PHYSICAL REVIEW B VOLUME 10, NUMBER 8 15 OCTOBER 1974

Vibrational absorption of tunneling molecular defects in crystals.*
I. Tunneling molecules in electric fields (KCl:OH$^-$)

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(Received 19 October 1973)

We shall discuss the general question of how orientational tunneling of substitutional molecular crystal defects affects the vibrational absorption of the molecule and its behavior under electric fields or stress. As a model case, ⟨100⟩ oriented dipoles are considered with a tunneling splitting Δ sizable enough to contribute to the low-temperature width of the vibrational absorption. It is shown that field application should cause drastic anisotropic changes in the spectral structure of this system: while the "main transition" (with strength of order 1) becomes narrowed under field application, weak satellite absorption ("paraelectric resonance sidebands") of strength $\propto(\Delta/pE)^2$ should become shifted out of the vibrational spectrum in such a way that the second-moment contribution (from tunneling) of the total absorption remains constant. For the main vibrational transitions (the only ones observed so far), the tunneling model predicts second-moment decreases under field (or stress) application, the magnitude of which is highly anisotropic in terms of dipole, field, and polarization direction. These general considerations are applied to previously uninterpreted electrooptical measurements on the OH$^-$ vibrational absorption in KCl. The available data for various field directions and $\|$ and $\perp$ polarization are found in agreement with the above analysis, and allow a determination of the tunneling parameter Δ and a dipole orientation which agrees with other experiments. Previously assumed serious contradictions between vibrational band width and tunneling splitting can be resolved within the model taking into account random background strain or fields in the crystal.

I. INTRODUCTION

Electrooptical and elastooptical measurements have played a major role in the study of molecular dipole defects in alkali-halide crystals. In essentially all cases treated so far, the field- or stress-induced changes of the optical absorption (or refractive index) have been treated and interpreted in terms of a simple "*classical reorientation-dichroism model*": Field or stress alignment of the permanent electric or elastic dipole moments leads to an alignment of the anisotropic absorption (or refractive index) components of the defects. As a consequence, the initially isotropic optical behavior of the randomly oriented defect system changes into the dichroic (or birefringent) behavior of the aligned system, with different optical response for light polarized parallel ($\|$) and perpendicular ($\perp$) to the applied perturbation. This simple picture of the *alignment of permanent anisotropic absorption components* implies that only changes of the absorption strength *(zero-moment changes)* should be introduced. The model further yields in a straightforward way the anisotropy of the effect (e.g., predicting vanishing electro- and elastooptical effects for ⟨100⟩ dipoles under ⟨111⟩ field or stress).

For OH$^-$ dipoles in alkali halides, which have been investigated most comprehensively with optical techniques, electro- and/or elastooptical effects have been studied in the uv electronic absorption[1-3] and by the electronic Kerr[4] and Pockels effects,[5] in the near-ir vibrational absorption,[6,7] the far-ir librational absorption[8] and the combination vibration-libration absorption.[9,10] In about all of these cases, pure zero-moment absorption changes under stress and field have indeed been observed. From the anisotropy and magnitude of this "classical" reorientation dichroism, the symmetry and magnitude of the electric dipole p and elastic dipole α of the OH$^-$ has been derived for various host lattice systems.

This classical reorientation dichroism should occur alone only for the high-field (or stress) range, in which the orientational eigenstates of the molecule can be well described by strongly localized directed dipole states. It is well established, however, that the molecular defects reorient by tunneling, so that their eigenstates at zero field and stress should be linear combinations of the directed dipole states without electric dipole character ("tunneling states").[11] The initial multiplet of tunneling states, split by a characteristic tunneling-splitting parameter Δ, is transformed by the applied field E or stress S into the directed dipole states. This transformation takes place in the low-field (or stress) region in which the perturbation energy pE (or αS) is comparable to the tunneling splitting Δ. As the selection rules are different for the tunneling and directed dipole states, changes in the optical behavior can, in principle, be expected in this low-field range.

For the broad electronic and librational absorption bands of the OH$^-$ (about 4000- and 20-cm^{-1} width, respectively), the small effects from the tunneling splitting (in the 0.1-cm^{-1} range) will hardly be detectable. The absorption due to the linear stretching vibration of the OH$^-$ molecule at 2.7 μm, however, becomes extremely sharp at low temperatures[6] with a width comparable to estimated Δ values. High-resolution measurements of the field- and stress-induced dichroism of this narrow absorption band in RbCl and KBr yielded, however, again a pure zero-moment change classical reorientation dichroism.[6] For these two systems the tunneling splitting is not known, but expected to be very small, estimated from the observed long dipole/lattice relaxation time.[12,13]

In contrast to this, a larger tunneling splitting Δ is expected in KCl:OH$^-$ from the short relaxation time, and has been derived from paraelectric resonance[14]($\Delta = 0.18$ cm^{-1}) and specific heat[15] ($\Delta = 0.25$ cm^{-1}) measurements. (Δ is the splitting between the T_{1u} and E_g tunneling states; the $A_{1g} - T_{1u}$ splitting in the high-barrier limit is 2Δ). For the KCl system, indeed peculiar anisotropic lineshape changes of the narrow vibrational absorption ($H = 0.17$ cm^{-1}) under small fields were observed, which have been reported previously,[6] without having been understood and analyzed.

Even more clear cut, for our considerations, is the situation of the CN$^-$ molecule, which has been studied in a variety of alkali halides, particularly in KCl.[16] Measurements with various techniques gave conclusive evidence for a large tunneling splitting of about 1 cm^{-1} for the KCl:CN$^-$ system. The large width of the CN$^-$ vibrational absorption at low temperature ($H \approx 2.5$ cm^{-1}) was therefore attributed to the unresolved tunneling splitting of the molecule. In spite of the fact that here clearly the tunneling splitting contributes decisively to the absorption shape, stress-[17] and field-[18] application have been reported to cause only zero-moment absorption changes, and thus have been interpreted essentially in terms of a classical reorientation model.

