In calculating the 1s-2p excitation energy for the U_2 center, one is primarily interested in a reasonably accurate description of the ground state. The model of the 2p state is not too critical, because the ionization energy of this state is much less than that of the ground state due to the large dielectric constant for such large-radius states. On the other hand, the ground state is very sensitive to the dielectric-constant function, in particular to the electronic polarization part of this function. The k-dependent dielectric-constant functions seem to be the most reliable of the dielectric functions we have considered for such small radius states and give calculated 1s-2p energies whose agreement with the observed U_2 bands is no worse than the transferred electron model of Kerkhoff, Martienssen, and Sander.[5] We recalculated the overlap integrals of the 1s state with the surrounding Cl^- and K^+ ions, using Slater functions for the ion orbitals. We find that the renormalization of the ground-state wave function due to overlap with nearest neighbors increases $|\psi(0)|^2$ by 13%. This gives values of $|\psi(0)|^2/|\psi_H(0)|^2$ of 0.796, 0.926, and 0.779 for the Penn, Azuma, and Hermanson potentials, respectively, where $|\psi_H(0)|^2$ is the wave-function amplitude for free hydrogen. Our values are lower than the experimental value of 0.976,[5] whereas Mimura and Uemura's[2] value of 1.10 and Spaeth's[6] value of 1.19 are too large. However, one would not expect a variational calculation to give a very accurate numerical value of $|\psi(0)|^2$. The value of $|\psi(0)|^2/|\psi_H(0)|^2$ calculated neglecting overlap are tabulated in Table I.

Using the k-dependent dielectric constants, we find that the 2p states have radii of $(5–6)a_0$ (Table I), as compared with a nearest-neighbor distance of $\sim 5a_0$ (assuming no lattice distortion). Neglecting overlap effects, we calculated a 2p energy of -0.35 eV for the Penn potential in KCl (potential IV). If one takes the extreme case of a large-radius wave function by accounting for the overlap effects by replacing m by m^*, taking $m^*=0.5m$, a 2p energy of -0.14 eV is obtained, with $1/\lambda=12.31\ a_0$. The use of effective-mass theory for so compact a state is questionable, even though the core effects would be minimized by the p character of this state. The actual state of affairs lies between the two extremes of no overlap and very considerable overlap. However, it is doubtful that overlap affects the calculated 1s-2p energies by more than a few tenths of an eV.

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Libration of the Hydroxyl Ion in Alkali Halide Crystals*

MILES V. KLEIN, BRENT WEDDING,† AND MICHAEL A. LEVINE‡
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

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This paper presents experimental data for a direct absorption band near 300 cm^{-1} due to the hydroxyl ion in several alkali halides. This excitation is also seen as a combination band 300 cm^{-1} above the 3600-cm^{-1} O—H stretching band. The lines are broad, even at helium temperatures, and seem to be Lorentzian. Dichroism induced by a static electric field indicates that the transition dipole moment is perpendicular to the O—H axis. The Devonshire model is unable to explain the OH^--OD^- isotope shifts, and predicts more than the one strong band which is seen. A simple torsional harmonic-oscillator model can explain relatively well the isotope shifts and the oscillator strengths for both the direct librator and the librational sideband. Better agreement can be obtained by assuming some anharmonicity in the angular potential energy and/or assuming a slight displacement of the axis of rotational oscillation from the c.m. The temperature dependence of the linewidths may indicate a coupling between the torsional librational oscillator and the "30-cm^{-1}" or "non-Devonshire" levels studied earlier.

I. INTRODUCTION

THE hydroxyl ion substitutes for a halide ion in alkali halide crystals where it exhibits a wide variety of energy levels due to internal stretching vibrations and to external motions with respect to its surroundings. The main stretching band near 3600 cm^{-1} together with combination bands at slightly higher frequencies have been discussed in detail in an earlier paper[1] (hereinafter referred to as I), which also gives more detailed references to previous work on OH^-. A sideband appears near 3900 cm^{-1} that has been assigned to a (stretching+libration) combination band.[2] A pure libration band has also been observed near 300 cm^{-1}.[3]

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† Present address: Technical Staffs Division, Corning Glass Works, Corning, N. Y. 14830.

‡ Present address: Aerojet General Corporation, Azusa, Calif. 91702.

[1] B. Wedding and M. V. Klein, Phys. Rev. **177**, 1274 (1969).

[2] B. Wedding and M. V. Klein, Bull. Am. Phys. Soc. **11**, 228 (1966).

[3] D. Harrison and F. Lüty, Bull. Am. Phys. Soc. **12**, 82 (1967).

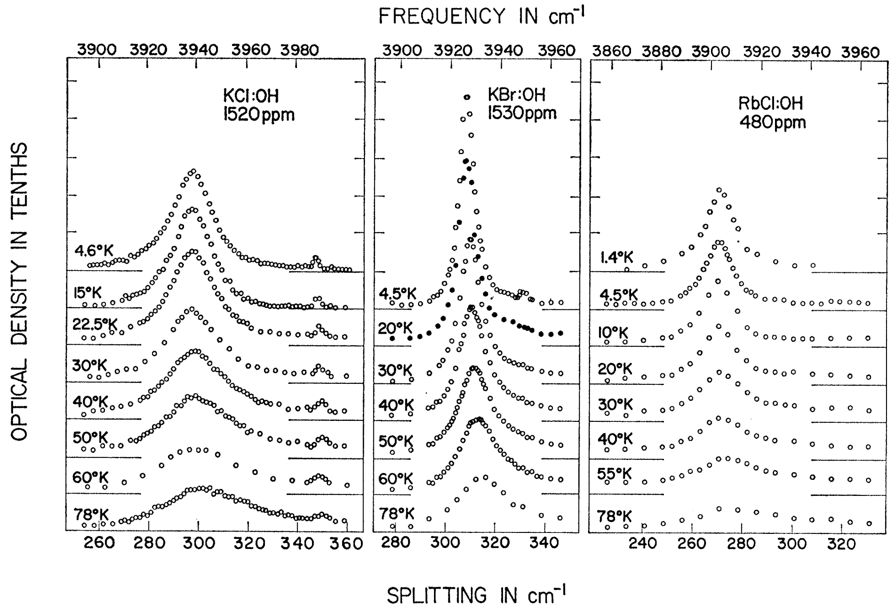

FIG. 1. Librational sidebands due to OH^- in three alkali halide crystals. The lower scales give the splittings from the main stretching bands. Crystal thicknesses were 1.4, 1.35, and 1.4 cm for KCl, KBr, and RbCl, respectively.

