Free-electron-laser studies of the relaxation of H^- and D^- local modes in CaF_2, SrF_2, and BaF_2

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We report a three-pulse, pump-probe experiment on H^- and D^- local modes in CaF_2, SrF_2, and BaF_2 using the Dutch free electron laser, FELIX. The 10-K lifetimes of the H^- local modes were measured as 43 ± 5, 170 ± 15, and 212 ± 20 ps for CaF_2, SrF_2, and BaF_2, respectively. For D^-, the corresponding 10-K lifetimes are 3.8 ± 0.5, 10.5 ± 0.5, and 11.6 ± 0.5 ps. Three-phonon anharmonic decay accounts for the temperature dependence of the H^- lifetimes, while two-phonon anharmonic decay is expected to apply for the D^- lifetimes. However, the D^- in BaF_2 lifetime is anomalous in requiring the three-phonon decay occasioned by a close resonance of this D^- mode with a three-phonon lattice peak. From a combination of lifetime and linewidth measurements, the pure dephasing rates of these hydrogenic local modes have been determined and well accounted for by elastic band-phonon scattering processes.

I. INTRODUCTION

The localized modes of vibration of defects in crystals have been studied extensively by infrared absorption[1,2] and Raman scattering.[3] However, few time-resolved measurements have been reported and little is known about the dynamics of this class of vibrations, which play a significant role in the nonradiative decay of optically active defects in liquids and solids.[4] We present measurements of the lifetimes of H^- and D^- local modes in CaF_2, SrF_2, and BaF_2 crystals. The term "hydrogenic" is used to cover both H^- and D^- local modes.

Local modes occur when a light ion is introduced into a crystalline lattice with unaltered force constants between the light ion and its neighbors. Local modes have been observed for a wide variety of materials, including III–V semiconductor compounds doped with Be, B, C, or Si,[5] ionic crystals containing transition-metal ions such as Cr^{3+} in $SrTiO_3$ (Ref. 6) and ionic crystals such as CaF_2, SrF_2, and BaF_2 with H^- and D^- ions.[1]

For hydrogenic ions in CaF_2, SrF_2, and BaF_2, the hydrogenic center present is formed by the substitutional replacement of an F^- by a hydrogenic ion. The hydrogenic ion has tetrahedral (T_d) symmetry and a single fundamental vibrational mode is observed in infrared absorption. To a good approximation, this vibrational mode may be regarded as a vibration of a single light ion with the rest of the lattice taken as static.

Previous time-resolved studies have been reported for CaF_2:H^- crystals.[7–9] Carbon-dioxide-laser saturation studies of the H^- local mode reported a strong temperature dependence of the saturation intensity I_S, but virtually no change in the derived lifetime of 17 ps between 10 and 110 K.[7] The determination of this local-mode lifetime from absorption saturation of the H^- line is rather indirect and involves assumptions about the absorption, which affects its value. The first study[8] utilizing infrared-light pulses shorter than the H^- lifetime in a pump-probe technique determined a longer 10-K lifetime of 45 ps.

Recent work here at FELIX (Ref. 9) using four-wave mixing techniques in both the time and frequency domain has demonstrated "negative-time" quantum beats arising from vibrational ladder climbing under free-electron laser (FEL) excitation. These so called "negative-time" oscillations occur only for essentially homogeneously broadened lines.

The principal result of this paper is measurement and analysis of the lifetimes of both H^- and D^- local modes for CaF_2, SrF_2, and BaF_2 as a function of temperature. The hydrogenic local-mode lifetimes are determined by decay of the hydrogenic local modes into several host lattice-band modes, such that the frequencies satisfy energy conservation.[1] For D^- local modes, decay into two band modes is possible, whereas for the H^- local modes at least three are required. The temperature dependences of these lifetimes are fitted to anharmonic-decay processes in Sec. III A.

Measurements of the local-mode infrared absorption lines as a function of temperature are also reported. The measured linewidths are broader than those derived from the measured lifetimes T_1 because of the presence of additional broadening processes. The principal contribution to the linewidths is from processes in which band phonons are elastically scattered off the hydrogenic defect without changing the vibrational state of the hydrogenic ion.[1] This scattering removes the local mode from its initial or final state giving a reduced lifetime T_2. These scattering processes have a T^2 dependence at high temperature, in agreement with observation.[1] The temperature-dependent linewidths for the hydrogenic local modes are analyzed in Sec. III B. From a combination of the infrared-absorption linewidths and the lifetimes measured with FELIX, the elastic-scattering dephasing contributions can be separated from those due to anharmonic decay.
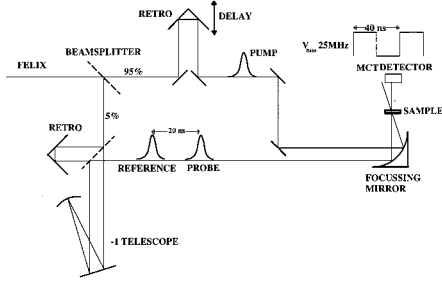
FIG. 1. Schematic diagram of the three-beam pump-probe experimental setup.

