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Comment on ''Universal two-state reorientational dynamics of diatomic hydrides in fcc salt crystals''

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In a recent paper, Mungan *et al.* [Phys. Rev. B **54**, 9204 (1996)] have proposed a model of ''universal two-state reorientational dynamics of diatomic hydrides in fcc salt crystals,'' based experimentally on an observed disappearance of librational ir absorption around 150 K. For the only presented example of OH^- defects in RbCl hosts, we show by comparison to our measurements that this claimed disappearance is not valid even up to $T=350$ K. Moreover, we show by accurate spectral data of two other examples (OH^- and OD^- in KBr) that the claimed universal validity of the proposed ''thermally activated jump-rotational-diffusion model'' is not true for OH^- and OD^- in fcc alkali-chloride and bromide crystals and that there is no contrast to the OH^-/OD^- dynamic behavior in bcc CsCl hosts. [S0163-1829(97)01833-X]

In two recent papers[1,2] and unpublished work,[3] Mungan *et al.* have proposed a ''universal two-state reorientational dynamics'' for a variety of diatomic hydride defects in various fcc alkali-halide hosts. The concept of this model was developed as an analogy to a defect-host system of extremely high thermal instability, Ag^+ in KI, which by extensive studies over 25 years have been shown to change from a ''vacancy-centered'' to an ''off-center'' configuration between 1.2 and 20 K. Besides thorough theoretical treatments[4] of this system, a hopping process between the two different states was experimentally proven by electronic UV absorption, Raman scattering, dielectric response, and far-ir resonant- and gap-mode data, which all change with identical T dependence in this narrow T range.[4] It is evident that such a ''bistability'' requires a very particular defect-lattice interaction, expected to change drastically under variation of host-anion, -cation, and defect size. This is well established, e.g., for Ag^+, Cu^+, and Li^+point-ion defects, which alternate in different hosts between well-defined on- and off-center positions. Only in very particular ''borderline systems,'' coexistence of both configurations may occur, or can be achieved (e.g., in RbCl:Ag^+) ''artificially'' using fine-tuning of their interaction potential by appropriately chosen hydrostatic pressure.[5,6]

In recognition of these results from well-studied and -understood model systems, it is hard to accept the hypothesis[1–3] that a large group of chalcogen-hydride anions substituted into alkali halides should all give rise to a similar thermally unstable and coexisting two-state behavior involving off-center positions. Arguments against this are based on the fact that the treated OH^-, SH^-, SeH^-, and TeH^-ions are isoelectronic and comparable in size and mass to the F^-, Cl^-, Br^-, and I^-host anions, respectively. While the F^--like OH^- can easily occupy off-center positions in chlorides, bromides, and iodides, an off-center potential for the Br^--like SeH^- ion will surely not exist in KCl hosts. By extended electro- and elasto-optical experiments,[7–9] drastic differences in three important properties have indeed been established for small OH^- ions versus the large SH^-, SeH^-, and TeH^- ions: (a) large *electric dipole moment* values of $\sim$0.6–1.2 e Å (particularly from off-center displacements) versus very small ones ($p \leqslant 0.01$ e Å), (b) ellipsoidal versus disk-shaped *elastic dipole tensors*, and (c) *orientational potential* with six $\langle 100 \rangle$ minima vs an eightfold potential with $\langle 111 \rangle$ minima. Though these properties were established in most cases only for the $T<20$ K range, there is one important published exception: The stress dichroism due to paraelastic alignment of SH^-in KCl was measured up to 100 K, showing, by its Curie-law $1/T$ dependence total persistence of its low-temperature elastic state, a $\langle 111 \rangle$-oriented disk-shaped elastic dipole tensor.[10] This rules out in our opinion the thermally activated transition into a new orientational diffusive state, as postulated for this system in Fig. 11(b) of Ref. 1. More accurate and conclusive high-T stress-optical experiments on several XH^- test systems are running at present in our laboratory and will be published separately.[11]

