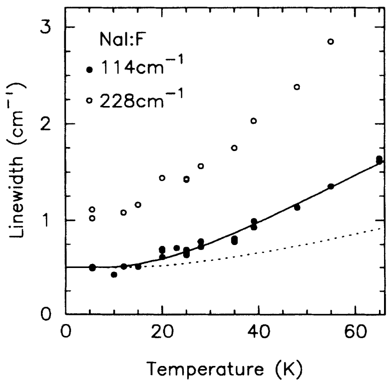

FIG. 7. Linewidth of the 114 cm^{-1}-gapmode in NaI (•) as a function of the temperature. (···) Expected temperature dependence of the two-phonon down conversion [Eq. (3.1)]. (—) Theoretical fit to the expression (3.3) which combines two-phonon down- and up-conversion contributions. The linewidth of the first overtone at $2 \times \nu$ (○) is also shown.

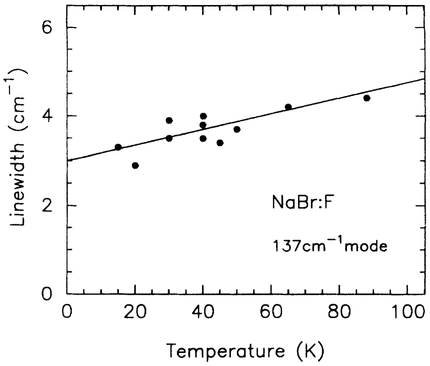

FIG. 8. Temperature dependence for the linewidth of the resonant mode in NaBr.

In view of the strong variation of the linewidth with temperature, determination of the local heating is of crucial importance for NaI at the lowest temperatures. This effect can probably explain an earlier large value (2.5 cm^{-1}) reported for the linewidth of the local mode in NaI at 10 K under 60 mW HeNe laser power.[23] It must also be mentioned that the latter measurements were performed with an experimental resolution of 5 cm^{-1}. The laser power incident on the samples has been limited in the linewidth measurements to 1 mW in order to avoid unwanted local heating effects. Temperatures lower than 15 K cannot be accurately determined from the anti-Stokes spectrum, because of the absence of a mode with sufficiently low frequency. Local heating effects could nevertheless be excluded in those cases, since measurements with a five times lower incident power resulted in essentially the same linewidth.

C. Vibrational cooling rate

The finite lifetime of the excitation determines the natural breadth of the spectral line. Different mechanisms may obscure this contribution. An inhomogeneous broadening can be present due to differences in the environment of different F centers. For NaBr the same linewidth was measured in samples colored by different coloration techniques (additive coloration, x-ray irradiation, hydrogenation, and subsequent $U \rightarrow F$ conversion). This indicates a negligible contribution of the inhomogeneous broadening. For NaI, no coloration procedure, alternative to the hydrogenation and subsequent x-ray irradiation, was available and no comparison could be made between different samples. The hydrogen concentration reached in NaI was much lower than in NaBr. Also, the line shape of the gapmode in NaI and the resonant mode in NaBr fit much better a Lorentzian than a Gaussian line shape (Sec. III A and Figs. 5 and 6). This fact further supports the conclusion that inhomogeneous line broadening can be neglected in both crystals.

Homogeneous broadening can be related to two different relaxation processes: population decay and pure dephasing processes. Both contributions are introduced by anharmonic terms in the potential energy.[26,27] The first class of processes includes the decay of the local excitation in two (or more) phonons, while the latter represents the contribution from phonon scattering which randomizes the phase of the local mode without changing its occupation number. The two contributions show a different temperature behavior. The main difference is found in the low-temperature range. The former one contains terms independent of the phonon population (i.e., down conversion to two lower-energy phonons), which yield a temperature independent contribution to the linewidth. By contrast, the pure dephasing process always requires an excited phonon to be scattered, leading to a vanishing contribution at zero temperature.[27] When the two-phonon down-conversion processes are allowed by energy conservation, they dominate at low temperatures. This is demonstrated by the different linewidths of the H_s^- and D_s^- vibrations in several alkali halides.[28,29]