In this work we will address ourselves to the question of how the orientational tunneling motion of substitutional molecules in a crystal affects their vibrational absorption under small applied field or stress. In the present paper we will first analyze in general the absorption changes for dipoles under electric fields, derived from the tunneling model, and will express the results in terms of simple and generally valid rules for the moments of the absorption. Subsequently, we will use this model to discuss and analyze the earlier results on the field-induced absorption changes in KCl:OH$^-$. This analysis, which includes qualitatively the effects from background strain and field, will remove the previous apparent contradiction between measured tunneling splitting and vibrational absorption width, and allows an estimate of Δ from the electro-optical data.

In Paper II of this work, we will first analyze in general the absorption changes for tunneling elastic dipoles under applied stress. We then will present extended new experimental material on the first and second harmonic vibration of CN$^-$ molecules in KCl and its dichroism under applied stress. The experimental reinvestigation of this problem was prompted by the serious and basic contradiction between the previous experimental results[16-18] and the expectations derived from the tunneling model. The treatment of this new material will serve as a prototype example for a system with large—and optically resolvable—tunneling structure, which makes it particularly useful to test the ideas and the model derived in the present paper.

II. TUNNELING MOTION AND VIBRATIONAL ABSORPTION OF ⟨100⟩ ORIENTED MOLECULES UNDER FIELDS OF DIFFERENT SYMMETRY

In Fig. 1 we will illustrate in the upper part the energy levels for the stretching vibration absorption of a ⟨100⟩ oriented diatomic molecule. Starting from the sharp ground and excited state levels of the localized vibration (with energy separation $h\nu_0$), tunneling among nearest-neighbor dipole sites (90° tunneling) leads to a splitting of the sixfold orientational degeneracy of both these states, producing the well-known multiplet of three tunneling states with A_{1g}, T_{1u}, and E_g symmetry and splitting of Δ and 2Δ.[11] [For convenience, the same splitting parameter Δ has been assumed for the ground and excited (*) vibrational state in the following; all considerations, however, can be easily extended to the more general case $\Delta^* \neq \Delta$.] The four dipole-allowed strong vibrational transitions are indicated as A, B, C, D. The right-hand side illustrates the splitting of the tunneling states under applied $E_{\langle 100\rangle}$, and the resulting optical transitions for light polarized $\parallel$ and $\perp$ to the applied field. These transitions (and the ones in the following figures) have been determined from the generally accepted wave functions[11] for ⟨100⟩ dipoles under strong electric fields ($pE > \Delta$), by calculation of the dipole matrix element for optical transitions up to the order of $(\Delta/pE)^2$ in strength. By determining similarly the allowed transitions between the low-field ($pE < \Delta$) wave functions, one can easily find the gradual evolution of the high-field transitions from the original transitions between the tunneling states at $E = 0$. This is illustrated in the lower part of Fig. 1, which shows the optical transition histogram at $E=0$, the shift of these transitions under applied $E_{\langle 100\rangle}$ field, and the transition histogram corresponding to the high-field ($pE>\Delta$) range. We limit our considerations to the case $kT \gg pE$, i.e., *absence of any field alignment* and note the following:

(a) For $E=0$, the four strong transitions A, B, C, D, (if not resolved)[19] give rise to an absorption band, the width of which can be characterized by a second moment $\langle U^2\rangle_{E=0}=2\Delta^2$ (or if $\Delta^*\neq\Delta$, $\langle U^2\rangle=\Delta^2+\Delta^{*2}$). As one can expect (in the absence of other broadening mechanism), the width of the band is determined by the energy uncertainties Δ and Δ^* in the two vibrational states.

(b) Under field application, the energies and wave functions of the states change, so that the original transitions shift and change in strength, and new transitions appear. For light polarization $\parallel E$, field localization of the dipoles leads to the appearance of the (initially forbidden) classical transition at $h\nu_0$, while the initial A, B, C, D transitions become shifted outwards under loss of their absorption strength. For $\perp$ polarization, the two strong transitions B and C remain unshifted, as the field does not affect the tunneling of the dipoles $\perp$ to the applied field.

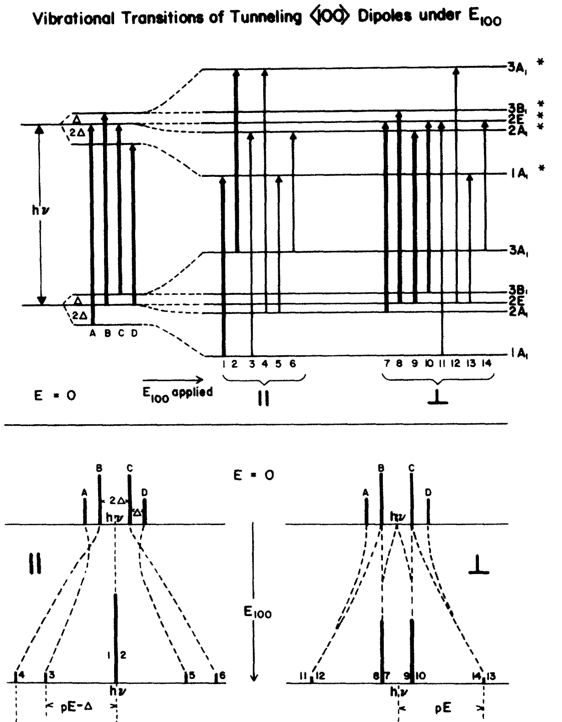

FIG. 1. Vibrational transitions of a tunneling ⟨100⟩ dipole under field application $E_{\langle 100\rangle}$. Upper part: Level diagram for vibrational ground and excited state with splitting by tunneling and applied $E_{\langle 100\rangle}$, showing the allowed optical transitions. (Strong arrows: "main absorptions"; weak arrows: "satellite absorptions".) Lower part: Absorption histogram for $E=0$ and $E_{\langle 100\rangle}$ applied, in parallel (||) and perpendicular ($\perp$) polarization.

