Reorientational tunneling and elastic-dipole properties of OH⁻ and OD⁻ molecular defects in alkali fluorides

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A microscopic model of OH⁻ and OD⁻ molecular defects and their reorientational tunneling has been determined in alkali fluoride crystals, using high-resolution Fourier transform infrared studies of their stretching mode absorptions. In LiF, NaF, and KF hosts, the measured integrated stress dichroisms yield symmetries and values of their elastic dipoles, which are found to be ''disk-shaped'' $\langle 111 \rangle$ oriented tensors aligning with a Curie law parallel to an applied $\langle 111 \rangle$ stress. Analyses of the spectral band shapes and their changes under stress alignment and T variation allow us to estimate their tunneling splittings Δ and vibrational lifetimes τ. This is best detectable in LiF:OH⁻, for which the separation and width of two well-resolved Lorentzian bands at 2–20 K yield $\Delta = 1.2$ cm⁻¹ and $\tau \approx 9$ ps. Isotope variation H→D reduces strongly the tunneling splitting by at least a factor of 6 in LiF and NaF. A general model for $\langle 111 \rangle$ oriented elastic dipole disks with 70° tunneling between nearest neighbor orientations is derived which may become valid for OH⁻/OD⁻ in all five alkali fluorides. [S0163-1829(97)51834-0]

In the extended paraelectric and paraelastic studies of OH⁻ defects in alkali halides over a period of 33 years,[1] the whole group of alkali-fluoride hosts has been nearly totally left out. The reason for this was partially due to discouraging negative electro-optical results, which were in strong contrast to the important paraelectric dichroism[2] and Kerr effect[3] results in all alkali-chlorides, -bromides, and -iodides studied so far. Neither the electronic (UV) nor stretching-mode (IR) absorption of OH⁻ in LiF, NaF, and CsF hosts showed detectable electrodichroism due to OH⁻ dipole alignment under fields up to $\sim 10^5$ V/cm and temperatures down to ~ 1.3 K.[4] Similarly, paraelectric resonance experiments in LiF:OH⁻ yielded negative results.[5] In both these studies it was suggested that high potential barriers for the OH⁻ on the substitutional site of small F⁻ ions make its field alignment or microwave-induced reorientation impossible. The question whether this could be achieved only at higher T by thermally activated processes was tested and ruled out with very sensitive thermally stimulated depolarization current experiments with negative results.[6] In contrast and contradiction to this, thermal conductivity[7] and dielectric[8] measurements of LiF:OH⁻ indicated by a low-temperature heat-conductivity dip and saturating dielectric response, respectively, the presence of defects with some tunneling splitting estimated in the 1–2 cm⁻¹ regime. These two encouraging results, however, remained ''singularities'' which were never tested or confirmed with other techniques, or extended to OH⁻→OD⁻ isotope or alkali-fluoride host material variation.

We have started a systematic study, trying to determine with different techniques values and symmetries of the electric and elastic dipoles as well as tunneling splittings and reorientational potentials of both OH⁻ and OD⁻ defects in all five fcc alkali fluorides. We report here significant results of optical and elasto-optical studies, so far mainly obtained in the two most simple hosts LiF and NaF. Disregarding their OH⁻/OD⁻ electronic absorption in the vacuum UV (which