Experimental results on both the librational sideband and the pure libration band will be presented and discussed in this paper.[4]

We shall show that the Devonshire model gives a poor fit to our data compared to that obtained from a simple model of the OH^- ion undergoing torsional oscillation about an axis at or near the molecular c.m. within a nearly harmonic minimum of the angular potential energy.

II. EXPERIMENTAL TECHNIQUE

The librational sideband measurements at low temperature were taken as part of the main stretching-band measurements described in I, and some room-temperature data were taken on a Cary Model 14 spectrophotometer using a thicker sample cut from the same boule.

Infrared data in the 300 cm^{-1} region were taken with a Beckman IR11 double-beam spectrophotometer used with a beam condenser. There was no chopping of the light beam between sample and detector; thus "negative light" effects due to absorption by a cold sample of radiation emitted by a warm detector were avoided. Wave numbers were calibrated using H_2O bands. The doped sample and an undoped reference crystal could be moved in and out of the beam while inside the cryostat. Cooling was achieved via helium exchange gas in contact with a 4.2°K bath or by direct contact of the crystals with a cold finger at the bottom of the helium bath.

III. RESULTS

In Table I are listed the peak positions for the librator in several alkali halides. Discussion of the last column will be postponed until later. The librational sidebands in KCl, KBr, and RbCl were strong enough to permit measurement over a wide range of temperature. The sideband in NaCl (see Fig. 8 of I) and one tentatively assigned in KI were weak even at helium temperature.

Spectra taken between liquid-helium and liquid-nitrogen temperatures are shown in Fig. 1. We have fewer results on the direct librational band. Absorption curves for KBr are shown in Fig. 2. Within experimental error, the sideband has the same shape and the same temperature-dependent shift as the direct librational band. At low temperatures the line shapes are Lorentzian, and they broaden more rapidly on the high-energy side as the temperature is increased. An example of the Lorentzian fit to the KCl sideband is shown in Fig. 3.

TABLE I. Librational frequencies.

	OH^-		OD^-		
Host crystal	Librational frequency (cm^{-1})	Sideband splitting (cm^{-1})	Librational frequency (cm^{-1})	Sideband splitting (cm^{-1})	Devonshire K value (cm^{-1})[a]
RbCl	272.0±1	270.5±0.5	[b]	[c]	490
KCl	[b]	297.5±0.5	[b]	231.5±2	560/450[d]
NaCl	[b]	390.0±0.5	[b]	[e]	750
KBr	312.7±0.5	309.7±0.3	236.3±0.5	233.0±1.5	570/470[d]
KI	284±1[f]	279±1[f]	[b]	[c]	520

[a] Using $B(OH^-) = 18.9$ cm^{-1} and $B(OD^-) = 10.0$ cm^{-1} fit to $T_{1u} \rightarrow T_{2g}$.
[b] Cannot be readily measured in transmission.
[c] Samples not available.
[d] Double entries give OH^-/OD^-.
[e] Zero oscillator strength (see Ref. 1).
[f] Tentative librational assignment (see text).

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[4] For a review of much recent work and detailed spectra on KBr:OH^- see F. Lüty, J. Phys. (Paris) Suppl. C-4, 28, 120 (1967). A listing of librator frequencies, widths, and sideband splittings for eight-crystal systems will be found in the abstract by F. Lüty in International Symposium on Color Centers, Rome, 1968 (unpublished).

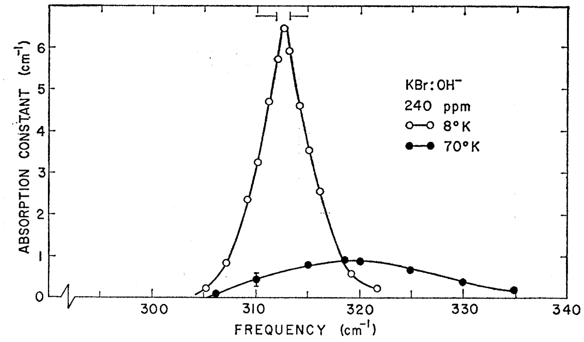

FIG. 2. The direct OH⁻ librational absorption band in KBr at two temperatures.

The librational sideband shows no significant changes upon cooling from helium temperature to 1.4°K, as is shown in Fig. 1 for RbCl. This was also found for KCl and NaCl, and is not shown.

A weak, narrow band may be seen in some of the sideband spectra above the main band. (See the KCl and KBr curves in Fig. 1.) We have no explanation at present for this extra band beyond the suspicion that it may be because of OH⁻ near an impurity.

The dichroism induced in the librational sideband by a ⟨100⟩ electric field is shown in Figs. 4 and 5 for KCl and RbCl.[5] These data were taken simultaneously with the data on the dichroism of the "30 cm^{-1}" sideband shown in Figs. 2 and 5 of I. As discussed there, temperatures were low enough for essentially complete alignment to have been attained; then one expects

$$\Delta\alpha(\perp)=0.5\alpha;\quad \Delta\alpha(\|)=-\alpha.$$

The data in Figs. 4 and 5 may be interpreted by assuming that about 75% of the OH⁻ dipoles align in KCl and that 50% align in RbCl. The dichroism results on the 30 cm^{-1} band in I suggest fractional alignments of 67 and 20%, respectively; these latter numbers are less accurate because of the weakness of the 30 cm^{-1} sideband. The shift in the NaCl librational-sideband intensity with applied field was similar, but the weakness of the band prevented our getting quantitative results.