The lineshapes of both the H^- and D^- infrared absorption lines are essentially Lorentzian. For a homogeneously broadened Lorentzian line, the linewidth Γ is related to the homogeneous dephasing time T_2 by $\Gamma = 1/\pi T_2$. This homogeneous dephasing time T_2 has contributions[10] both from the vibrational lifetime T_1 and from the pure dephasing time T_2^*,

$$\frac{1}{\pi T_2} = \frac{1}{\pi T_2^*} + \frac{1}{2\pi T_1}.$$

As the measured linewidths determine T_2, while the T_1 lifetimes are measured directly, the pure dephasing times T_2^* can be derived. These pure dephasing times are analyzed as a function of temperature in Sec. III C.

As elastic scattering of phonons is a process that vanishes at the lowest temperatures, the measured 10-K lifetimes should concur with those derived from the residual linewidths. However, the measured linewidths remain larger by about a factor of 2 as a probable consequence of residual crystal inhomogeneities. Four-wave-mixing measurements were carried out to determine the free polarization decay width to compare with the narrowest infrared linewidth obtained and these are discussed in Sec. III D.

II. EXPERIMENT

The CaF_2, SrF_2, and BaF_2 crystals were offcuts purchased from Optovac Inc. H^- or D^- ions were introduced by heating these crystal offcuts in contact with molten aluminum to $850\,°C$ in $\frac{2}{3}$ atm of H_2 or D_2 for periods of up to an hour.[11] This sufficed to give an optimal 90% absorption depth at 10 K for the respective local-mode lines. The crystals were cleaved to obtain samples with minimal surface scattering.

Infrared absorption spectra were measured at either 0.1 or $0.25\ cm^{-1}$ resolution with a Bio-Rad FTS-40 FTIR spectrometer. The crystal samples were cooled by thermal conduction with the 10-K stage of a CTS LTS 0.1 closed-cycle helium cryostat.

The pump-probe experiments were performed using FELIX at FOM "Rijnhuizen" at Nieuwegein in The Netherlands. The output of FELIX is a train of 6 μs length "macropulses" at a repetition rate of 5 Hz. Each macropulse comprises a train of "micropulses," each with a width adjustable between 500 fs and 10 ps with a pulse separation of 40 ns. To counter fluctuations in the macropulse output, a three-pulse pump, probe, and reference-beam technique[12]
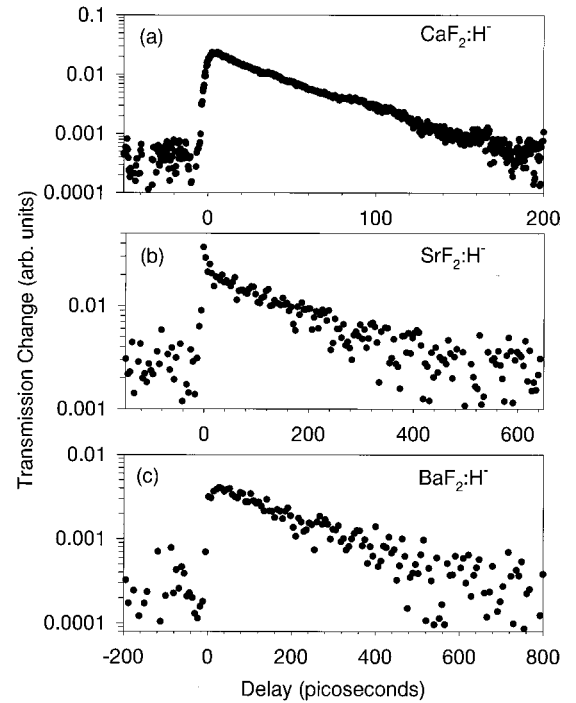

FIG. 2. Probe transmission as a function of delay between the pump and probe pulses as measured at 10 K for H^- modes in (a) CaF_2 (b) SrF_2, and (c) BaF_2.