cannot differentiate the two isotopes and still has questionable polarization behavior[2]), we have chosen high-resolution (0.1 cm⁻¹) Fourier transform infrared (FTIR) spectroscopy of their stretching mode (SM) absorption [with well-separated $\omega(\text{OH}^-)$ and $\omega(\text{OD}^-)$ frequencies and its definite polarization parallel to the molecular axes]. Figure 1 shows in double-logarithmic scale the T dependence of the full width at half maximum (FWHM) of this OH⁻ and OD⁻ absorption in LiF and NaF. In distinct contrast to the SM properties in alkali chlorides or bromides,[9,10] our four systems show a very peculiar twofold temperature behavior: nearly constant FWHM values from 2 K up to about 70 K, followed by thermal broadening with a simple $T^{1.6-2.2}$ power law under preservation of Lorentzian band shape.
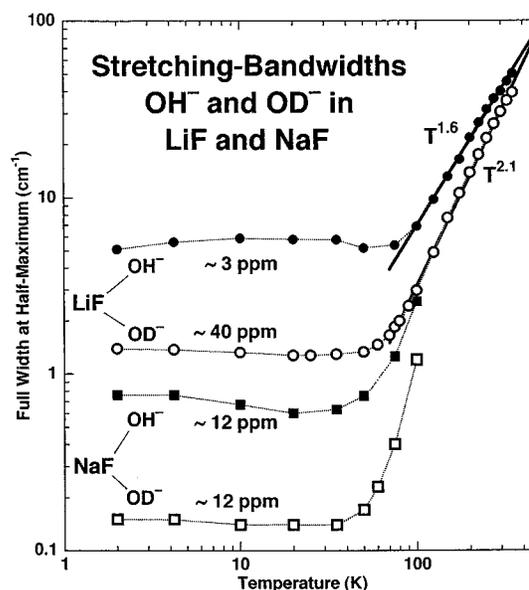
FIG. 1. Temperature dependence of stretching bandwidths of OH⁻ and OD⁻ defects in LiF and NaF.
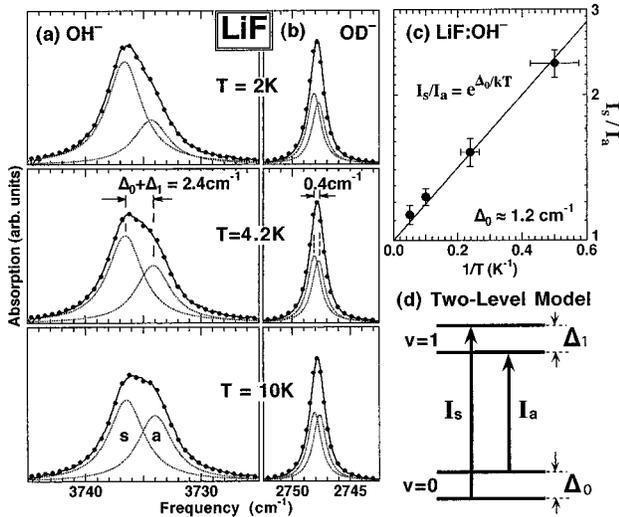
FIG. 2. SM spectra and curve fittings of (a) OH⁻ and (b) OD⁻ defects in LiF at $T = 2$, 4, and 10 K. (c) Boltzmann plot of intensity ratio I_s/I_a and (d) schematic level diagram for I_s and I_a transitions of OH⁻ in LiF.

We first focus on the $T < 80$ K results in Fig. 1, measured in both hosts at small molecular concentrations to exclude defect interactions. Selecting the LiF host for best possible band shape analysis, we show in Figs. 2(a) and 2(b) the measured OH⁻ and OD⁻ SM absorption at three different temperatures, 2, 4.2, and 10 K (full curves). The clearly visible substructure of the OH⁻ absorption can be easily decomposed with computer curve fitting into two Lorentzian bands ("a" and "s," dotted curves), such that their sum (displayed by points ●) fits very accurately the measurements over the whole spectral range. Within experimental accuracy, the separation of the two subbands ($\Delta\omega = 2.4$ cm⁻¹) and their equal half widths of 3.7 cm⁻¹ remain constant between 2 and 20 K.[11] Changing with T, however, is their relative integrated strength I_s/I_a, which in logarithmic plot vs $1/T$ [Fig. 2(c)] yields a Boltzmann behavior with activation energy of $\Delta_0 = 1.2$ cm⁻¹. A simple two-level tunneling model [Fig. 2(d)] accords well with these results: Splitting of the vibrational states $v = 0$ and $v = 1$ by Δ_0 and Δ_1 splits the $0 \rightarrow 1$ transition into Stokes and anti-Stokes absorption lines "s" and "a" of separation $\Delta\omega = \Delta_0 + \Delta_1$, and of relative strength I_s/I_a determined by the Boltzmann equilibrium in the Δ_0 split ground-state doublet. From our data we obtain the same value $\Delta = 1.2$ cm⁻¹ for the $v = 0$ and $v = 1$ state (as expected for independent tunneling and vibrational motion of the molecule).