In Fig. 2, the situation for ⟨100⟩ dipoles is similarly examined for the case of a ⟨111⟩ applied field. While for a *classical* directed ⟨100⟩ dipole model a ⟨111⟩ field should *not produce any electrooptical effect,* the transformation from tunneling to directed dipole states produces strong spectral changes (different for polarization $\parallel$ and $\perp$ to E), which are qualitatively similar to the $E_{\langle 100\rangle}$ case in Fig. 1. Note that here (in contrast to the $E_{\langle 100\rangle}$ case) the field application does *not* remove the tunneling splitting within any of the newly formed state multiplets. Nevertheless, the induced transformation in the character of the states by the field changes the selection rules in such a way that for light polarization $\parallel E_{\langle 111\rangle}$ the unshifted $A_1\rightarrow A_1^*$ transition at $h\nu_0$ becomes the only strong allowed transition.

Figure 3 examines in a similar way the situation for ⟨100⟩ dipoles under ⟨110⟩ applied electric fields. In this case three different absorption spectra should result, for light polarized parallel to the [110] field and polarized in the two inequivalent directions [1$\bar{1}$0] and [001] perpendicular to the

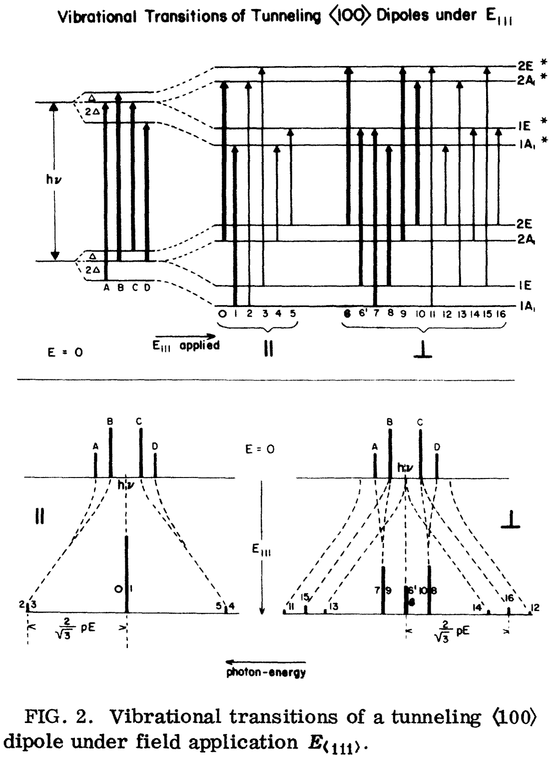

FIG. 2. Vibrational transitions of a tunneling ⟨100⟩ dipole under field application $E_{\langle 111\rangle}$.

field. In Fig. 4, an example is illustrated for uniaxial stress, applied in ⟨100⟩ direction to (cigar-shaped) ⟨100⟩ elastic dipoles. The nature of the stress-induced absorption changes is very similar to the field-induced changes in Figs. 1–3. We mention here the stress effect in view of its parallelity to the electric field effects, but will treat it in more detail in Paper II.

A general feature of all these (and other possible) transition pictures is evident. Starting from the tunneling transitions A, B, C, D, which are within a factor of 2 equal in strength and splitting, field and stress application (pE or $\alpha S > \Delta$) produces a pattern of transitions with *highly unequal spacing and strength,* containing two essential parts: (a) strong transitions (strength of the order of one) close to the center frequency $h\nu_0$, which do not shift any more for large E and S (*"main absorption"*); (b) weak *satellite absorptions,* which are shifted out of the center $h\nu_0$ under simultaneous decrease of their strength. For $pE > \Delta$ the shift becomes $\propto pE$ and their strength $\propto (\Delta/pE)^2$.

In spite of the considerable differences in the details of the transition spectra, some general features can be easily recognized and expressed in terms of moments of the total absorption. In the absence of alignment ($kT \gg pE$) the integrated absorption area (zero moment) for each polarization direction is unchanged by field or stress. In the absence of a change of the vibrational frequency ν_0 by the field or stress, the center of gravity (first moment) of the absorption is unchanged. While this is fairly trivial, it is not that evident that a similar conservation law holds for the second moment also. In spite of the strong changes in spectral distribution of the transition structure, the *second moment of the total absorption is unchanged by field or stress,* and remains $\langle U^2\rangle_E = \langle U^2\rangle_S = \langle U^2\rangle_{E=0} = \Delta^2 + \Delta^{*2}$. This can be easily verified by calculating the second moment summing over all allowed transitions predicted by the tunneling model for any situation of field, stress or light polarization. Physically, this empirical second-moment conservation law makes sense. Though field or stress application changes the character and energy of the states and localizes the dipoles, it does *not* change or remove the inherent tunneling effect Δ and Δ^* of the system, so that the energy uncertainty of the total absorption is still determined by $\langle U^2\rangle_{\text{total}} = \Delta^2 + \Delta^{*2}$ (for pE or $\alpha S \gg kT$).[20]

The existence of the weak satellite absorptions which should become shifted out of the main absorption by the electric field or stress, has not been recognized so far and has never been experimentally verified. Their role is an important one in several respects.