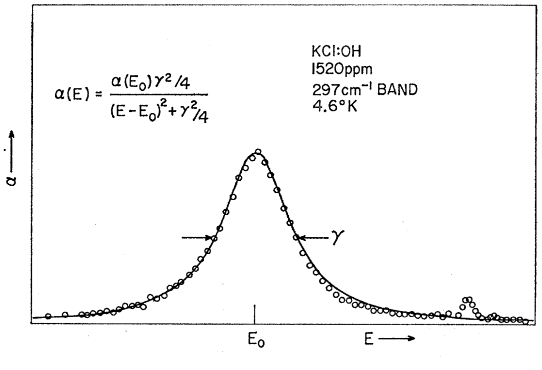

FIG. 3. Lorentzian fit to the OH⁻ librational sideband in KCl.

From Figs. 1 and 2 one can see that the librator shifts to higher frequencies at higher temperatures. Shifts of the sideband upon warming from helium to nitrogen temperature amounted to 6 cm^{-1} for KBr and 3 cm^{-1} for KCl and RbCl. The respective shifts from helium to room temperature were 28, 23, and 48 cm^{-1}. These positive shifts are much larger than the small negative shifts of the main stretching band.[1] The direct KBr librator also shifts by +6 cm^{-1} between helium and nitrogen temperatures.

Values for the librational splittings and direct librator frequencies are listed in Table I for OH⁻ and OD⁻ ions in several alkali halide crystals. The large isotope shifts were first reported for the librational sideband in Ref. 2 and for the direct librator in the first paper cited in Ref. 4.

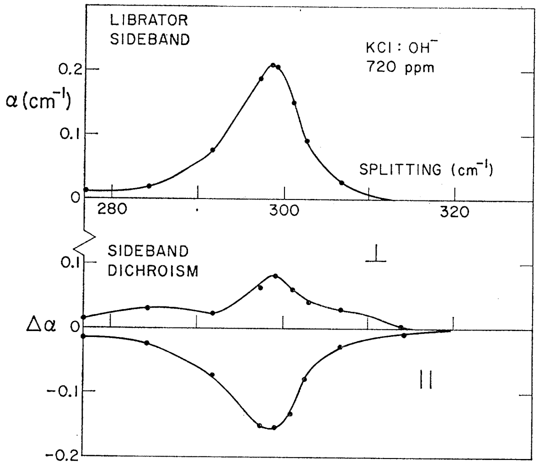

FIG. 4. Upper curve: librational sideband in KCl:OH⁻. Lower curves: dichroism induced at 1.4°K in the sideband by an applied ⟨100⟩ electric field E_a of 73 kV/cm. The symbols ⊥ and || refer to E_{light}, respectively, perpendicular and parallel to E_a.

Linewidths of the direct librator and of the librational sideband are compared in Fig. 6. To a first approximation they are the same, for example, γ in KBr is 20±2 cm^{-1} at 70°K for both bands. Since the main stretching band has a width of 7 cm^{-1} at this temperature,[1] one can conclude that the width of the 3600 cm^{-1} main band should not be subtracted from that of the 3900 cm^{-1} sideband to obtain the intrinsic width of the librator. The excited stretching-oscillator state and the excited (stretching+libration) combination-oscillator state apparently represent two different states with different decay mechanisms. The decay of the excited-combination state is very similar to that of the excited-librational state. It should be pointed out, however, that in KBr, where we have looked with greatest care, there is a small difference outside the experimental

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[5] The fact that the combination vibration-libration band is polarized perpendicular to the OH⁻ axis was first shown by stress dichroism measurements [H. Härtel, thesis, Stuttgart, 1966 (unpublished)].

errors between widths at low temperatures: γ is 5.2 cm^{-1} for the direct librator at 8°K and 6.7 cm^{-1} for the sideband at 4.2 and 1.4°K.

Sideband widths for KCl, RbCl, and KBr are compared in Fig. 7 with and without the width of the main band subtracted. At room temperature the γ's are almost the same for the three host crystals; whereas at low temperatures they differ markedly: γ(KCl) is three times γ(KBr) and 1.5 times γ(RbCl). For OD$^-$ dopings the sidebands at 8°K have the following values: $\gamma(\text{KBr})=13$ cm^{-1} and $\gamma(\text{KCl})=28\pm7$ cm^{-1}. The direct OD$^-$ librator in KBr has a width of 10.7 cm^{-1}. The 28 cm^{-1} value for the width of KCl:OD$^-$ makes it difficult to locate precisely the librational sideband peak in KCl:OD$^-$; hence the ±2 cm^{-1} error estimate in Table I.

In KI the hydroxyl ion behaves differently. Both the 279 cm^{-1} sideband and the 284 cm^{-1} direct band are about six times weaker than the corresponding bands for the other crystals in Table I. The lines are also narrower—3 cm^{-1} at helium temperature compared with 6.7, 13, and 20 cm^{-1}, respectively, for KBr, RbCl, and KCl. We estimate the direct band to be 5 ± 1.5 cm^{-1} higher than the sideband splitting as contrasted to shifts of 1.5 ± 1.3 and 3.0 ± 0.6 cm^{-1} for RbCl and KBr from Table I.