In distinct contrast to this OH⁻ behavior, the much narrower SM absorption of OD⁻ in LiF shows no direct indication for a two-band structure [Fig. 2(b)]. Its band shape of width $H = 1.43$ cm⁻¹ can be fitted (with similarly small rms error) either by a single Lorentzian, or by pairs of Lorentzians of slightly decreasing width $\bar{H}$ and increasing separation $\Delta\omega$ up to $\Delta\omega_{max} = 0.25H = 0.36$ cm⁻¹. In spite of large uncertainty, this yields with $\Delta\omega_{max}/2 = \Delta_{max}(OD^-) = 0.18$ cm⁻¹ an upper limit for tunneling splitting $\Delta(OD^-)$: at least a factor of 6 smaller than the $\Delta(OH^-) = 1.2$ cm⁻¹ value. In the NaF host, the proceedingly smaller half width of OH⁻ and OD⁻ absorption (see Fig. 1) makes estimates of Δ from

band shapes even more uncertain. Using as a boundary the above $\Delta\omega \lesssim 0.25H$ relation, we obtain at least rough estimates about the upper limit tunneling splittings Δ, listed in Table I together with the values in the LiF host.

Evidently, the as yet unknown nature and symmetries of the discussed tunneling processes and states must still be determined. Expecting that orientational tunneling occurs and the molecules introduce sizable anisotropic elastic lattice deformations ("elastic dipole tensors λ"), we have measured their paraelastic alignment under stress of different symmetries. As the axis λ_1 of these tensors coincides in directions with the molecular axis and its stretching motion, their alignment can be monitored directly by the stress-induced integrated absorption changes $I(S)/I(0)$ of the stretch band.[12] Figure 3 summarizes this stress-optical dichroism for OH⁻ and NaF and LiF as a function of S (at 4 K) and of temperature (at $S = 600$ atm). The observed total absence of any dichroism for S_{100} and its achieved size and sign for S_{111} clearly show that OH⁻ in these hosts form "disk-shaped" elastic dipole tensors which align with their

TABLE I. Summary of the Δ, α_{111}, $\bar{H}$, and τ results, obtained from spectral and elasto-optical measurements at 4 K for OH⁻/OD⁻ defects in LiF and NaF.

		LiF		NaF	
		OH⁻	OD⁻	OH⁻	OD⁻
Δ [cm⁻¹]	from band shape	1.2	$\lesssim 0.2$	$\lesssim 0.10$	$\lesssim 0.02$
	from stress align.	1.2	$\gtrsim 0.15$	$\gtrsim 0.08$	
	α_{111} [10^{-24} cm³]	−3.3	−3.3	−2.4	
	$\bar{H}$ [cm⁻¹]	3.7	∼1.3	∼0.70	∼0.12
	$\tau = (c\bar{H})^{-1}$ [ps]	9.0	∼26	∼50	∼280
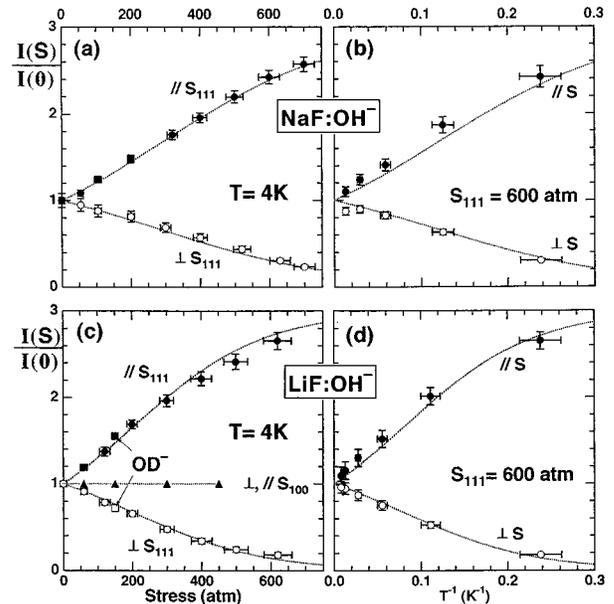
FIG. 3. Integrated OH⁻ absorption ratio $I(S)/I(0)$ in LiF and NaF under variation of S and T, measured parallel and perpendicular polarized to the applied stress S. The curves are calculated and fitted for the $\langle 111 \rangle$ elastic-dipole model as described in text.
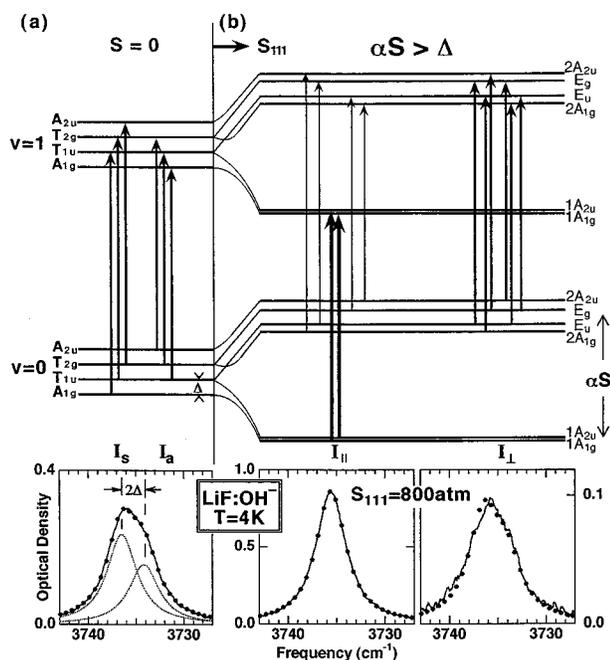
FIG. 4. Energy levels of tunneling states of $\langle 111 \rangle$ oriented disk-shaped elastic dipoles for (a) $S=0$ and (b) $S>\Delta/\alpha$ compared in both these cases to measured and decomposed absorption spectra of LiF:OH$^-$ at 4 K.