was employed, as shown in Fig. 1. From the input FELIX pulse, both probe and reference beams are split off with the appropriate BaF_2 or ZnSe beamsplitters. The reference pulse is delayed by 20 ns with respect to the probe pulse and back reflected to the beamsplitter with a -1 telescope onto the probe-beam position. Thus, both the probe and the reference pulses follow the same optical path, travel through the sample at the same position and are detected by the same liquid N_2 cooled MCT detector. The detector bias is modulated at 25 MHz, synchronized to FELIX. This results in signals with opposite phase for the probe and reference beams. When the system is in balance, the integrating electronics give an apparent zero output signal. The three beams are focused onto the sample with an off-axis parabolic mirror of 17 cm focal length. Samples were cooled with an Oxford Instruments "Microstat" flow cryostat equipped with a model ITC503 controller to provide variable temperatures.

III. RESULTS AND ANALYSIS

A. Vibrational lifetimes (T_1)

1. H^- in CaF_2, SrF_2, and BaF_2

The pump-probe experiments were performed with excitation of the H^- local-mode fundamentals for all three host crystals. Figures 2(a)–2(c) shows the normalized probe transmission as a function of the time delay between the pump and probe pulses for samples at 10 K. Under certain conditions, the transients show a sharp feature around $t=0$, which results from coherent coupling between the pump and probe beams (a consequence of which is self-diffraction of

the pump beam into the probe-beam path). This effect causes no problems for the interpretation of the observed signal, but yields no information about the population decay time of the H^- mode.

10 K lifetimes of H^- *local modes.* Single exponential fits to the data yield population decay (T_1) lifetimes at 10 K for the H^- modes of 43 ± 5, 170 ± 15, and 212 ± 20 ps for CaF_2, SrF_2, and BaF_2, respectively. The value of 43 ps inferred for the H^- lifetime for CaF_2 is in excellent agreement with the reported value of 45 ps,[8] while the values for SrF_2 and BaF_2 are new measurements.

The primary deexcitation pathway for H^- local modes is direct anharmonic decay into host-lattice band modes. As these band modes have cutoff energies[13–15] of 460, 370, and 335 cm^{-1} for CaF_2, SrF_2, and BaF_2, respectively, the lowest-order anharmonic process possible for H^- local modes is decay into three band modes.

It is notable that the H^- lifetimes are substantially longer for SrF_2 and BaF_2. As the anharmonic constants for H^- local modes for all three host crystals are similar,[16] the difference in these lifetimes is attributed to the relative placement of the H^- local-mode frequencies with respect to the peaks in the three-phonon density of states of the respective host crystals. Hence the faster decay of H^- mode in CaF_2 is attributed to the presence of favorable decay paths.

Temperature-dependent lifetimes for H^- *local modes.* As yet, there are no reported temperature-dependent lifetime measurements for H^- local modes above 110 K, at which temperature the decay rate is not expected to have varied significantly from the residual (10 K) value. The only temperature-dependent study thus far reported found only a small temperature variation to 110 K.[7]

The temperature-dependence of the three-phonon anharmonic decay rate $[T_1]^{-1}$ is governed by the Bose-Einstein factors $n_i = [\exp(\hbar\omega_i/kT) - 1]^{-1}$ for band modes of energy $\hbar\omega_i$,

$$[T_1]^{-1} = [T_1^0]^{-1}[(1+n_1)(1+n_2)(1+n_3) - n_1 n_2 n_3],$$

where $[T_1^0]^{-1}$ is the zero-temperature decay rate, which we approximate with the measured 10 K value above.