(i) The satellite absorptions can be regarded as the *"paraelectric resonance* (PER) *sidebands"* of

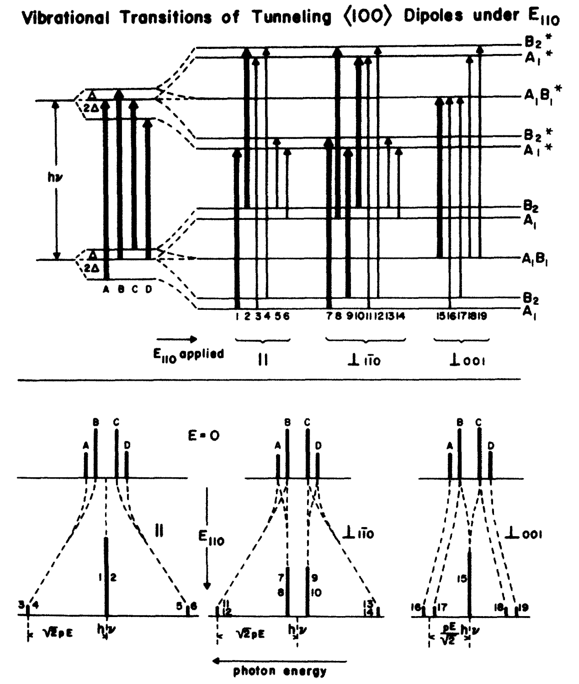

FIG. 3. Vibrational transitions of a tunneling ⟨100⟩ dipole under field application $E_{\langle 110\rangle}$.

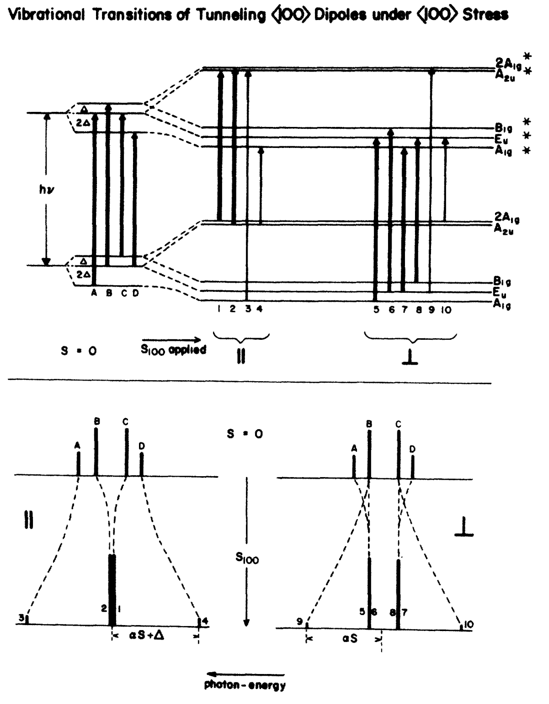

FIG. 4. Vibrational transitions of a tunneling ⟨100⟩ dipole under uniaxial stress application $S_{\langle 100\rangle}$.

the stretching vibration absorption. They correspond in energy directly to the PER transitions, added to (or subtracted from) the vibrational transition $h\nu_0$ and follow the same selection rules as the PER transitions. Their detection would allow "PER spectroscopy shifted into the near ir range" (with its advantage of continuously variable frequency).

(ii) The width of the satellite transitions is expected to be similar to the PER transitions (0.5–1.0 cm^{-1}). The reason for their larger width compared to the main absorption under field is that background strain will shift the energy difference of the levels producing the satellite transition much more than the transition energy of the main absorption. (This argument is similar to the one used in PER work for the difference in width of the $1A \to 2A_1$ vs $1A_1 \to 3A_1$ transition...).

(iii) As the satellite transition corresponds (in the high-field $pE > \Delta$ limit) to a vibrational transition under simultaneous 90° flip of the dipole, pumping of this transition (e.g., with a high-power laser) could be used as a method to optically reorient the dipoles—especially in systems with long relaxation times.

(iv) By the application of field or stress, the second-moment contribution $\langle U^2\rangle = 2\Delta^2$ from tunneling becomes—partially or totally—transferred into the satellite absorptions. For large $E_{\langle 100\rangle}$ fields and ∥ light polarization, for instance (see Fig. 1), the normalized strength of each satellite is $0.5 \times (\Delta/pE)^2$ and their distance from the center absorption at $h\nu_0$ is $\sim pE$, so that their second-moment contribution is $4\times 0.5(\Delta/pE)^2 \times (pE)^2 = 2\Delta^2$. The main absorption at $h\nu_0$ has become a classical sharp vibrational transition, which no longer carries any information about the tunneling splitting.

In all experiments under field and stress, done so far, only the main vibrational transitions (with strength of the order ~1) have been observed. Thus for practical purposes we are interested in the field- and stress-induced second-moment changes of these observable main transitions. With the *sum-rule for the second moment of the total absorption* established, it is easy to derive the field- or stress-induced second-moment changes $\langle\Delta U^2\rangle$ for the two absorptions *parts* (main and satellite), which must be equal and opposite: $\langle \Delta U^2\rangle_{\text{satell.}} = -\langle \Delta U^2\rangle_{\text{main}}$. As can be seen readily from Figs. 1–4, field or stress application reduces (for both light polarizations) the second moment of the main absorption and transfers it to the satellites. In Table I we list the normalized second-moment change under field application $\langle\Delta U^2\rangle_E / \langle U^2\rangle_{E=0}$ for the main absorption of ⟨100⟩, ⟨110⟩, and ⟨111⟩ dipoles, which can be easily derived from the tunneling model. As can be seen, the main absorption loses its total second-moment contribution from tunneling for *all* dipole and field directions in the ∥ observation. For the ⊥ polarization, the second-moment decrease lies between zero and the full second-moment contribution, depending on field and dipole direction. Note that this quantum-mechanical electrooptical effect is present even in the cases where the classical (zero-moment) alignment effect is absent due to symmetry (e.g., for ⟨100⟩ dipoles in ⟨111⟩ fields). While for ⟨100⟩ and ⟨111⟩ dipoles only nearest-neighbor tunneling has been considered in Table I, we list for ⟨110⟩ dipoles both the case of nearest-neighbor (60°) and next-nearest-neighbor (90°) tunneling. As can be seen, the expected narrowing effects in ⊥ polarization should be distinctively different for the two tunneling cases.

For applied stress, the induced second-moment change is for both ∥ and ⊥ polarization anisotropic under variation of dipole and stress direction. We will treat this case in more detail in Paper II.