FIG. 5. Comparison of alkali halide anion sizes with proper shape and size of OH$^-$ ion; the latter is obtained from S. Okazaki *et al.*, J. Chem. Phys. **92**, 15 (1990).

axes parallel to the S_{111} compression. As indicated by the dotted curves in Fig. 3, both measured S and T dependences can be fitted very well with the relations

$$I(S)/I(0)_{\parallel} = (3+e^a)/(1+3e^a), \qquad (1)$$

$$I(S)/I(0)_{\perp} = 1.5 - \tfrac{1}{2}I(S)/I(0)_{\parallel} \qquad (2)$$

(with $a=8\alpha S/9kT$), calculated for paraelastic alignment of interaction-free elastic dipole tensors. The resulting negative splitting factors α_{111} obtained from best fit are listed in Table I. (First exploratory S_{100} and S_{111} experiments in KF:OH$^-$ yield similar results, with α_{111} close to -7×10^{-24} cm^3.)

This information from classical paraelastic alignment allows us to replace the simple two-level model [Fig. 2(d)] by a realistic three-dimensional eight-well model of $\langle 111 \rangle$ oriented dipoles [Fig. 4(a)]. The presence of reorientational tunneling will split the eightfold-degenerate localized states into tunneling states of A_{1g}, T_{1u}, T_{2g}, and A_{2u} symmetry, with energy-splitting values between them determined by the tunneling probabilities through the possible 70°, 110°, and 180° reorientation angles.[13] Calculated electric dipole transitions between these levels should appear as ''fine structure'' on top of the $0\rightarrow1$ vibrational absorption. In case 70° tunneling is predominant, the levels split equidistant by Δ in energy, and the simple vibrational fine structure should be a doublet of Stokes and anti-Stokes shifted lines of separation 2Δ and relative strength $\exp(\Delta/kT)$. Our exact observation of this in LiF:OH$^-$ confirms that only 70° tunneling between nearest-neighbor positions plays a role.[14]

Application of S_{111} converts this Δ tunneling system of O_h symmetry into two different trigonal tunneling multiplets which separate under increasing S by $U_S=\alpha S$. In Fig. 4(b) we plot for our $\langle 111 \rangle$ oriented disk-shaped tensor the calcu-