Figure 3(a) shows the calculated and experimental temperature-dependent decay rate for the H^- mode in CaF_2. An excellent fit is obtained for the specific choice of three equal phonon energies of 322 cm^{-1}, which is coincidental with the $(LO)L$ point,[17] and for $[T_1^0]^{-1}$ set at 23 520 MHz. Equally good agreement is obtained for a range of different phonon combinations summing to 965 cm^{-1}, which indicate that several pathways are available for the decay of the H^- mode in CaF_2. The temperature dependences of the H^- decay rates for SrF_2 and BaF_2 are shown in Figs. 3(b) and 3(c), respectively. For both SrF_2 and BaF_2, the measured decay rates increase more rapidly with temperature than for CaF_2, with increases up to a factor of 4 by 300 K rather than just 2. This indicates that lower-energy phonons are required as accepting modes, with the three-phonon summations being combinations of low- with high-energy phonons. To ad-
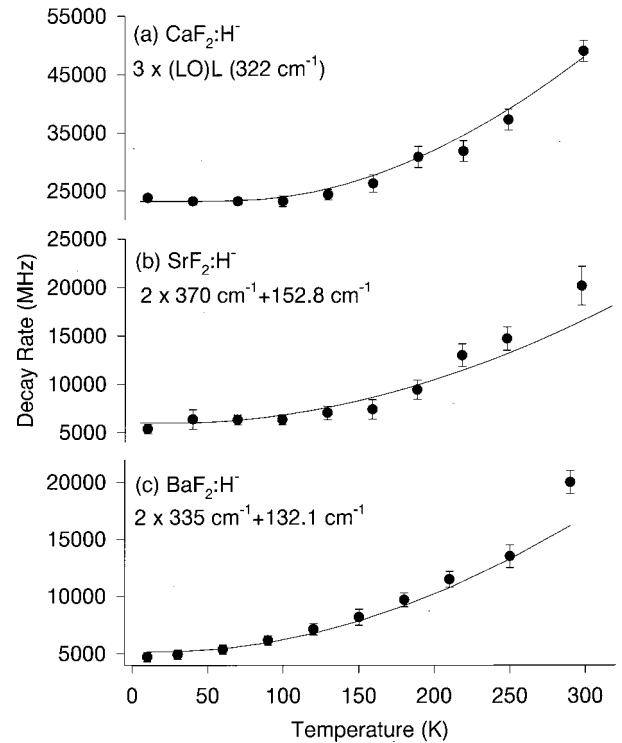

FIG. 3. Temperature dependence of the decay rates (in MHz) for the H^- modes in (a) CaF_2, (b) SrF_2, and (c) BaF_2.

equately account for the temperature-dependent decay rates, the two high-energy phonons each need to be set to the maximum host-lattice frequency.

Figure 3(b) shows the fit of the H^- rate in SrF_2 for decay into two 370-cm^{-1} phonons and one 152.8-cm^{-1} phonon and with $[T_1^0]^{-1}$ set to 6000 MHz. Figure 3(c) gives the corresponding fit of the H^- rate in BaF_2 for decay into two 335-cm^{-1} phonons and one 132.1-cm^{-1} phonon with $[T_1^0]^{-1}$ set to 5200 MHz. In both cases, acceptable fits are obtained. Other choices of three lattice-phonon combinations with the three phonon energies closer to one-third of the respective local-mode energy give significantly degraded fits. The choice of two high-frequency phonons and one low-frequency phonon is essential to give any acceptable fits.

2. D^- in CaF_2, SrF_2, and BaF_2

The pump-probe experiments for D^- local modes were carried out for excitation of the respective D^- fundamentals, which are located on broad absorption bands of the host lattices. For excitation of these D^- modes, the samples had to be thinned to 200 μm to obtain more than 10% transmission of the FEL beam through the samples. These underlying lattice absorptions cause dispersion of the FEL pulse and limit the temporal resolution.

10-K lifetimes for D^- *local modes.* Figures 4(a)–4(c) show the normalized-probe absorption as a function of the time delay between the pump and probe pulses for D^- samples at 10 K. Single exponential fits to the data yield T_1 lifetimes at 10 K of 3.8 ± 0.5, 10.5 ± 0.5, and 11.6 ± 0.5 ps for CaF_2, SrF_2, and BaF_2, respectively.
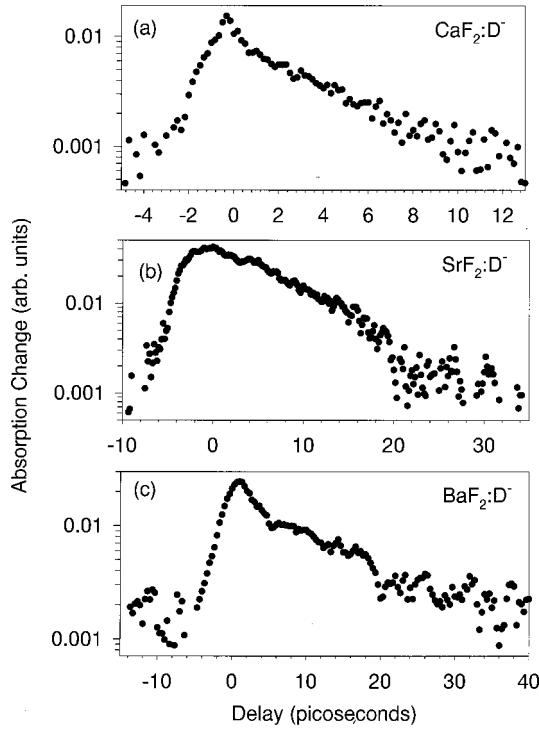
FIG. 4. Probe transmission as a function of delay between the pump and probe pulses as measured at 10 K for D^- modes in (a) CaF_2, (b) SrF_2, and (c) BaF_2.