It is evident that the observation of these predicted field- or stress-induced narrowing effects of the main vibrational absorption and their anisotropy should, in principle, allow the determination of the tunneling angle and splitting, as well as of the symmetry and magnitude of the dipole moment.

III. DISCUSSION OF NONCLASSICAL BEHAVIOR OF OH^- VIBRATIONAL ABSORPTION IN KCl

The OH^- vibrational absorption in KBr and RbCl displays under field or stress application an optical dichroism in agreement with the reorientation behavior of a classical diatomic vibrator: The field-

TABLE I. Normalized field-induced second-moment changes $\langle\Delta U^2\rangle_E / \langle U^2\rangle_{E=0}$ of the main absorption, derived from the tunneling model (for $kT \gg pE \gg \Delta$).

Dipole	Field	$\frac{\langle\Delta U^2\rangle_E}{\langle U^2\rangle_0}$ ∥ polar.	$\frac{\langle\Delta U^2\rangle_E}{\langle U^2\rangle_0}$ ⊥ polar.
⟨100⟩	$E_{\langle 100\rangle}$	−1	−0.5
	$E_{\langle 111\rangle}$	−1	−0.25
	$E_{\langle 110\rangle}$	−1	$-0.5(\perp_{\bar{1}10})$ $-1(\perp_{001})$
⟨111⟩	$E_{\langle 100\rangle}$	−1	0
	$E_{\langle 111\rangle}$	−1	−1
	$E_{\langle 110\rangle}$	−1	$-1(\perp_{\bar{1}10})$ $0(\perp_{001})$
⟨110⟩ 60° tunnel.	$E_{\langle 100\rangle}$	−1	−0.5
	$E_{\langle 111\rangle}$	−1	0
	$E_{\langle 110\rangle}$	−1	$-0.5(\perp_{1\bar{1}0})$ $-1(\perp_{001})$
⟨110⟩ 90° tunnel.	$E_{\langle 100\rangle}$	−1	0
	$E_{\langle 111\rangle}$	−1	−1
	$E_{\langle 110\rangle}$	−1	$-0.5(\perp_{1\bar{1}0})$ $0(\perp_{001})$

or stress-induced absorption changes[21] (if measured with appropriate high resolution) follow the spectral shape of the original absorption band, with the magnitude, direction, and anisotropy of these zero-moment changes in quantitative agreement with the classical paraelectric alignment model.[6]

A clear deviation from this classical reorientation dichroism was found for the KCl:OH$^-$ system,[6] as summarized in Fig. 5. The original vibrational absorption band [Fig. 5(a)] becomes more narrow under field application. Figure 5(b) shows the spectral dependence of the absorption change, caused by a small electric field (of the same magnitude), applied in three different directions. For all directions of field and light polarization a similar ΔK spectrum, corresponding to a second-moment decrease, is observed. The magnitude of the effect in $\parallel$ polarization varies very little with the field direction, though being slightly higher for $\langle 111 \rangle$ fields. In $\perp$ polarization the effect is smaller; compared to the corresponding $\parallel$ effect it is reduced by a factor 5 ± 0.5 for $E_{\langle 111 \rangle}$ [Fig. 5(b)], and by a factor of (2 ± 0.5) for $E_{\langle 100 \rangle}$ (Fig. 12, Ref. 6). For larger E/T values [Fig. 5(c)], one finds superimposed on this initial narrowing effect the field-induced zero-moment change due to dipole alignment. Similarly, application of uniaxial stress $S_{\langle 100 \rangle}$ leads to a sizable initial narrowing effect of the band (stronger again for $\parallel$ polarization) in addition to the zero-moment change from stress alignment. In Fig. 6(a) the measured field-induced absorption increase in the center of the band is shown as a function of $E_{\langle 100 \rangle}$.

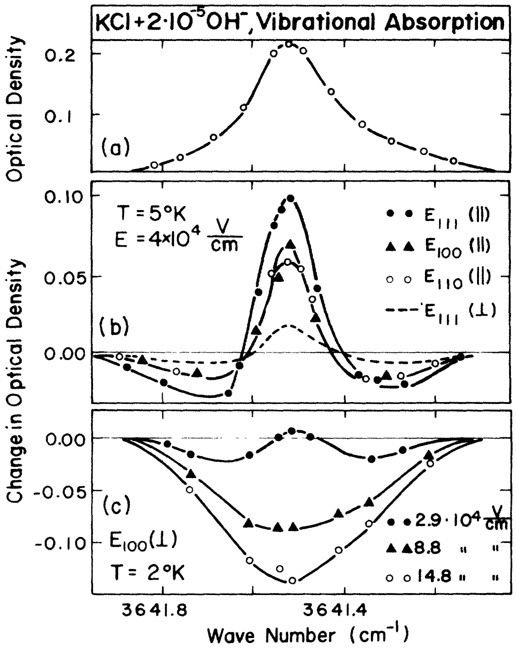

FIG. 5. Summary of the electrooptical behavior of the OH$^-$ vibrational absorption in KCl (Ref. 6). (2×10^{-5} Mol parts KOH in KCl.) (a) Absorption spectrum at 4 °K. (b) Spectral change of the optical absorption under small electric field, applied in $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ direction at 5 °K, measured in $\parallel$ and $\perp$ polarization. (c) Spectral change of the optical absorption under $\langle 100 \rangle$ fields of different strength, measured in $\perp$ polarization at 2 °K.

The understanding of these—so far completely uninterpreted—results follows in a straightforward way from the discussion in Sec. I. In contrast to the classically behaving KBr:OH$^-$ and RbCl:OH$^-$ systems, the tunneling splitting is sizable for KCl:OH$^-$, so that nonclassical electro- and elasto-optical behavior can be expected. We imply (as we did earlier in Sec. I) that in all optical measurements only the main transitions (with strength of the order 1) have been observed, and that the very weak (and possibly more broadened) PER sidebands, tuned out of the center $h\nu_0$ by the field, were not detected. With this assumption, the observed narrowing in Fig. 4(b) can be attributed to the second-moment decrease, expected from the tunneling model for the main transitions (Figs. 1–3 and Table I).