lated conversion and splitting of levels, indicating for $\alpha S>\Delta$ the allowed electric dipole transitions polarized parallel and perpendicular to S. Under neglect of the splittings within each multiplet, the integrated absorption strengths parallel and perpendicular to S yield the classical S/T stress alignment of our defects in Fig. 3. Beyond this, however, distinct changes of the optical band shape are expected.[15] For parallel polarization and $\alpha S>kT$, the weak contributions from the upper multiplet essentially preserve their splitting but become thermally depopulated, while the $1A_{1g}$ and $1A_{2u}$ states of the dipoles aligned into the S_{111} direction lose their initial tunneling splitting Δ. As indicated in Fig. 4(b), the measured strongly increased parallel absorption at 800 atm/4 K has indeed lost its 2Δ separated double Lorentzian structure and fits nearly accurately a single Lorentzian of unchanged width ($\bullet\bullet$). In contrast to this, the remainder of the perpendicular absorption from unaligned dipoles keeps essentially its width and structure from $S=0$, as expected from the level diagram. These observed band-shape changes under stress alignment confirm perfectly our presented nearest neighbor orientational tunneling model for LiF:OH$^-$. In spite of an unresolved double structure in the other systems, slight narrowing effects under alignment into the S_{111} directions have been also observed for parallel polarization in LiF:OD$^-$ and NaF:OH$^-$. This leads at least to rough estimates of their Δ values, which lie close to the ''upper limit values''obtained from the $S=0$ band-shape analysis, as summarized in Table I. More accurate Δ(OD$^-$) values will be obtained from *dielectric* experiments down to $kT<\Delta$ (started in collaboration with another group[16]), which will also yield electric-dipole moment values, expected to be very small to account for the negative electro-optical results.[4]

The large half widths $\bar{H}>\Delta$ and Lorentzian shape of our SM absorptions indicate homogeneous broadening due to short lifetimes $\tau=(c\bar{H})^{-1}$ as listed together with $\bar{H}$ values at 4 K in Table I. Obviously, an ultrafast (ps) nonradiative decay of the photoexcited $v=1$ state takes place, in both hosts more rapid for OH$^-$ compared to OD$^-$. In order to determine the nature and isotope dependence of this decay mechanism,

we have started to study the coupling of OH^-/OD^- defects to lattice phonons and librational modes with two complimentary techniques: SM absorption sideband and polarized Raman spectroscopy. Both these approaches will yield symmetry, strength, and spectral distribution of the phonon coupling and librational motion of our molecules.

The final goal of this work is not only a full understanding of the OH^-/OD^- physical properties in all five fcc alkali fluorides, but also comparison to their behavior in alkali chlorides and alkali bromides.[1] The main reason for drastic differences in these two classes of hosts is illustrated in Fig. 5—extremely tight fit of the egg-shaped OH^- molecule into the F^- vacancy versus a very loose fit into the Cl^- and Br^- lattice sites. In the latter group of hosts, sizable off-center shifts give rise to large (displacement+molecular) electric dipoles[2] and cigar-shaped elastic-dipole tensors of $\langle 100 \rangle$ symmetry.[12] Orientational tunneling not only involves complicated angular and translational motion of the molecule, but also needs renormalization of Δ to a much smaller Δ^* value to take care of the reorientation of strong gerade and ungerade distortions in the surrounding lattice.[17] This ''dressing effect'' obscures (or may even invert[18]) the large difference $\Delta(OH^-) > \Delta(OD^-)$ expected for the tunneling of the ''bare molecule.''

As we show in this work, all these extensively studied OH^- properties change drastically under variation to the smallest host anion F^-. In the LiF, NaF, and KF systems studied so far, substituted OH^- molecules form, without off-center shifts, $\langle 111 \rangle$ oriented defects with small electric-dipole moments and disk-shaped T_{2g} elastic-dipole tensors. The reason for their new $\langle 111 \rangle$ orientation is quite easily understood from the $\sim 12\%$ larger axial size of OH^- compared to the F^- host ion, which would require for $\langle 100 \rangle$ orientation high repulsion energy and strong E_g symmetry lattice deformation. It is harder, and a challenge for theory, to answer the question why the elongated OH^- molecule (see Fig. 5) in the $\langle 111 \rangle$ orientation gives rise to a disk-shaped lattice deformation of T_{2g} symmetry. Contrary to conclusions derived from earlier negative results,[4–6] the strong spatial confinement of OH^- in the alkali fluorides allows still large reorientational tunneling within the eight-well potential with $\langle 111 \rangle$ minima. Strong preference of nearest-neighbor 70° tunneling through $\langle 110 \rangle$ orientation is easily understood from the above-mentioned high-energy barrier for $\langle 100 \rangle$ orientation, necessary to be crossed in next-nearest-neighbor 110° tunneling. The observed large tunneling variation under $OH^- \rightarrow OD^-$ isotope exchange clearly indicates that its tunneling involves very little translation and/or ''dressing'' by motion of lattice deformations, but is mostly performed by the mass of H or D. Obviously, results from the currently started dielectric and Raman experiments (and extension to the still missing RbF and CsF hosts) will be important for construction of more detailed microscopic defect and tunneling models as well as realistic rotational potentials.

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