Renk has seen a series of sharp bands in the gap between acoustical and optical branches in KI:OH$^-$.[6] The strongest band that was at 69.5 cm^{-1} had a width of 2 cm^{-1} and an integrated area A of about 5 cm^{-2}. He did not give a value for the OH$^-$ concentration in the crystal, but the doping level in the melt was $\frac{1}{2}$ mole %. One of our KI:KOH crystals had a roughly similar melt doping and contained 90 parts per million (ppm) OH$^-$. In this crystal we found a band at 70 cm^{-1} with an instrument-limited width of 3 cm^{-1} and an area A of 1.0 cm^{-2}, and the 284 cm^{-1} band had an integrated area of 3.5 cm^{-2}. We did not have the sensitivity to observe the other bands reported by Renk. The 69.5 cm^{-1} line and the other weaker lines in the gap of KI:KOH have been interpreted as librational modes and translational localized modes. If this is so, then the librator in KI is obviously quite different from that in KCl, KBr, and RbCl, and one will have to find another explanation for the 284 cm^{-1} line in KI:KOH. We suggest that rather than being related to the librator, the gap bands in KI:KOH may be similar to the broad bands that have been observed at 67 and 87 cm^{-1} in KBr:KOH.[7] Two comments may be useful when assigning explanations to these bands. One is that in KI the hydroxyl ion has different properties than in other alkali halides, for instance its ultraviolet dichroism is different[8] and its main O—H stretching spectrum is different.[1] The other comment is that KI is sure to contain a relatively large amount of Br$^-$ and Cl$^-$ impurities and perhaps other impurities as well; any weak bands having areas of a few cm^{-2} might be due to interactions between hydroxyl ions and such impurities.

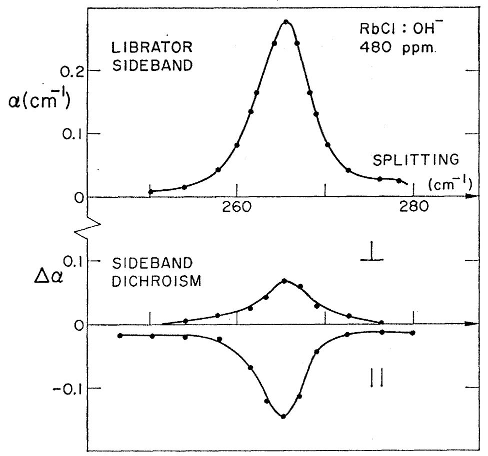

FIG. 5. Upper curve: librational sideband in RbCl:OH$^-$. Lower curves: dichroism induced at 1.4°K in the sideband by an applied ⟨100⟩ electric field E_a of 45 kV/cm. The symbols ⊥ and ‖ refer to E_{light}, respectively, perpendicular and parallel to E_a.

In Table II are gathered some experimental values for the areas under the absorption curves and the oscillator strengths. The area A is expressed as cm^{-2} per 1000 ppm. The oscillator strength f was calculated

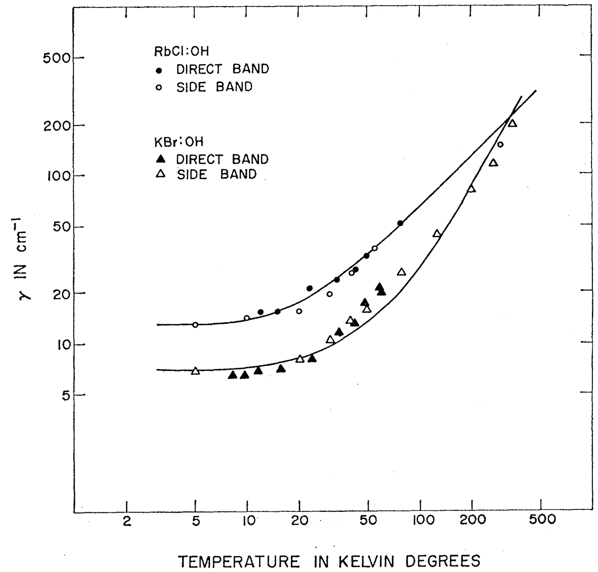

FIG. 6. Widths γ (full width at half-maximum) for the direct librational band and for the librational sideband for OH$^-$ in RbCl and KBr. The circles and triangles represent experimental data. The solid lines are discussed in the text.

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[6] K. F. Renk, Phys. Letters **20**, 137 (1966). See also R. G. J. Grisar, K. P. Reiners, K. F. Renk, and L. Genzel, Phys. Status Solidi **23**, 613 (1967).

[7] D. R. Bosomworth, Solid State Commun. **5**, 681 (1967).

[8] U. Kuhn and F. Lüty, Solid State Commun. **2**, 281 (1964); H. Paus and F. Lüty, Phys. Status Solidi **12**, 341 (1965); F. Lüty and K. F. Weinmann, Bull. Am. Phys. Soc. **12**, 82 (1967).

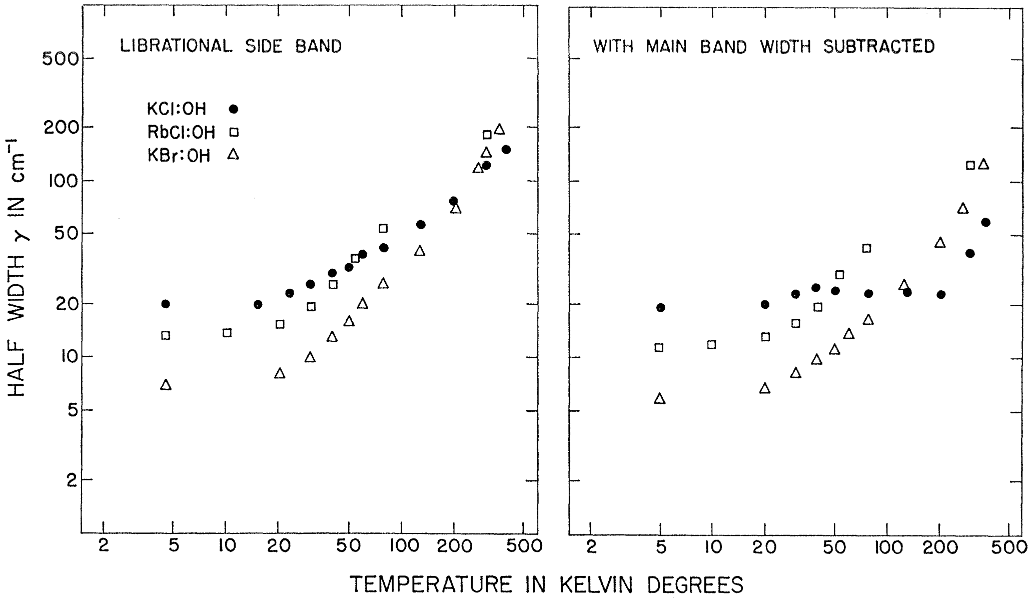

FIG. 7. Widths of the librational sidebands for OH^- in KCl, RbCl, and KBr, with and without the widths of the main stretching subtracted.