For $\langle 100 \rangle$ dipoles, small applied fields ($pE < \Delta$), and light polarization $\parallel$ to E, the tunneling model predicts that the (initially forbidden) sharp $1A_1 \rightarrow 1A_1^*$ transition should appear under field application with a strength $(pE/3\Delta)^2$ for light polarization $\parallel E$. We assume that the increase in the center of the ΔK spectrum in Fig. 5(b) is caused by the appearance of this classical transition. If we normalize this field-induced absorption increase in the center of the band $\Delta K(E)$ to its maximum saturation value (for large E) ΔK_{max}, and plot this normalized $\Delta K(E)/\Delta K_{\text{max}}$ ratio in double logarithmic scale [Fig. 6(b)], one obtains indeed a good initial $(pE)^2$ dependence. Comparison of this measured dependence to the expected $(pE/3\Delta)^2$ yields a tunneling parameter $\Delta = 0.26$ cm^{-1} (corresponding to 0.38 °K). For large fields ($pE \gg \Delta$), the tunneling model predicts that the strength of the $1A_1 \rightarrow 1A_1^*$ transition should approach saturation with $[1 - \gamma(\Delta/pE)^2]$, with the factor γ depending on the field direction. For the $\langle 100 \rangle$-field case, the expected $1 - 2(\Delta/pE)^2$ dependence is indicated in Fig. 6(b) in the high-field range for the determined Δ value, yielding a quite good agreement with the experimental behavior.

The narrowing effect of the main absorption is predicted by the tunneling model to be in $\perp$ polarization smaller than in $\parallel$ polarization in most cases (see Table I). For $\langle 100 \rangle$ dipoles the factor between $\parallel$ and $\perp$ polarization is predicted to be 4 for $E_{\langle 111 \rangle}$ and 2 for $E_{\langle 100 \rangle}$. The experimental values (5 and 2, respectively) are in close agreement with this.

In summary, it can be stated that the observed narrowing effect under applied field and its dependence on field strength and field direction and on light polarization (Figs. 5 and 6) is in good agreement with the tunneling model. The effect is found to be approximately isotropic in $\parallel$ polarization. The relative reduction of the effect for $\perp$ polarization is in good agreement with the prediction for $\langle 100\rangle$ dipoles; Table I shows that $\langle 111\rangle$ or $\langle 110\rangle$ dipoles should produce very different second-moment changes in $\perp$ polarization, so that the observed effects give in fact clear evidence for a $\langle 100\rangle$ dipole model. The obtained magnitude for the tunneling splitting ($\Delta = 0.26\ \mathrm{cm}^{-1}$) is in close agreement with the values derived from PER ($\Delta = 0.18\mathrm{cm}^{-1}$) and specific-heat measurements ($\Delta = 0.25\ \mathrm{cm}^{-1}$).

This good agreement of several experimental features with the tunneling model is in striking contrast to an apparent severe disagreement, which seems to invalidate all prior interpretations. As has been pointed out previously,[6,16] there seems to exist a serious contradiction between the observed small halfwidth H of the vibrational band and the relatively large value of the tunneling splitting Δ. The obtained Δ value of about $0.26\ \mathrm{cm}^{-1}$ would predict for the unresolved four-line spectrum of $E = S = 0$ a band with a halfwidth of $H \approx 3.3\Delta = 0.83\ \mathrm{cm}^{-1}$. The high-resolution measurements of Härtel yielded, however, a halfwidth of the OH^- vibrational band in KCl of $H = 0.17\ \mathrm{cm}^{-1}$ at 2 °K. This measured halfwidth value would allow only a Δ value of $0.05\ \mathrm{cm}^{-1}$, about a factor 4–5 smaller than the derived values (0.17 to 0.26) mentioned before.

This apparent discrepancy can be explained and removed, using the considerations from Sec. II, if one regards the well-known presence of random background stress and electric fields in the crystals. An absorption spectrum of a crystal with random background stress or fields can be visualized as a superposition of spectra, as given in Figs. 1–4, under various random stress or field situations. The presence of stress or field of various strength and direction produce one *identical* effect: They make the initially forbidden classical transition $1A_1 \rightarrow 1A_1^*$ allowed (for particular polarization directions), and thus will add up a strong optical transition at $h\nu_0$. This increase of the classical $h\nu_0$ transition will be accompanied by a quasi-continuous spectrum of satellite absorptions, the envelope of which being determined by the distribution function of the random background stress or field.

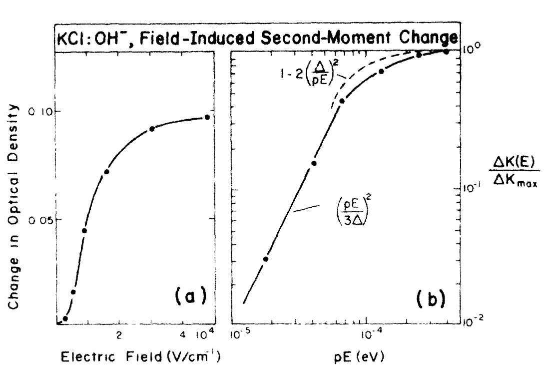

FIG. 6. (a) Field-induced absorption increase measured at the maximum of the OH^- band in KCl as a function of $E_{\langle 100\rangle}$. (b) Plot of the field-induced absorption change [from (a)], normalized to its maximum value, in double logarithmic scale.

Figure 7 gives a qualitative illustration of this: on the left-hand side is indicated the ideal vibrational absorption spectrum for $\langle 100\rangle$ dipoles with (unresolved) tunneling structure Δ and halfwidth $H \approx 3.3 \times \Delta$. On the right-hand side is indicated schematically the absorption for the same system under the influence of random stress and field. The halfwidth, reduced by about a factor of 4, is no longer determined by the tunneling splitting Δ, but by the width of the classical $1A_1 \rightarrow 1A_1^*$ transition, which has become partially allowed by the background stress and field. What remains constant in the two situations (besides the zeroth and first moment) is the *second moment* of the total absorption, produced in (a) directly by the tunneling splitting, and in (b) by the distribution of satellite absorptions.