Besides the above-discussed arguments against the universal validity of the two-state model for very different defect and lattice systems, we question in this Comment the experimental results which led to its postulation. While in the KI:Ag^+ model case many optical properties change with identical dependence in a narrow T range,[4] in the treated XH^- systems it is basically only one: Their ir absorptions due to a librational motion of XH^-(or XD^-) around its center of mass are claimed to disappear between 0 and 150 K. In Ref. 1, this is shown spectrally in Figs. 1–7 and 9, while Fig. 11 summarizes the T dependence of the ''disappearing effect'' and its (four-parameter) fit to the proposed model. A claimed ''reappearance'' of this lost librational absorption in the form of a generalized Debye spectrum in the millimeter wave region has been measured only for a single system of KBr:SH^- in Fig. 10 of Ref. 1. We focus here mainly on the OH^-/OD^- species, which have been studied in Refs. 1 and 3 only for a single case (RbCl:OH^-) by observing the librational mode at $\sim$270 cm^{-1} either as a direct ir transition or as a sideband of the OH^- stretching mode. Both these approaches have been already extensively used $\sim$30 years ago in librational studies of several OH^- and OD^- defects. In these early sideband studies,[12,13] no disappearing effect of

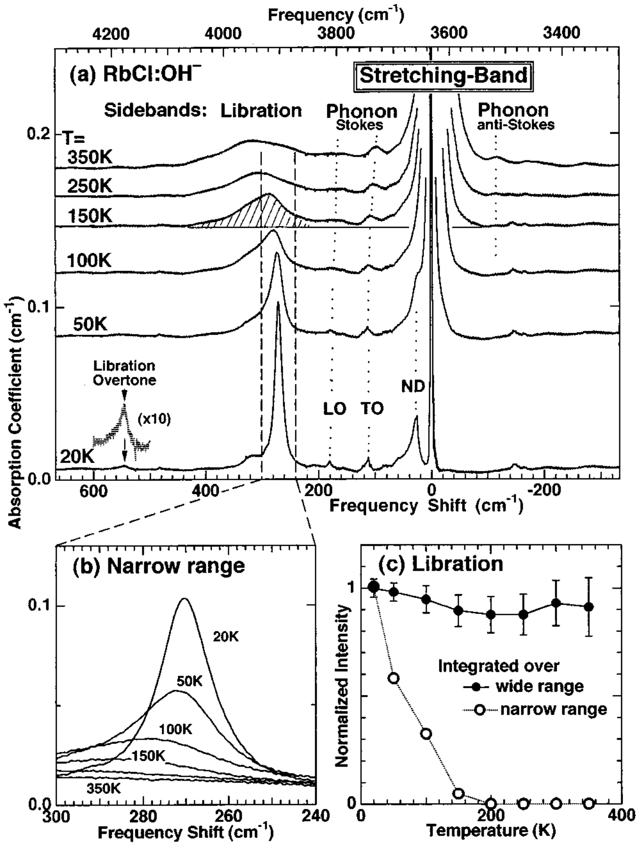

FIG. 1. Near ir absorption of $\mathrm{RbCl}^{+}+2\times10^{-4}\ \mathrm{OH}^{-}$ under a temperature variation of 20–350 K. (a) Spectra of OH$^-$ stretching band and all observable sidebands (Ref. 14). (b) Librational sideband in 7 times expanded but narrow spectral range. (c) Temperature dependence of libration sideband intensity, integrated over a properly chosen wide (solid circles) and improper narrow (open circles) spectral range.

librational sidebands has been observed in KCl, KBr, and RbCl. The severe contradiction to the new Fourier transform infrared (FTIR) measurements in RbCl:OH$^-$ is suggested by the authors of Ref. 1 to arise from ''uncorrected overall base line shifts'' in the old data.