from the equation

$$f=(Amc^2/Ne^2\pi)9n/(n^2+2)^2$$

using the reduced mass m.[9,10] Included in the table are experimental results on the main stretching band from I, our estimates of the A and f values associated with the main peaks of the far infrared non-Devonshire bands as measured by Bosomworth,[7] and our values for the non-Devonshire sidebands of the main stretching band.

The values of A for the sideband are constant between helium temperature and about 200°K. They then approximately double upon further warming to room temperature. On the other hand, A for the direct librator seems to decrease by approximately 30% between 8 and 70°K, although the data are not very precise.

IV. DISCUSSION

Ultraviolet dichroism measurements have shown that, except possibly for KI:KOH, the hydroxyl ion in alkali halides lines up in $\langle 100\rangle$ directions.[8] Our dichroism results on the librational sideband show that the transition moment is perpendicular to the O—H axis.[5] The OH^-/OD^- isotope effect suggests that most of the motion is associated with the hydrogen part of the molecular ion. The torsional-harmonic oscillator is a simple model with these features and one that we believe represents a good starting approximation to the true state of affairs.

A. Torsional Harmonic Oscillator

In this model the hydroxyl ion oscillates about its fixed c.m., the O—H axis making an instantaneous angle θ with one of the $\langle 100\rangle$ directions. Assume a harmonic potential energy of the form

$$V(\theta)=\tfrac{1}{2}C\theta^2.$$

Then the librational frequency is $\omega=\sqrt{(C/I)}$, where $I=m_{\rm H}R^2$ is the moment of inertia, $m_{\rm H}=M_{\rm O}M_{\rm H}/(M_{\rm O}+M_{\rm H})$ is the reduced mass, and R is the O—H internuclear spacing.

The isotope shift would then be given by

$$[\omega(OH^-)/\omega(OD^-)]=(m_{\rm H}/m_{\rm D})^{1/2}=1.375.$$

The predicted values of $\omega(OD^-)$ are lower than observed, for instance in KBr the predicted value is 227.5 cm^{-1} compared with the experimental value of 236.3 cm^{-1}. As a first approximation, however, the agreement is not bad.

The vibrational sidebands have splittings slightly smaller than the frequencies of the direct librational bands presumably because of the increased moment of inertia of the vibrating molecule. For a diatomic molecule, it is customary to introduce the rotational constant

$$B_e=\hbar^2/2I_e=\hbar^2/2mR_e^2.$$

The subscript e refers to the classical equilibrium values. In the vth vibrational state the effective value of B is defined in terms of the expectation value

$$B_v=(\hbar^2/2m)\langle v|1/R^2|v\rangle.$$

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[9] This is the expression most often used for both color centers and far infrared resonances. For a derivation see Ref. 10.

[10] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Co., Inc., New York, 1940), p. 644ff.

Table II. Areas under absorption bands (A, in cm^{-2} per 1000 ppm) and oscillator strengths (f).

	Direct librator (8°K)		Librational sideband (5°K)		Main stretching band (78°K)		Direct "non-Devonshire" (1.7°K)		"Non-Devonshire" sideband (5°K)	
System	A	f_l	A	f_{s+l}	A	f_s	A	f_x	A	f_{s+x}
KBr:OH$^-$	230	2.5×10^{-2}	7	0.7×10^{-3}	33	3.3×10^{-3}	160	11×10^{-3}	$\sim$2.3	0.23×10^{-3}
KBr:OD$^-$	160	3.3×10^{-2}		···	8	1.7×10^{-3}	250	8×10^{-3}		···
RbCl:OH$^-$	187	2.2×10^{-2}	12	1.3×10^{-3}	53	5.7×10^{-3}	125	5.5×10^{-3}	$\sim$4	0.43×10^{-3}
KI:OH$^-$	31	3.7×10^{-3}	1.0	0.17×10^{-3}	18	3.0×10^{-3}		···		···
KCl:OH$^-$		···	8.8	0.75×10^{-3}	55	4.7×10^{-3}	140	8.4×10^{-3}	$\sim$5	0.42×10^{-3}
NaCl:OH$^-$ (1900 ppm)		···	2.6	0.16×10^{-3}	10	0.65×10^{-3}	200	14×10^{-3}	$\sim$5	0.06×10^{-3}
Theory OH$^-$		5.9×10^{-2}		0.83×10^{-3}		6.8×10^{-3}				
Theory OD$^-$		8.2×10^{-2}		0.21×10^{-3}		2.7×10^{-3}				

B_v is given approximately by[11]

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}).$$

The parameter α_e depends on the cubic-anharmonic coefficient V_3 in the stretching potential

$$V(R-R_e) = \tfrac{1}{2}K(R-R_e)^2 + (1/3!)V_3(R-R_e)^3 + \cdots.$$

On the basis of his calculation of electronic wave functions and energies for OH$^-$, Cade has made the following predictions[12]:

$$B_e = 19.2 \pm 0.2 \text{ cm}^{-1}$$

and $\alpha_e = 0.8$ cm^{-1}. Thus, in the $v=0$ vibrational state we have

$$B_0 = 18.8 \text{ cm}^{-1},$$

and in the $v=1$ state we have

$$B_1 = B_0 - \alpha_e = 18.0 \text{ cm}^{-1}.$$

Now apply the torsional-oscillator model and assume that C is a constant independent of R. Then, since the frequency of the librator obeys

$$\omega \propto I^{-1/2} \propto B^{1/2},$$

we find for the frequency shift

$$\delta(\omega) = \omega(\text{librator}) - \omega(\text{sideband}) = \omega(v=0) - \omega(v=1),$$

the result being

$$\delta\omega/\omega = \tfrac{1}{2}[(B_0 - B_1)/B_0] = 2.1\times10^{-2}.$$

The experimental values from Table I are

$$\begin{aligned} \delta\omega/\omega &= (0.5\pm0.4)\times10^{-2} \quad \text{for RbCl} \\ &= (1\pm0.25)\times10^{-2} \quad \text{for KBr} \\ &= (2\pm0.5)\times10^{-2} \quad \text{for KI}. \end{aligned}$$

The best experimental result (for KBr) is about half the predicted result.