Within the assumption of anharmonic coupling, the following temperature dependence is expected for the two-phonon down-conversion process:[28,27]

$$\Gamma_{\text{down}} = \Gamma_0 \left(1 + \frac{2}{\exp(\hbar\omega_d/kT) - 1}\right), \tag{3.1}$$

where ω_d is an effective frequency for the down-conversion process which is in general close to half the frequency of the decaying mode.[28] The temperature dependence for the linewidth of the gapmode in NaI is shown in Fig. 7. The expected temperature dependence of the two-phonon down-conversion [Eq. (3.1)] is also shown, corresponding to Γ_0=0.5 cm^{-1} and ω_d=57 cm^{-1}. The discrepancy between the experimental points and the two-phonon down-conversion curve points to the contribution of other processes to the line broadening. For the gapmode in NaI up-conversion processes are also allowed by energy conservation, in contrast to the cases of the relaxation of the H_s^- and D_s^- local mode.[28,29] In the latter processes a phonon and a gapmode decay in a phonon of higher energy. Neglecting the contribution from the inverse process, namely the decay of an optical phonon into a gapmode plus an acoustic phonon quantum, the linebroadening arising from up-conversion processes can be written as[30]

$$\Gamma_{\text{up}} = \frac{A}{\exp(\hbar\omega_u/kT) - 1}. \tag{3.2}$$

In principle, the up-conversion processes can involve phonons from a larger range of frequencies in the acoustic band. As such, the effective frequency ω_u is in general different from ω_d. Since the frequency spectrum of acoustic phonon modes for NaI is steeply peaked at about 55 cm^{-1},[24] the effective frequencies ω_u and ω_d are expected to be not too much different in this case. For this reason the experimental data have been fitted to the following expression which combines expressions (3.1) and (3.2):

$$\Gamma = \Gamma_0 + \frac{c}{\exp(\hbar\tilde{\omega}/kT) - 1}. \tag{3.3}$$

The best fit of expression (3.3) to the experimental data has been obtained for the value of the effective frequency $\tilde{\omega}$=53 cm^{-1} and c=2.32 (Fig. 7). Although the result of the fit appears in a reasonable agreement with the expectations, the latter interpretation of the temperature dependence of the linewidth should be accepted with some caution. Especially at higher temperatures a contribution from the dephasing processes cannot be excluded.

Important information can be obtained from the low-temperature limit of the linewidth. Assuming that the dominant contribution of coupling of the F-center electron to the lattice is related to the gapmode (see Sec. IV B for a discussion of this assumption), the vibrational cooling rate V_1 of the F center in NaI can be related to the width of the gapmode. At low temperatures, the relaxation time V_1^{-1} of the vibrational cooling is equal to Γ_0^{-1}=10.5 ps.

Different from the case of NaI, the 137-cm^{-1} resonant mode of the F center in NaBr does not display a pronounced temperature dependence. This is probably related to its position within the optical phonon band: One should consider the resonant mode rather as a spectrum of phonon modes with different frequencies than as a lifetime broadened normal mode.[28] In this case, the vibrational cooling can be considered as a loss of the amplitude of the effective coordinate due to the dephasing of its constituent phonon modes with different frequencies.[27] Also in this case the cooling rate is proportional to the width of the resonant mode, within the assumption that the latter gives the dominant contribution to the resonant Raman spectrum. The vibrational lifetime of the individual phonon modes can be much longer. Under certain conditions one can describe the damping of the effective coordinate as a step-by-step one-phonon relaxation and the vibrational relaxation rate of the nth vibrational level approximately equals[3,8]

$$V_n = nV_1 = n\pi\Delta\omega. \tag{3.4}$$

A requirement is that

$$n\Delta\omega \ll \omega_{\text{eff}}, \tag{3.5}$$

which means that the levels of the effective mode must be well separated.