It is evident from this that the characterization of the absorption by a *halfwidth* can be completely inaccurate and misleading. What is needed instead

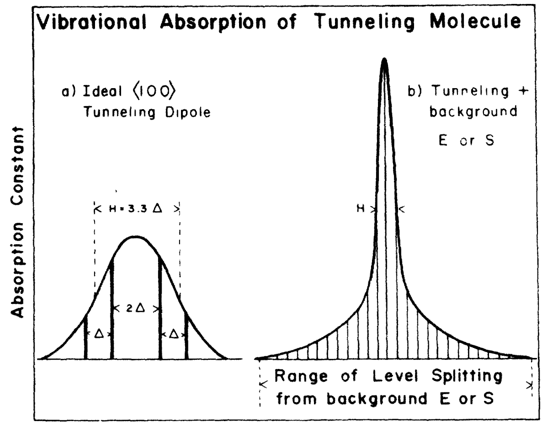

FIG. 7. Illustration of the effect of random background stress or field on the vibrational absorption of a tunneling $\langle 100\rangle$ dipole molecule. (a) Absorption spectrum for $E = S = 0$ with (unresolved) tunneling splitting Δ and halfwidth $H \approx 3.3 \times \Delta$. (b) Same absorption in the presence of random background stress and/or field (schematically).

for an estimate of the tunneling splitting from the optical data is an exact measurement of the absorption shape into its outmost wings, and determination of its *total second moment*. [This band-shape argument is drastically evident when comparing absorption bands of the same halfwidth, but of different analytical shape: While for a Gaussian shape $\langle U^2\rangle = (8\ln 2)^{-1}H^2$ or $H = 3.3\Delta$, the Lorentzian band decays as $(E-\overline{E})^{-2}$ and therefore has an infinite second moment!]

The small measured halfwidth ($H \sim 0.17\ \text{cm}^{-1}$) of the OH^- vibrational band is therefore not at all inconsistent with a larger value of the tunneling splitting. A situation $H < \Delta$ just demonstrates that internal stress—or field perturbations—have already converted the "tunneling spectrum" [Fig. 7(a)] into the spectrum of Fig. 7(b), in which the main absorption consists to a good part of the classical localized dipole transition at $h\nu_0$, and a good part of the second-moment contribution from tunneling has been transferred into very weak (and possibly unmeasurable) satellite absorptions. It is evident that for this situation the magnitude of the field- or stress-induced narrowing (second-moment change) of the *main* absorption will also be considerably less than the predicted maximum value $\langle \Delta U^2\rangle = -2\Delta^2$.

Thus it is impossible in this situation to derive an estimate on Δ either from the observed width of the band or from the size of the field-induced narrowing effect $\langle \Delta U^2\rangle_E$. In our treatment we have, in fact, disregarded the observed size of $\langle \Delta U^2\rangle_E$ (which is strongly reduced by the already existent background perturbations). Instead, we have analyzed only the *relative electric field dependence* of the normalized $\langle \Delta U^2\rangle_E$ effect, comparing it to the $(pE/3\Delta)^2$ and $1-2(\Delta/pE)^2$ dependence predicted by the tunneling model (Fig. 6). This relative field variation is found in good agreement with Δ values obtained from other techniques. The evident result that the *field dependence* of $\langle \Delta U^2\rangle_E$ is much less affected by background perturbations compared to the *size* of $\langle \Delta U^2\rangle_E$, would have to be justified by calculations of the problem including random fields or strain.

A quantitative measurement of the OH^- band into its outmost weak absorption tails in order to obtain its true second moment is virtually impossible due to the fact that the band is accompanied by a series of weak sidebands with about 1.5–2-cm^{-1} splitting.[22] The question, if these sidebands are absorption properties of the *isolated* OH^- *defect*, is of central importance for our problem: If the answer is yes, this side structure could be satellite absorption produced by background strain or fields, and had to be counted in the determination of the second moment of the absorption. In this case, most of the second moment of the OH^- absorption would in fact come from this sideband structure.

Investigations which are presently under way[23] indicate, however, that these sidebands are most probably produced by close pairs of interacting OH^- dipoles, so that they should be discarded for the isolated OH^- spectrum. Their presence, however, makes it still very hard to accurately determine the weak absorption tails from the isolated OH^- defect, and thus precludes an estimate of the tunneling splitting from an accurately measured second moment of the vibrational absorption.

Towards higher temperatures, the OH^- vibrational absorption broadens very drastically[6] (by about one order going from 2 to 25 °K). As the basic tunneling and dipole properties (i.e., Δ and p) should not be changed by the temperature, our considerations about field- or stress-induced absorption changes should be valid at high temperatures as well (e.g., field application should still produce a small narrowing effect on the strongly phonon-broadened absorption band).

Figure 8 summarizes the results from a previous field measurement,[24] performed on the OH^- vibrational absorption in KCl in the 20–40 °K range, where the bandwidth is about 1–4 cm^{-1}. For this broad band it seemed appropriate to use a wide spectral bandwidth (of about 1 cm^{-1}), so that the large light intensity allowed the use of the highly advantageous field-modulation technique. Figure 8(a) shows the result of such a broad band modulation spectrum. It represents, indeed, closely a decrease of the second band moment, with an obtained $\langle \Delta U^2\rangle$ value similar to the one obtained at low temperatures.