An alternative to the assumption that C = constant is the assumption $C \propto R^2$. For a simple mechanical model of the forces producing the torsional oscillation, assume a series of harmonic springs with spring constants $k_1, k_2, \cdots$ acting at right angles to the O—H axis at distances $d_1, d_2, \cdots$ from the c.m. C is then given by

$$C = \textstyle\sum_i k_i d_i^2.$$

Thus, C will be proportional to R^2 if the distances d_i remain directly proportional to R as the molecule vibrates. Then the librational frequency will be independent of R; this is not the case experimentally. The experimental results suggest that the distances for the springs that contribute most importantly to C vary somewhat like $R^{1/2}$.

In the torsional-oscillator model the oscillator strength for the direct librational band would be

$$f = (2/3)(e_r/e)^2,$$

where e_r is the charge associated with the equilibrium dipole moment p_e as measured from the c.m., i.e.,

$$e_r = p_e/R_e.$$

This result will be discussed in somewhat more detail below. The factor $\frac{2}{3}$ results from the assumed symmetry of the dipole orientation and from the transverse nature of the librational oscillator.

A theoretical estimate of e_r may be obtained from Cade's calculations of the equilibrium dipole moment with respect to the center of the molecule.[12] The results are

$$\begin{aligned} (e_r/e) &= 0.298 \quad \text{for OH}^-, \\ &= 0.350 \quad \text{for OD}^-. \end{aligned}$$

The resulting f values are shown in Table II. They are two to three times larger than the experimental values.

B. Devonshire Model

In 1935, Devonshire solved the quantum mechanical problem of a diatomic molecule rotating about its center of mass in an angular potential well of octahedral symmetry.[13] The potential he used can be written most

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[11] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand, Princeton, N. J., 1950), 2nd ed., p. 106.

[12] Paul Cade, J. Chem. Phys. **47**, 2390 (1967).

[13] A. F. Devonshire, Proc. Roy. Soc. (London) **A153**, 601 (1936).

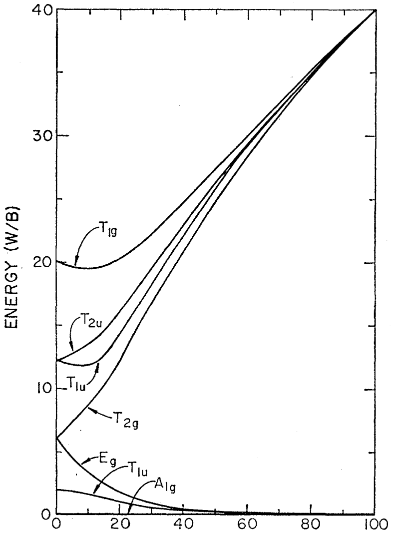

FIG. 8. Devonshire energy levels as calculated by Sauer (Ref. 14). For convenience the zero of energy is taken as the A_{1g} ground state. The curves apply for positive values of the Devonshire potential parameter $K=kB$, which give ⟨100⟩ potential energy minima. Energies are expressed in units of the rotational constant B.

simply in the form

$$V=-\tfrac{1}{2}K\left[5\frac{X^4+Y^4+Z^4}{R^4}-3\right],$$

where $(X,Y,Z)/R$ are the components of the unit vector along the O—H axis. The Devonshire calculation has recently been repeated and extended by Sauer,[14] and the pertinent energy levels are plotted in Fig. 8. The abcissa k is the Devonshire strength parameter K in units of the rotational constant B; the ordinate gives the energy levels in units of B above the ground-state level (which has A_{1g} symmetry).

The free rotor levels at $k=0$ gradually transform into several more or less distinct manifolds for large positive values of k. In this case, the classical equilibrium positions for the hydroxyl ion are along the 6⟨100⟩ directions. Quantum-mechanical tunneling among these 6 equilibrium directions produces the lowest-lying manifold of A_{1g}, T_{1u}, and E_g levels. This same set of tunneling levels is obtained from any model that localizes the ion along potential-energy minima in ⟨100⟩ directions with nonzero transition amplitudes between states corresponding to ions in different minima. Such models are sometimes called "tight-binding" or "LCAO" (linear combination of atomic orbitals) models.[15] The LCAO basis states for the lowest manifold are $l=0$ librational ground states in the six potential wells. The next manifold of states occuring for large k (T_{2g}, T_{1u}, T_{2u}, and T_{1g}) may be described in a LCAO model as tunneling among basis states corresponding to first excited ($l=1$) librational states within each ⟨100⟩ angular potential well.[14]

Neither Devonshire nor Sauer has published dipole matrix elements between different levels. For $k=0$, the selection rule is of course that $\Delta J=\pm 1$. One might expect that the strongest transitions for nonzero k will result from transitions that adiabatically transform to $\Delta J=\pm 1$ transitions as $k\rightarrow 0$. The first such transition from the $l=0$ manifold to the $l=1$ manifold is $T_{1u}\rightarrow T_{2g}$. It seems natural to fit the experimental librational frequencies to this transition. The k values that result are about 30 for OH$^-$ and 45 for OD$^-$. In the large-k limit the ΔJ selection rule is replaced by the results of a tight-binding calculation, which says roughly that all $l=0$ to $l=1$ transitions allowed by cubic symmetry are equally strong. Thus in the large-k limit, in addition to the $T_{1u}\rightarrow T_{2g}$ transition already mentioned, there should be transitions from the other ground-state levels A_{1g} and E_g to T_{1u} in the first excited state, and these should be separated by energies greater than our experimental widths. This is one prediction of the Devonshire model which is not observed. It could be salvaged by going to larger values of k, so that the levels in the first excited-state manifold would be closer. As discussed in the next paragraph, the resulting isotope shifts would be unrealistic.