From the Raman data one derives the timescale of the vibrational relaxation V_1^{-1}=0.6 ps for NaBr and V_1^{-1}=10.5 ps for NaI. This is in the same order of magnitude as the configurational relaxation in the excited state of several analogous systems like the F_A center in KCl:Li (13 ps),[17] the Tl$^+$ center in KBr, and the F_2 center in NaF and LiF (~ 2 ps)[18] or of the lifetimes of the pseudolocal modes of Cu$^+$ in NaF (0.31 ps, 3.3 ps, and 5.3 ps, for the different local modes).[31]

IV. THEORETICAL CONSIDERATIONS

A. Efficiency of the crossover process

Within the model of an electronic transitions during vibrational relaxation, the lifetime of the effective vibrational coordinate is the rate-determining process in the recovery of the ground state. The experimental values of the vibrational lifetime are much smaller than the time constants of the ground-state recovery which have been established to be in the order of 10 ns.[11,13] Therefore, one concludes that the observed ground-state recovery arises from the electronic relaxation from the RES and that the crossover process cannot be the dominating relaxation mechanism.

Obviously, this conclusion does not solve the discrepancy between theoretical and experimental results. As a first remark on the theoretical considerations, we note that Bartram and Stoneham[3] assume in their model an instantaneous electronic transition rate at the crossing point. The efficiency η_e of reaching the RES is then determined by the branching ratio, the ratio between the cooling rate in the excited and ground electronic states at the crossover point. If in addition the nonradiative relaxation from the RES is not efficient, η_e is also equal to the emission efficiency. The model has the advantage of considering back transitions from the ground state, but it takes only electronic transitions into account at the crossing point itself. Omitting back transitions, Leung and Song performed a calculation of η_e considering, during the vibrational cooling, electronic transitions from all vibrational levels in the electronic excited state.[5] They made the calculation only for one value of the parameters. Their choice for the vibrational cooling rate was 36 and 2 times slower than the one experimentally established from the linewidth measurements of Sec. III C for NaBr and NaI, respectively.

To evaluate how critically the conclusions depend on these assumptions and on the particular choice of the parameters, we calculated the probability of the F center to reach the RES, as a function of the vibrational cooling rate with respect to the electronic transition rate. Electronic transitions to the ground state, as well as back transitions, were taken into account for all vibrational states. The electronic nonradiative transition rate W_n can be expressed as[5]

$$\begin{aligned} W_n &= W_0 \, |\langle n, e | n+p, g \rangle|^2 \\ &= W_0 e^{-S} \frac{n!}{(n+p)!} S^p [L_n^p(S)]^2 . \end{aligned} \tag{4.1}$$

In the latter expression, the parameter W_0 represents the mixing of the ground and excited electronic wave functions under the influence of the electron-phonon coupling. The second factor is the square of the overlap integral of the two displaced harmonic oscillator wave functions expressed in terms of the Laguerre polynomials $L_n^p(S)$, with S the Huang-Rhys factor and p the energy difference between the excited and ground electronic state in units of vibrational-energy quanta. We can write the probability $\eta_{i,n}$ for the system to make a transition one vibrational level downward within the same electronic state i from the nth vibrational level, by the following recursive formulas:

$$\eta_{e,n} = \frac{V_n\big((V_{n+p} + kW_n)\eta_{e,n+1} + kW_n \eta_{g,p+n+1}\big)}{V_{n+p}(V_n + W_n) + kW_n V_n} , \tag{4.2}$$

$$\eta_{g,p+n} = \frac{V_{p+n}\big((V_n + W_n)\eta_{g,p+n+1} + W_n \eta_{e,n+1}\big)}{V_{n+p}(V_n + W_n) + kW_n V_n} . \tag{4.3}$$

An *ad hoc* parameter k is introduced in the expression, to switch the electronic back transitions from the ground state on and off, respectively, for $k = 1$ and $k = 0$.

Expression (4.2) for n=1 is the probability of reaching the relaxed excited state. Within the crossover model it coincides with the emission efficiency η_e. The result of the calculation for the F center in NaBr and NaI is displayed in Fig. 9 for both k=1 and k=0. The same values for S and p are used as in Ref. 5.