FIG. 5. Temperature dependence of the decay rates (in GHz) for D^- modes in (a) CaF_2 and (b) BaF_2.

Temperature-dependent lifetimes for D^- local modes. Figures 5(a) and 5(b) show the measured D^- temperature-dependent decay rates for CaF_2 and BaF_2, respectively, which could be measured up to 200 K. The temperature dependence of the D^- fundamental for SrF_2 could only be tracked to 100 K due to its proximity to a lattice-absorption peak. No decrease in the lifetime to 100 K was observed.

D^- local modes decay through two phonon anharmonic processes, whose temperature-dependent rate $[T_1]^{-1}$ is

$$[T_1]^{-1}=[T_1^0]^{-1}[(1+n_1)(1+n_2)-n_1 n_2],$$

where $[T_1^0]^{-1}$ is the zero-temperature decay rate and n_i are the Bose-Einstein occupation factors. Figure 5(a) shows the fitted curve for the D^- mode of CaF_2 for decay into two phonons of energies 394 and 300.5 cm^{-1} and for a high and low-frequency combination of 462 and 232.5 cm^{-1}. Either of these phonon combinations give good fits to the experimental data, with a $[T_1^0]^{-1}$ of 263 GHz.

In contrast, the temperature dependence of the D^- mode in BaF_2 could not be accounted for by two-phonon anharmonic decay, regardless of the choice of lattice-phonon energies. Figure 5(b) shows a representative two-phonon combination. The temperature dependence of the D^- mode in BaF_2 could be better fitted by decay into three equal-energy TO lattice phonons of energy 191.7 cm^{-1} with a $[T_1^0]^{-1}$ of 86.2 GHz. It appears that three-phonon anharmonic decay of the D^- mode in BaF_2 is enhanced by its fortuitious coincidence in energy with three 192 cm^{-1} lattice modes, which give a three-phonon peak, sufficient for these to provide the
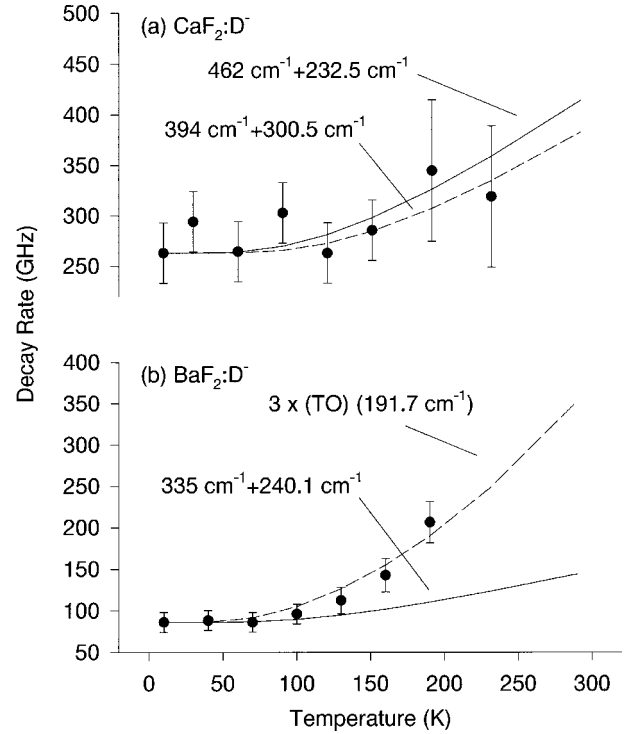
principal decay path. Two-phonon decay would still be present, but to a lesser degree. Evidently, energy resonance between a local mode and lattice phonons can be an important factor governing nonradiative decay processes. Such observations have been made[18] for the case of Cr^{4+} local modes in Mg_2SiO_4.

No temperature-dependent T_1 lifetimes could measured for D^- in SrF_2. Nevertheless, the similarity of the temperature-dependent infrared linewidths for D^- in SrF_2 and BaF_2, together with the similar 10-K lifetimes of 10.5 and 11.6 ps, respectively, suggest that the D^- mode in SrF_2 would have comparable three-phonon resonances to those found for the D^- mode in BaF_2.

B. Vibrational linewidths (T_2)

For all three hosts, the H^- local mode infrared lines have narrow residual linewidths of less than 0.3 cm^{-1} at 10 K. Lightly hydrogenated crystals give the narrowest linewidths and the spectra of these are shown in Figs. 6(a)–6(c).