Another wrong prediction of the Devonshire model concerns the isotope shifts. If one fits the $T_{1u}(l=0)\rightarrow T_{2g}(l=1)$ frequency to the experimental librator frequency using Fig. 8 and B values of 18.9 cm^{-1} for OH$^-$ and 10 cm^{-1} for OD$^-$, one obtains values for the Devonshire barrier-parameter K given in the last column of Table I. Note that the values for OH$^-$ and OD$^-$ do not agree, contrary to expectations that the angular potential should be independent of hydrogen mass, at least to a good approximation. If the OH$^-$ K value is used to predict the OD$^-$ librational frequency in KBr, the result is $\omega(\mathrm{OD}^-)=274$ cm^{-1}; the experimental value is 236.3 cm^{-1}. Recall that the torsional harmonic-oscillator model predicted $\omega(\mathrm{OD}^-)=227.5$ cm^{-1}, in better agreement. Larger Devonshire K values and hence smaller B values can be obtained by postulating that the c.m. is displaced from the center of symmetry of the potential and participates in the motion. This would solve the problem of the "missing transitions" discussed in the previous paragraph, but it would lead to an even weaker isotope shift than that predicted by the ordinary Devonshire model.

The Devonshire potential may be fitted to a power series in the angle of deviation from the ⟨100⟩ equilibrium position. For small angles and for large K values this series would yield an explicit representation of the anharmonic angular potential in which the libration must occur. This particular anharmonic potential was shown above to give too small an OH—OD

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[14] P. Sauer, Z. Physik **194**, 360 (1966).

[15] P. Sauer, O. Schirmer, and J. Schneider, Phys. Status Solidi **16**, 79 (1966); H. B. Shore, Phys. Rev. **151**, 570 (1966).

isotope shift, whereas a harmonic potential gives too large a shift. The experimental shift could be explained by adding an *ad hoc* quartic term proportional to θ^4 to the harmonic term $\frac{1}{2}C\theta^2$ and making the coefficient of this quartic term somewhat less than that in an expansion of the Devonshire potential. At present we have no additional results that depend on the value of the quartic term to serve as a test of this possibility.

C. Additional Remarks about Isotope Shifts and Oscillator Strengths

The isotope shifts could be explained in a purely harmonic model if the c.m. is allowed to participate in the librational motion; the result would be torsional oscillation about an axis not located at the c.m. This axis could be a fixed distance d from the c.m. (and hence at different locations for OH^- and OD^-) or at a fixed point in the molecule. In the former case, for example, one finds

$$|d/R|=0.11 \quad \text{for} \quad \text{KBr},$$

$$|d/R|=0.15 \quad \text{for} \quad \text{KCl}.$$

In the latter case, if it is assumed that the fixed center of rotation is shifted a distance d from the c.m. towards the oxygen nucleus, one finds from the experimental isotope shifts

$$d/R=0.22,\ 0.27 \quad \text{for} \quad OH^-,\ OD^- \quad \text{in KBr},$$

and

$$d/R=0.28,\ 0.34 \quad \text{for} \quad OH^-,\ OD^- \quad \text{in KCl}.$$

Any participation of the c.m. in the librational motion will change the effective charge e^* and hence the oscillator strength

$$f=\tfrac{2}{3}(e^*/e)^2,$$

since a charge $(-e)$ will be associated with the c.m. motion. For instance, if the center of rotation is shifted a distance d from the c.m. towards the oxygen nucleus, the effective charge would be given by

$$e^*=e_r-ed/R.$$

To explain the experimental librational-oscillator strength for KBr:OH^- we would need $d/R=0.10$.

In any discussion of the oscillator strength, it is important to keep in mind that the electrical properties of the surrounding ions are included in the expression we have used for f only to the extent that they may be described by the Lorentz local field

$$E_l=E+\tfrac{1}{3}(4\pi P)=\tfrac{1}{3}(n^2+2)E.$$

Since the hydroxyl ion will have less than cubic symmetry, the use of the Lorentz local field may not be justified.

A comment should be made about our use of e_r, the effective charge for rotation of a free hydroxyl ion about its c.m. The angular zero-point motion associated with the librator is expected to be large; for example, with the torsional-oscillator model we find

$$\theta_{\text{rms}}=\langle\theta^2\rangle^{1/2}=0.24 \text{ rad}$$

for the ground state and

$$\theta_{\text{rms}}=\sqrt{3}\times 0.24 \text{ rad}$$

for the first excited state. At these relatively large angles there may be an appreciable distortion of the electron distribution of the hydroxyl ion due to interactions with its surroundings. This distortion would affect primarily the nonbonding π electrons, which have relatively little influence on the O-H stretching frequency or equilibrium spacing. The result might cause the effective value of e_r to differ from the free ion value.