A very surprising result, however, evolved when these measurements were repeated with high optical resolution (which then allowed only dc field techniques) [Fig. 8(b)]. The ΔK spectrum is found to consist of a very small *decrease* of the temperature broadened OH^- band [not detectable in the scale of Fig. 8(b)], and an absorption *increase* in the form of a narrow spike close to the center of the band. [Figure 8(a) showed this same ΔK spectrum, only under completely inadequate resolution conditions.] The field-induced absorption spike, which is shown separately in Fig. 8(c) for various temperatures, is about an order of magnitude narrower than the original absorption band. A full interpretation of these peculiar spectral properties of the field-induced absorption change seems not readily available. Neglecting, however, the details of the spectral dependence and regarding only the moment of the ΔK spectrum, the effect apparently constitutes the—roughly temperature independent—second-moment decrease predicted by the tunneling model. This illustrates the validity of the rules

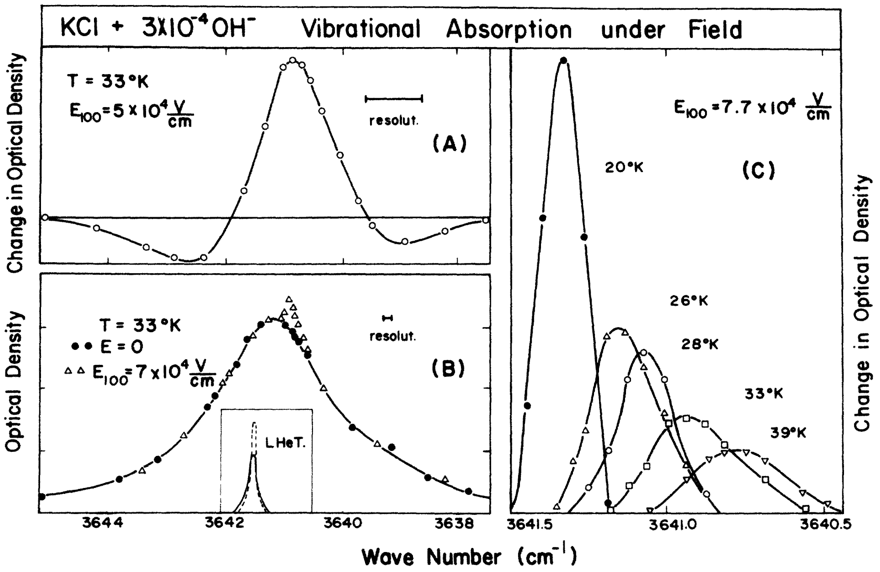

FIG. 8. OH^- vibrational absorption in KCl under field application $E_{\langle 100\rangle}$ at higher temperatures (Ref. 24) (3×10^{-4} Mol parts KOH in KCl). (a) Spectral change of the absorption under ac field modulation, measured at 33 °K with an optical resolution of about 1 cm^{-1}. (b) Optical absorption at $E = 0$ and under applied dc field $E_{\langle 100\rangle}$, measured at 33 °K with a resolution of about 0.15 cm^{-1}. (For comparison, the insert shows the equivalent measurement at 4 °K, solid line: $E = 0$, dotted line: $E_{\langle 100\rangle}$ applied.) (c) Field-induced absorption spike on the band, measured under the same field $E_{\langle 100\rangle}$ at different temperatures.

for the moment changes, even in a case where the details of the spectral changes are not understood.

More detailed experiments on the field (or stress?) induced transformation of the temperature-broadened absorption band into a narrow absorption spike are under way, in order to achieve a full understanding of this interesting effect.

Finally, the field-modulation experiment of Handler and Aspnes,[25] performed with the OH^- vibrational absorption in KBr at room temperature, should be mentioned in this connection. They observed under ⟨100⟩, ⟨110⟩, and ⟨111⟩ electric fields in parallel polarization a slight band narrowing ($\Delta K/K \approx 10^{-5}$), which they argue to be not compatible with a ⟨100⟩ model, checking it only in terms of its expected classical (zero-moment) dichroism. This narrowing effect for all field directions, however, is in qualitative agreement with the quantum-mechanical effects from the tunneling model and with the discussed KCl:OH^- low-temperature results.

ACKNOWLEDGMENTS

The author is indebted to Professor B. G. Dick and Dr. H. U. Beyeler for fruitful and stimulating discussions on the subject of this paper.

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*Work supported by NSF Grant No. GH33704X. Helium gas was provided by a departmental grant from the ONR.

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[19] It is sometimes questioned if in a very "quick" near ir excitation experiment a tunneling state (which needs several "slow" tunneling times to become defined as an eigenstate) can really be observed in terms of its particular selection rules. Evidently, in order that this can occur, the "interaction time" of the photon with the defect must be *long* compared to the tunneling time. As the "length" of the photon, i.e., its interaction time, is determined by its spectral width, this time-argument is just an equivalent statement for the trivial fact that the spectral width of the light must be small against Δ, in order to resolve the tunneling structure.

[20] If the condition $kT \gg pE$ is dropped and dipole alignment is present, these simple moment rules become changed in an easily predictable way. A net dipole alignment is directly measured by zero-moment changes for light polarized $\parallel$ and $\perp$ to the perturbation. Moreover, the freezing out of the higher field-split levels in the vibrational ground state will remove from the transition pattern all the anti-Stokes satellite absorptions and thus will decrease the second moment of the total absorption. For a simple case like $E_{\langle 100\rangle}$ and polarization $\parallel$ to E (Fig. 1), in which the lowest field-split multiplet is a single level, the second moment of the total absorption changes from $\langle U^2\rangle_{E=0} = \Delta^2 + \Delta^{*2}$ under dipole alignment to $\langle U^2\rangle_{E/T\to\infty} = \Delta^{*2}$. In this case the freezing out of all higher levels of the vibrational ground state removes all energy uncertainty of and information about the ground state tunneling splitting Δ, so that the width of the resulting absorption is determined only by the tunneling splitting Δ^* of the excited vibrational state. For convenience of analysis, however, one will always attempt to separate the classical reorientation dichroism from the optical effects due to quantum-mechanical mixing of the dipole states, as we do in this work.

[21] The stress introduces additionally small shifts (first-moment changes) of the absorption (Ref. 6), due to the change of the distance of the nearest neighbors around the OH^- ion.

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