It is clear that, if the back transitions are included in the calculation, the vibrational cooling should be extremely slow in comparison with the interstate coupling to explain values as small as the experimentally observed η_e in the order of 10^{-3}.[9] For the particular choice $\Delta\omega = 5\times10^{10}$ s^{-1} and $W_0 = 10^{13}$ s^{-1} as in Ref. 5, back transitions raise the number of F centers reaching the RES by a factor of 10 for NaI. It should be noted that the model of the vibrational cooling is valid under the assumption of step-by-step one-phonon relaxation, i.e., condition (3.5). If the experimental values of the resonances in the two crystals are used, relation (3.5) implies $n \ll 45$ for NaBr and $n \ll 160$ for NaI. It can be shown[5] that the electronic transition W_n reaches its maximum value at about n_x and decreases very rapidly below that level. Therefore, condition (3.5) must be fulfilled at least up to vibrational levels near the the crossing point. Since the vibrational quantum number at the crossing point n_x is 6 for NaBr and 4 for NaI, this is indeed the case for both host crystals in the excited electronic state. In contrast, n_x is in the order of 100 for the ground state. Instead of the one-phonon relaxation assumed in Sec. IV A, fast multiphonon relaxation may be expected after electronic transition to the ground state. As such, back transitions from the ground to the excited state may probably be neglected.

By comparison with vibronic coupling matrix elements

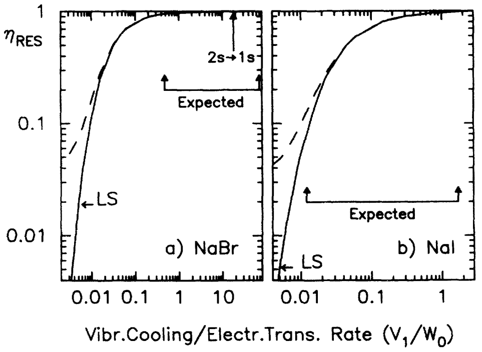

FIG. 9. Fraction $\eta_{\rm RES}$ of F centers reaching the RES calculated with (- - -) and without (——) back transition as a function of the ratio between the vibrational cooling V_1 and the electronic nonradiative rate W_0 for NaBr (a) and NaI (b). The values corresponding to the choice of parameters of Ref. 5 (LS) in both crystals and to the experimental results ($2s \rightarrow 1s$) from the ground-state recovery and the linewidth of the resonant mode for NaBr are shown. The range which is expected from the experimental vibrational relaxation rate and the electronic transition rate from the literature is also reported.

in aromatic hydrocarbon molecules,[14] the interstate coupling factor W_0 is expected in the range 2.6×10^{10}–4×10^{12} s^{-1} for NaBr and 5×10^{10}–8×10^{12} s^{-1} for NaI. If the experimental values of the width of the Raman lines [$V_1(\mathrm{NaI})=0.9\times10^{11}$ s^{-1} and $V_1(\mathrm{NaBr})=1.8\times10^{12}$ s^{-1}] are combined with the expected range for the interstate coupling factor W_0, it turns out that the value of η_e can vary from 0.85 to 1 in NaBr and from 0.05 to 1 in NaI (see Fig. 9). In the case of NaBr, the fraction of F centers reaching the RES is expected to be considerably higher than previously calculated. In this case W_0 can also be evaluated by comparison with the promoting factor for the $2s \rightarrow 1s$ transition which was obtained from the ground-state recovery measurements,[11] yielding a value of about 10^{11} s^{-1}.

In contrast to the case of NaBr, the crossover process might be the dominant nonradiative electronic relaxation process for the F center in NaI. The choice of the rates of the two competing processes that was made in Ref. 5 corresponds to the lower limit of the expected range of the ratio between the vibrational cooling factor $\Delta\omega$ and the interstate coupling factor W_0. In contrast, a full efficiency results if one considers the higher limit of the range for W_0 and the experimental value of the gapmode linewidth. The lack of accurate knowledge of the interstate coupling factor W_0 does not allow one to draw any conclusion from the theoretical estimates about the efficiency of reaching the RES. Therefore, there seems to be *no contradiction* between theory and the experimental evidences of Refs. 11, 13, and this work that the F center reaches the RES with a high efficiency.