In a comprehensive FTIR study of OH$^-$ and OD$^-$ in all alkali halide hosts running at present in our laboratory, we measure also all detectable sidebands of the stretching modes. Figure 1(a) shows our spectral results for RbCl:OH$^-$ measured at six different temperatures between 20 and 350 K. In the range of low-energy shifts from the stretching band, we observe—besides the important ''non-Devonshire'' (ND) absorption[12]—very weak LO and TO phonon sidebands (detectable also at higher temperature on the anti-Stokes side). The strongest sideband due to libration at ~270 cm^{-1} shows clearly, with rising temperature, *very strong broadening, increasing frequency shift from the stretch band, and persistence of its strength up to 350 K.* Though with rising T and broadening proper baseline determination becomes more uncertain, its position, e.g., at 150 K indicated in the figure is still very well defined. Our measured small one-phonon sidebands, which increase only slightly with temperature, make the assumption in Ref. 1 of ''temperature-dependent base line shifts below the libration absorption due to two-phonon sidebands'' meaningless. Careful integration of the librational band over the properly wide spectral range yields the curve (solid circles) in Fig. 1(c) for its intensity as a function of temperature. Within its well-recognized error bars (increasing with T), this curve shows essentially a *temperature-independent strength up to 350 K*—in total contrast to the error-bar-free ''disappearance effect'' in Fig. 11(c) of Ref. 1. The reason for this disagreement is in our opinion improper integration in Ref. 1, as clearly reflected in its Fig. 7(a). This shows the ''background-corrected librational sideband absorption spectra of RbCl:OH$^-$,'' plotted in a spectral range 240–300 cm^{-1}, much too narrow to account for the strong broadening and shift of the band with rising temperature. This becomes evident when we indicate this narrow region with dashed lines in our Fig. 1(a) measurement and show the resulting absorptions in this range spectrally explained in Fig. 1(b). When integrating improperly just over this small range, we obtain the incorrect intensity (T) curve (open circles) in Fig. 1(c), which closely resembles the ''disappearance curve'' in Fig. 11(a) of Ref. 1.

We have tested and confirmed this sideband behavior in several other fcc hosts, and show it as one more example in Fig. 2 for both OH$^-$ and OD$^-$ in KBr.[14] In these systems we see (besides weak isotope-independent LO and TO sidebands) the strong librational sideband at isotopically shifted positions for OH$^-$and OD$^-$, which strongly broaden, shift to higher energies, and preserve their strength under temperature increase up to 350 K.[15] It is obvious that the OD$^-$ libration (around 233 cm^{-1}) overlaps increasingly stronger with rising temperature the LO one-phone sideband and makes ''spectral separation'' and exact integration more uncertain. In summary of our presently running study,[16] we state that in all eight so far studied systems of both OH$^-$ and OD$^-$ ions in KCl, KBr, RbCl, and RbBr hosts, there is within experimental uncertainties *no indication for a librational sideband disappearance with rising temperature* up to 350 K.

This conclusion about the sideband behavior is not changed when observing the OH$^-$ libration as a direct ir transition, measured in Ref. 1 only for the RbCl:OH$^-$ system. Again, disregarding the strong temperature broadening and shift of the band, its plot over the same narrow (240–300 cm^{-1}) spectral range in Fig. 9 leads to an ''apparent disappearance effect.'' In all studies of direct librational transitions ~30 year ago,[13,17] no disappearance of the direct librational ir absorption with temperature increase was observed under proper wide-scale integration.

For completeness of experimental results, the extended Raman study of OH$^-$ in KCl and KBr should at least be mentioned.[18] In this approach, the observed direct librational transition cannot be determined quantitatively in strength due to its overlap with the strong two-phonon Raman response of the pure crystals. The observed weak libration-stretching combination band shows within error bars no decrease with rising temperature. In particular, the one in Fig. 3 of Ref. 18, mentioned in Ref. 1 ''to support our results,'' yields up to its highest measured temperature constant integrated intensity.