D. Oscillator Strength of the Librational Sideband

The simplest assumption to make for the stretching-libration combination band is that the instantaneous dipole moment lies along the O—H axis and has the value

$$p=p_e+(dp/dR)_e(R-R_e)=e_rR_e+e_s(R-R_e),$$
$$\text{with} \quad e_s=(dp/dR)e.$$

The dipole moment along the transverse direction of libration would then be

$$p_\theta=p\theta=e_rR_e\theta+e_s(R-R_e)\theta.$$

The oscillator strength may be calculated by comparing the matrix element of the dipole moment with that for a linear harmonic oscillator of (reduced) mass m, frequency ω, and charge e. When allowance is made for a geometrical orientation factor G, which would equal $\frac{1}{3}$ for the stretching band and $\frac{2}{3}$ for the pure librator or librational sideband, we obtain

$$f=G\langle g|p|e\rangle^2(2m\omega/e^2\hbar),$$

where $\langle g|p|e\rangle$ is the relevant matrix element of p. Thus, for the pure stretching band we use

$$p=e_s(R-R_e),$$

and find

$$\langle g|R-R_e|e\rangle^2=\hbar/2m\omega_s.$$

Thus,

$$f_s=\tfrac{1}{3}(e_s/e)^2$$

as in I. For the pure librator we use

$$p=p_\theta=e_rR_e\theta,$$

and find

$$\langle g|R_e\theta|e\rangle^2=\hbar/2m\omega_l.$$

This gives the result (used above)

$$f_l=\tfrac{2}{3}(e_r/e)^2.$$

For the stretching-librational combination band we write for the relevant part of the dipole moment

$$p = p_\theta = e_s(R - R_e)\theta ,$$

and assume a factorization

$$\langle g|\,(R-R_e)\theta\,|e\rangle = \langle g|R-R_e|e\rangle\langle g|\theta|e\rangle .$$

Then

$$\langle g|\,(R-R_e)\theta\,|e\rangle^2 = (h/2m\omega_s)(h/2mR_e^2\omega_l) .$$

Thus, we predict for the librational sideband

$$\begin{aligned} f_{s+l} &= \tfrac{2}{3}(e_s/e)^2(\omega_{l+s}/\omega_s)(h/2m\omega_l R_e^2) \\ &= f_s[(2\omega_{l+s}/\omega_s)(h/2m\omega_l R_e^2)] . \end{aligned}$$

The numerical results are

$$\begin{aligned} f_{s+l}/f_s &= 0.12 \quad \text{for OH}^- \\ &= 0.079 \quad \text{for OD}^- . \end{aligned}$$

These values have been inserted into Table II. We see that the experimental values for the ratio f_{s+l}/f_s and for f_{s+l} itself are not far from this theoretical prediction.

E. Temperature Dependence of the Linewidth

It is instructive to compare the OH^- librator with the deuterium *U* center in alkali halides, which has almost the same frequency.[16] For instance, the *U*-center localized mode in KBr:D^- is at 318 cm^{-1} compared with 313 cm^{-1} for the librator in KBr:OH^-. The width of the D^- line is 1–2 cm^{-1} at helium temperature and appears to be lifetime limited because of the decay of the excited-localized mode into two phonons. At higher temperatures, say 70°K and above, the width is proportional to T^2 for both H^- and D^- *U* centers. This suggests that the scattering mechanism is dominant. In this mechanism, a phonon, is scattered during the optical transition, and the line broadens as a result. The width should also be proportional to m^{-2} and hence twice as large for H^- as for D^-. This is what is observed experimentally.

The experimental situation for the OH^- librator is not as clear cut as that for the *U* center. The temperature dependence is different in different host crystals, as can be seen from Figs. 6 and 7. At high temperatures the width may be proportional to T^2 for KBr:OH^-, but certainly not for the other two host crystals. At low temperatures the OD^- widths are greater than the OH^- widths which may support a decay mechanism of some sort.

Quite apart from the question of whether the scattering mechanism is effective at high temperatures, is the need for an explanation of the large low-temperature widths, including the factor of three variation between KBr:OH^- and KCl:OH^-. The Lorentzian line shape suggests lifetime broadening. Decays into two phonons are energetically possible. There is not much range for the frequencies of the two phonons, since they must sum to the librational frequency and both be less than the maximum phonon frequency ω_m in the host crystal, which is 214, 173, and 165 cm^{-1} for KCl, RbCl, and KBr, respectively. The resulting expressions give a constant width for temperatures below 100°K. Note that the low-temperature widths decrease in the order KCl, RbCl, KBr, which is also the order of decreasing values for $(2\omega_m - \omega_l)$.

We can obtain a reasonable good fit to the data for KBr:OH^- using a three-phonon decay scheme, with one low-energy phonon of 28 cm^{-1} and with the other two roughly equal at about 135 cm^{-1}. The resulting expression when fitted to the low-temperature width gives the lower solid line in Fig. 6. Since 28 cm^{-1} is close to the broad 37 cm^{-1} non-Devonshire level in KBr:OH^-, it is interesting to speculate that the librational excitation decays to (or via) the non-Devonshire excitation with the emission of two-band phonons.

The three-phonon scheme does not work for the data from other host lattices. We can fit the width for RbCl:OH^- with the function $\coth(E/2kT)$ with $E = 29$ cm^{-1} (upper solid line in Fig. 6), but there is no apparent theoretical justification for this expression.

V. CONCLUSIONS

The difference between the frequencies of the direct librator and the splitting of the librational sideband can be understood in terms of the increased moment of inertia in the excited stretching-oscillator state.

The Devonshire model is unable to explain the OH^--OD^- isotope shifts. It also predicts additional strong lines, which are not seen experimentally.

A simple torsional harmonic-oscillator model yields the correct symmetry for the transition dipole moment and is able to produce rough agreement with the experimental oscillator strengths and isotope shifts. The isotope shifts could be explained by the anharmonicity of the angular potential, by a shift of the axis of rotation away from the c.m., or by both. The experimental oscillator strengths can be explained by a shift of the axis of rotation by about the same amount needed for the isotope shifts. The torsional oscillator model gives a good quantitative explanation for the oscillator strengths of the librational sideband.

The origin of the linewidths still remains an open question. There is some evidence that the non-Devonshire levels may play a role in limiting the lifetime of the excited librational state.

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[16] For a review of the experimental and theoretical status of the infrared U center, see M. V. Klein, in *Physics of Color Centers*, edited by W. B. Fowler (Academic Press Inc., New York, 1968), Chap. VII.