B. Contribution of the resonance and the gapmode to the effective configurational coordinate

Another important assumption in Sec. IV A is that most of the vibrational energy after optical excitation is contained in the narrow 114-cm^{-1} mode for NaI and the 137-cm^{-1} mode for NaBr. The Raman intensity I_i of a mode i and its energy in the excited state after optical excitation $S_i\omega_i$ are related to each other by[32]

$$I_i(T) \propto S_i\omega_i^2 \coth\left(\frac{\hbar\omega_i}{2kT}\right), \qquad (4.4)$$

where S_i gives the (linear) coupling strength of the i mode to the F-center transition. The relative contribution of this mode to the total configurational relaxation energy is therefore

$$\frac{S_i\omega_i}{S\omega_e} = \frac{I_i(0)\omega_i^{-1}}{\sum I_i(0)\omega_i^{-1}}. \qquad (4.5)$$

Applying (4.4) to the resonant Raman spectra of Figs. 3 and 4, it turns out that only 40% of the configurational energy is accepted by the intense narrow modes in both cases. As a result, the total width of the first-order Raman spectrum is several tens of cm^{-1}, which would imply that condition (3.5) is not fulfilled and that one should rather use the semiclassical theory of Sumi[7] to describe the relaxation process. One may doubt, however, whether it may be applied to a case in which a very pronounced structure is present. The situation is probably better described in a two-dimensional configurational diagram with the narrow mode as one coordinate and an effective phonon coordinate which accepts the rest of the configurational energy, as the other one. The latter relaxes very quickly due to the dephasing, whereas the vibrational excitation of the former one persists for the lifetime determined in Sec. IV A. It is possible to show, with the parameters appropriate for NaI and NaBr, that after dephasing of the effective phonon mode, the narrow mode still oscillates far above the crossing between the potential curves. Since far above the crossing point the calculation of Sec. IV A is not very sensitive to the exact excitation energy, the results remain relevant.

V. CONCLUSIONS

We were able to resolve the width of the 114-cm^{-1} gapmode and the 137-cm^{-1} resonance observed in the resonant Raman spectrum of the F center in NaI and NaBr, respectively. Their linewidth, extrapolated to zero temperature, could be related to the vibrational cooling of the F center after optical excitation. The present results show that the lifetime of the vibrational excitation is 10.5 ps for NaI and 0.6 ps for NaBr. Within the crossover model, the vibrational relaxation is the rate-determining process for the recovery of the ground state. Since the ground-state recovery is determined to be in the order of 10 ns by means of time-resolved measurements,[11,13] they cannot be interpreted in terms of a dynamical nonradiative process *during* the vibrational cooling in the excited state. In principle, the ground-state recovery measurements show the contributions from all different processes. Decay components with a time constant smaller than the time resolution used in the measurements, however, will possess a smaller amplitude in the measurements than their actual one. This may hide a contribution of the crossover process, if it is occurring on a timescale smaller than about 10 ps. The relation $\tau_r = \tau_0\eta_e^{-1}$ established between the RES lifetime τ_0, the emission efficiency η_e^{-1}, and the expected radiative lifetime τ_r limits the possible efficiency of such a contribution.[11] Considering the experimental error on these parameters, a contribution of the crossover process with a smaller or comparable efficiency as the nonradiative relaxation from the relaxed excited state, cannot yet be excluded. These conclusions apply if there is not much difference between the vibrational cooling in the ground and the excited states, since the resonant Raman measurements yield essential information about the ground state. A more rigorous proof would follow from time-resolved measurement of the RES absorption: The rise time of the RES absorption after pulsed optical excitation of the F center would yield the vibrational cooling rate in the excited state.

We also reconsidered the theoretical treatments of the nonradiative relaxation during lattice relaxation in the excited state. The result of the theoretical estimate turns out to depend quite critically on the vibrational relaxation and the electronic transition rate. Whereas the estimate of Ref. 5 is in agreement with the crossover process, another reasonable choice of the parameters can explain the opposite. The analysis of Ref. 33 leads essentially to the same conclusion for the F center in NaI and NaBr, although it is not mentioned explicitly in this way by the authors. For NaCl and KI the latter work needed the crossover process to explain the dependence of the emission efficiency on the excitation wavelength. It is surprising, however, that in the case of NaCl a slower vibrational relaxation rate was used than for NaBr and NaI, since the F center in NaCl does not possess a pronounced narrow structure in its resonant Raman spectrum. Therefore time-resolved measurements on the F center in NaCl as a function of the excitation wavelength would be very interesting to verify if the assumption that the crossover is the process responsible for the (partial) quenching of the F-center luminescence in NaCl is correct.

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