All D^- lines are relatively broad, with residual widths of more than 0.8 cm^{-1} at 10 K. All the D^- lines occur on broad infrared absorption bands of the host crystals, which are three-phonon lattice combinations with peaks centered at 740, 645, and 550 cm^{-1} for CaF_2, SrF_2, and BaF_2 respectively. As much D^- as possible was introduced into these crystals to minimize the spectral effect of these underlying absorptions [Figs. 6(d)–6(f)]. As shown in these figures, the D^- fundamentals for CaF_2 and BaF_2 are below and above their respective lattice peaks, while the D^- fundamental for SrF_2 is situated close to its lattice peak.
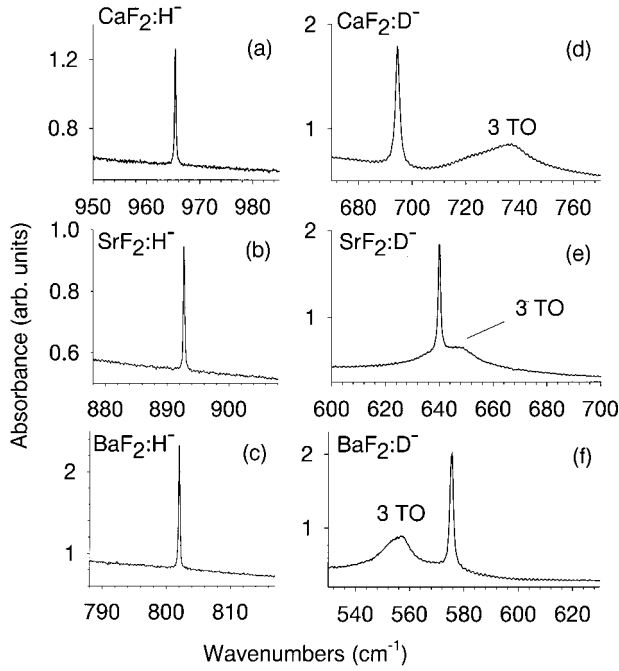
FIG. 6. 10 K infrared absorption line profiles for the H^- modes in (a) CaF_2, (b) SrF_2, (c) BaF_2 and for the D^- modes in (d) CaF_2, (e) SrF_2, and (f) BaF_2.

C. Pure dephasing times (T_2^*)

The pure-dephasing rates $[T_2^*]^{-1}$ can be extracted from the population decay rates $[T_1]^{-1}$ determined from pump-probe experiments and the rates $[T_2]^{-1}$ derived from the infrared-absorption linewidths. Pure dephasing results from the temporal evolution of the vibrational transition energy. Quantum fluctuations of the vibrational transition energy about the average cause the individual oscillators, which comprise the vibrational ensemble, to lose phase with one another. Pure dephasing can be considered as the adiabatic modulation of the vibrational energy levels, which is zero at zero temperature.

1. H^- in CaF_2, SrF_2, and BaF_2

Figures 7(a)–7(c) shows the experimentally derived pure dephasing rates for H^- in CaF_2, SrF_2, and BaF_2 as a function of temperature. As for the analysis[1] of the H^- local-mode linewidths, temperature-dependent dephasing is attributed to a two-phonon scattering process in which lattice phonons are scattered off the H^- defect without a change in its vibrational state. In the Debye approximation for the host-lattice band modes,[19] this process has a temperature dependence of the form

$$[T_2^*]^{-1} = a + A \left(\frac{T}{\Theta_D} \right)^7 \int_0^{\Theta_D/T} \frac{x^6 e^x}{(e^x - 1)^2} dx,$$