In summary, there is in our opinion no reliable experimental indication—neither from ir nor from Raman spectroscopy—for a rapid decrease of the libration of OH$^-$

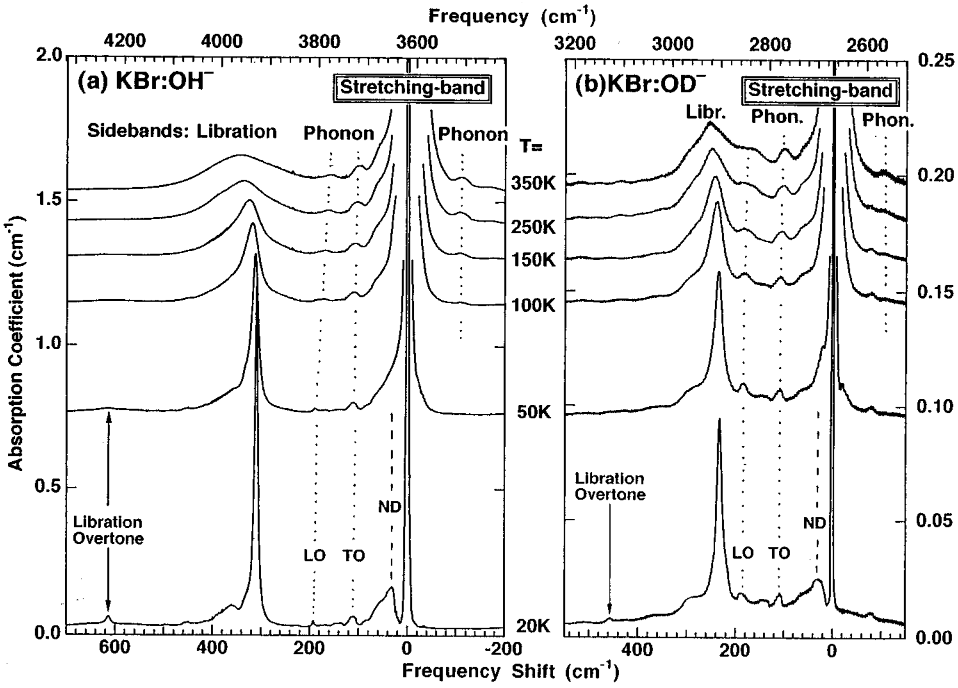

FIG. 2. Temperature variation (20–350 K) of stretching and sideband spectra (Ref. 14) in (a) KBr+1.5×10^{-3} OH$^-$ and (b) KBr+9×10^{-4} OD$^-$.

or OD$^-$ ions in fcc crystals with rising temperature. Contrary to the ir data in Refs. 1 and 3 claiming its vanishing around 150 K, we have measured particularly the libration-stretching combination bands in many systems and show for three examples that they persist in strength up to 350 K. This rules out, in our opinion, for these systems the validity of a postulated two-state model, based totally in its justification and parameter fit on the observation of a librational disappearance effect. Moreover, this removes the contrast (emphasized in Ref. 1) to the OH$^-$/OD$^-$ behavior in cesium halides, for which total persistence of the librational sidebands up to room temperature has already been measured and reported in our earlier work.[19]

Besides these experimental facts about the nonexisting librational disappearance, our result questions further the validity of the proposed two-state model. Our spectra in Figs. 1 and 2 show the observation of a weak overtone absorption ω_2 of the librational sideband ω_1, lying very closely to its double frequency ($\omega_2/\omega_1=546/270$ in RbCl:OH$^-$, 615/310 for KBr:OH$^-$, and 458/233 for KBr:OD$^-$).It is obvious that this $\omega_2$observation requires for any constructed orientational potential of the low-temperature-state energy barrier heights $U$with $U \gg \omega_2$. Evidently, the $U=542$ cm^{-1} value, derived in the two-state model of RbCl:OH$^-$ from librational disappearance in Ref. 1, is in total contradiction to the observed larger overtone value of$\omega_2=546$ cm^{-1}.

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[14] In both Figs. 1 and 2 we have removed for better clarity extremely sharp spectral lines close to the OH$^-$ or OD$^-$ stretching band or librational sideband. They are due to OH$^-$/OD$^-$defect pairs, treated in a separate publication [see A. Afanasiev and F. Luty, Solid State Commun. **98**, 531 (1996) and (unpublished)].

[15] It is worth mentioning that the ''old'' librational sideband results in Ref. 13 obtained with much simpler point-by-point ir instrumentation compared to modern FTIR technique—agrees quite closely with our new results in Fig. 1(a) and 2(a).

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