where Θ_D is the Debye temperature (with values of 516, 380, and 282 K adopted for CaF_2,[20] SrF_2,[21] and BaF_2,[22] respectively) and A is an elastic band-phonon scattering constant. As this process involves two band modes, its probabil-
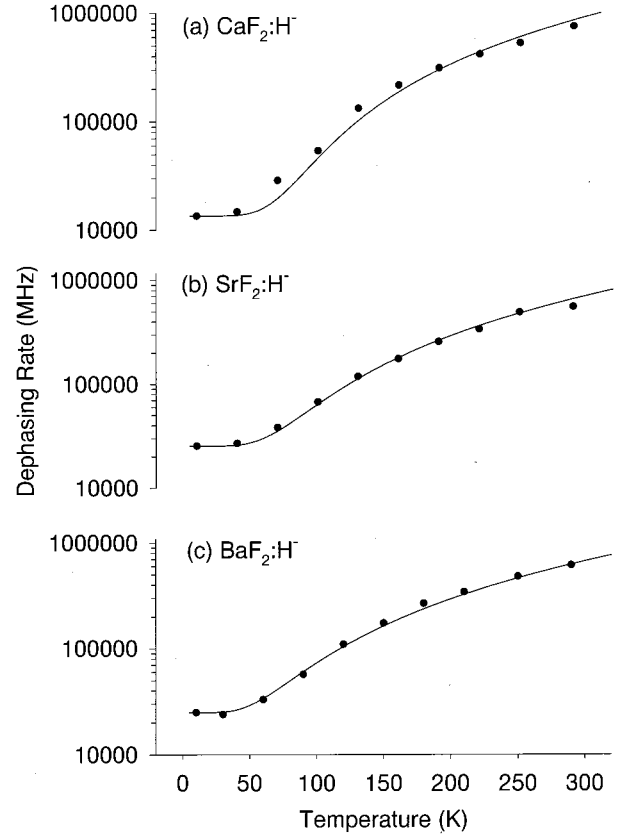

FIG. 7. Temperature dependence of the pure dephasing rates (in MHz) for H^- modes in (a) CaF_2, (b) SrF_2, and (c) BaF_2.

ity is proportional to T^2 at high temperatures and T^7 at low temperatures. An additional temperature-independent term a needs to be introduced to account for any residual linewidth contributions from crystal inhomogeneities. As shown in Figs. 8(a)–8(c), excellent fits are obtained for H^- modes in all three hosts with values for the constant A of 16, 6, and 3 THz for CaF_2, SrF_2, and BaF_2, respectively.

2. D^- in CaF_2, SrF_2, and BaF_2

Figures 8(a)–8(c) show the pure dephasing rates as a function of temperature for the D^- modes in CaF_2, SrF_2, and BaF_2. The rates shown for SrF_2 were obtained from predicted temperature-dependent lifetimes, derived on the assumption of three-phonon decay as for D^- in BaF_2. For SrF_2, the assumed anharmonic decay is into three 213-cm^{-1} TO phonons with a $[T_1^0]^{-1}$ value of 95 GHz derived from the measured 10.5 ps lifetime at 10 K.

All these pure dephasing times for D^- are well fitted by the lattice-phonon scattering process, with values for the constant A of 8.0, 1.7, and 1.3 THz for CaF_2, SrF_2, and BaF_2, respectively. The values derived for A for both the H^- and D^- modes in all three hosts are given in Table I. The value of A inferred for the D^- mode in SrF_2 is less certain because of the difficulty in accurately measuring the linewidth of this mode, whose transition is superimposed upon a broad host-lattice phonon band. Apart from this less accurate value for D^- in SrF_2, there is a overall decrease by a factor
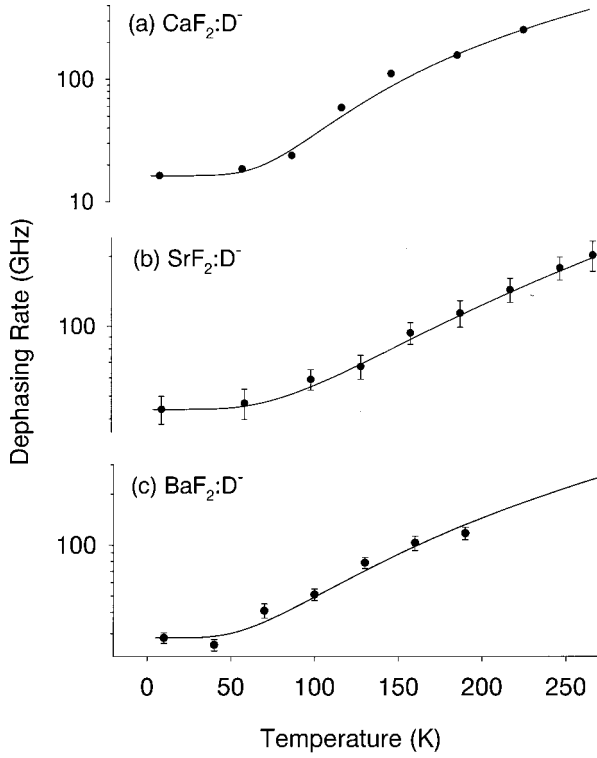
FIG. 8. Temperature dependence of the pure dephasing rates (in GHz) for D^- modes in (a) CaF_2, (b) SrF_2, and (c) BaF_2.

FIG. 9. 10-K free-induction decay of the H^- mode in CaF_2.

of 2 in the A values determined for the D^- modes as compared to those for the H^- modes. With the anharmonic potential-well constants essentially the same for both H^- and D^- modes,[16] the isotope-dependent terms M' and Ω of Eq. (7.27) of Ref. 1 readily account for this decrease.

The temperature-independent a term varies little with host crystal and is attributed to residual homogeneous broadening of the respective H^- and D^- modes.

D. Degenerate four-wave mixing experiments

Degenerate four-wave mixing techniques are a useful tool for measuring vibrational dynamics and our results have been detailed elsewhere.[9] For a purely homogeneously distributed ensemble of H^- oscillators, one measures the free-
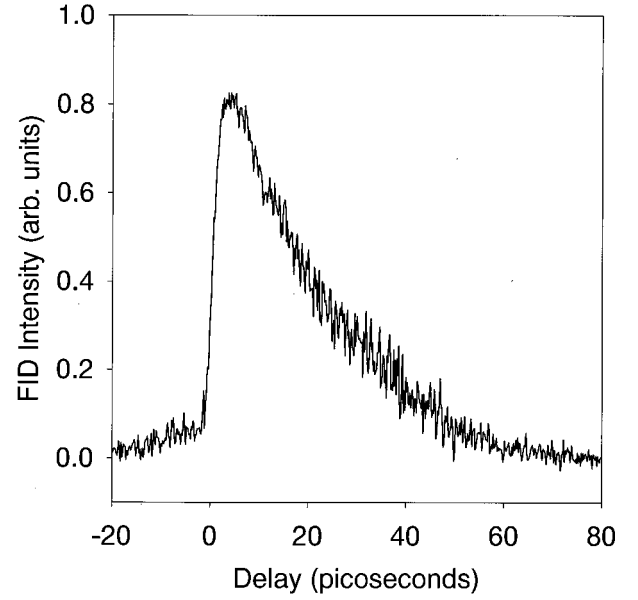
polarization (or free-induction) decay created in the medium upon excitation. This is expected to match that derived from the spectral linewidth. Figure 9 presents the infrared free-induction decay (IR-FID) measured for our best $CaF_2:H^-$ sample. As the infrared FID has a decay term of exp $(-2\tau/T_2)$, a value for T_2 of 49 ps is inferred with a derived linewidth of 0.22 cm^{-1} in excellent agreement with the measured infrared linewidth of 0.24 cm^{-1}. It is concluded that the H^- local mode in CaF_2 is almost wholly homogeneously broadened, with its 10-K width approaching the 0.15 cm^{-1} width derived from the measured T_1 lifetime.

IV. CONCLUSIONS

Measurements of temperature-dependent lifetimes and linewidths are reported for H^- and D^- modes in CaF_2, SrF_2, and BaF_2. The temperature-dependent lifetimes of the H^- local modes are accounted for by anharmonic decay into three band phonons. For CaF_2, the lifetime of the H^- mode is well fitted to anharmonic decay to three equal-energy

TABLE I. 10-K fundamental frequencies (cm^{-1} ± 0.1), lifetimes T_1 (picoseconds $\pm 10\%$) as measured at 10 and 300 K (unless otherwise indicated), elastic band-phonon scattering coupling constants, A (THz), and temperature-independent contributions a (MHz) for the H^- and D^- local modes in CaF_2, SrF_2, and BaF_2.

Crystal	Frequency	T_1 (ps)		A	a
		10 K	300 K		
$CaF_2:H^-$	965.2	43	20	16.0	13 550
$SrF_2:H^-$	892.8	170	50	6.0	25 300
$BaF_2:H^-$	802.1	212	54	3.0	25 000
$CaF_2:D^-$	694.5	3.8	3.1 (220 K)	8.0	16 350
$SrF_2:D^-$	640.1	10.5		1.7	43 600
$BaF_2:D^-$	575.1	11.6	4.8 (190 K)	1.3	28 300

phonons of one-third the local-mode energy. In contrast, the H^- modes in both SrF_2 and BaF_2 require combinations of two high-energy phonons and one low-energy phonon to account for their temperature-dependent lifetimes. The lifetime of the D^- mode in CaF_2 is only weakly dependent on temperature, consistent with its anharmonic decay into two lattice phonons. The D^- mode in BaF_2 is strikingly different, in that, the decrease of its lifetime with temperature could only be accounted for by its near resonance with three TO lattice phonons.

The pure dephasing rates of all of the hydrogenic local modes are accounted for by elastic band-phonon scattering processes, together with a small temperature-independent inhomogeneous contribution.

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