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Infrared absorption and rotational dynamics of OH^- and OD^- defects in cesium halides

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The rotational degrees of freedom of substitutional OH^- and OD^- defects in CsCl, CsBr, and CsI have been studied between 2 and 300 K using infrared absorption in the range of the 2.7 and 3.7-μm stretching absorption. In CsCl the first direct evidence for quasi-free-rotational behavior of OH^- in alkali-metal halides is found in the form of a vibration-rotation spectrum above 45 K, corresponding to a reorientational barrier of $\sim 30\ \mathrm{cm}^{-1}$. The small rotational constant of $B = 1\ \mathrm{cm}^{-1}$ without OH^--OD^- isotope shift, derived from the temperature dependence of the rotational P and R branches, indicates a considerably increased moment of inertia for OH^- and possibly off-center motion of the molecule around the H ion. High-frequency librational sidebands observed below and above 45 K and their isotope shifts indicate radial and angular modes superimposed on the rotational motion and can be explained with a simple double-librator model. In CsBr and CsI doped with OH^- and OD^-, high-frequency sidebands and isotope shifts expected from a harmonic-librator model for center-of-mass libration in high barrier potentials are found. The observed second harmonic of the stretching absorption in CsCl and CsBr allows determination of the mechanical and electrical anharmonicity parameters.

I. INTRODUCTION

The diatomic OH^- molecule substitutes for a halide ion in alkali-metal halides and has optical excitations in the uv, near-ir, and far-ir spectral ranges resulting from electronic and oscillatory modes.[1-8] The latter arise from internal vibrational modes and local modes of the whole molecule and lend themselves to investigation by Raman and infrared spectroscopy. Transitions corresponding to angular modes lie in the far ir ($0-600\ \mathrm{cm}^{-1}$) and are thus more difficult to observe. Much of the information about the angular motion of the molecule, however, is carried by sidebands of the vibrational transition (at 2.8 μm for OH^-) more readily accessible to measurements. The sidebands arise from a combination of vibrational and angular transitions.

A large amount of experimental and theoretical work has focused on the question of how the lattice affects the reorientation of the molecule.[9] The electrostatic, repulsive, and multipole interactions of the molecule with the host lattice that make up the crystal field of cubic symmetry alter the internal modes and impose a reorientational barrier on the defect that restricts the angular motion to reorientational tunneling, hindered rotation, or libration. As a less pronounced effect the internal modes are altered too. Various models have been proposed and used for different heights of the reorientational barrier; namely, the Devonshire,[10] Pauling,[11] harmonic-librator, and microscopic models.[12-14] Due to the large dipole moment of OH^- of $\sim 1\ e$ Å, the barrier is high compared to thermal energies thus leading to high-frequency angular oscillations in all previously studied host materials. An off-center position and center-of-mass modes of the molecule have been proposed to explain the low-frequency librational sidebands or non-Devonshire bands and the smaller than expected isotope shift in KCl.[6,15] Strongly damped free-rotor-like behavior has been suggested to account for the broad sidebands in the OH^- stretch band region at higher temperatures in NaCl and KCl.[16,15]

In this paper we present comprehensive infrared absorption data on the fundamental stretch bands, second-harmonic transitions, and librational sidebands of OH^- and OD^- in CsCl, CsBr, and CsI. Contrary to the situation in alkali halides with NaCl structure, very little is known about OH^- in CsCl-structure hosts. Previous uv electro-optic measurements performed only on the CsBr:OH^- system have indicated a $\langle 111 \rangle$ OH^- equilibrium orientation and very long low-temperature dipole-reorientation times[17] pointing to a deep angular potential well in this host. In contrast, our results in CsCl, a host material with only a 7% smaller anion vacancy to accommodate the OH^- molecule and identical nearest-neighbor ions, show a drastically changed dynamic behavior, thus presenting a challenge for existing theoretical models.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

The crystals were grown at the Utah Crystal Growth Laboratory by the Czochralski technique from Merck suprapure material under argon atmosphere, adding cesium hydroxide (CsOH, CsOD) to the melt. The amount of carbonate in the CsOH was reduced by precipitation of CsOH out of ethanol solution to values below 0.1% and 1% of the OH^- concentration in CsCl and CsI, respectively. The molar OH^- and OD^- concentrations in the crystals were determined using a standard acid-base titration technique and are as follows for all measurements: CsCl: 3.5×10^{-4} for OH^- and 3.3×10^{-4} for OD^-; CsBr: 5.7×10^{-4} for OH^- and 5.0×10^{-5} for OD^-. To assure that none of the sidebands were caused by OH^-

defects associated to alkali-metal impurities, atomic analysis for Na^+, K^+, and Rb^+ was performed and the impurity content found to be below 10 ppm (typical 2–5 ppm). In addition, CsCl was intentionally doped with NaOH, KOH, and RbOH and the cationic impurity bands compared with the spectra of pure CsOH-doped crystals. The OH^- absorption data were taken with a Cary 17 DX (resolution ~ 1 cm^{-1}), and the OD^- data with a Beckmann 4240 (resolution ~ 2 cm^{-1}) spectrophotometer.

A. CsCl

Figure 1 shows the absorption spectra for CsCl:OH^- in the vicinity of the fundamental stretch band at 3601.5 cm^{-1} over the temperature range 2–290 K. At 2 K we observe a sharp stretch band at 3601.5 cm^{-1} accompanied by a sideband shifted to higher energy by 16 cm^{-1}. As the temperature is increased to 30 K the sideband splitting reduces to 10 cm^{-1} and the stretch band broadens and decreases in height. Simultaneously, a low-energy sideband, the ground state of which is now thermally populated, appears with a separation of ~ 10 cm^{-1}. The observed strength ratio between the low- and high-energy sideband is smaller than the expected Boltzmann factor at 16 and 30 K. Above 45 K the spectrum changes in an exciting way. The stretch band corresponding to the pure vibrational transition $v=0\rightarrow 1$ (Q branch) becomes less intense and washed out, with the strongest absorption developing into the vibrational-rotational spectrum of a quasifree rotor with P and R branches corresponding to rotational transitions of $\Delta J=-1$ and $+1$, respectively. At higher temperature the splitting of the P and R branch maxima $\Delta\nu_{PR}^{\max}$ increases as the population maximum in the vibrational ground state moves to higher rotational levels.

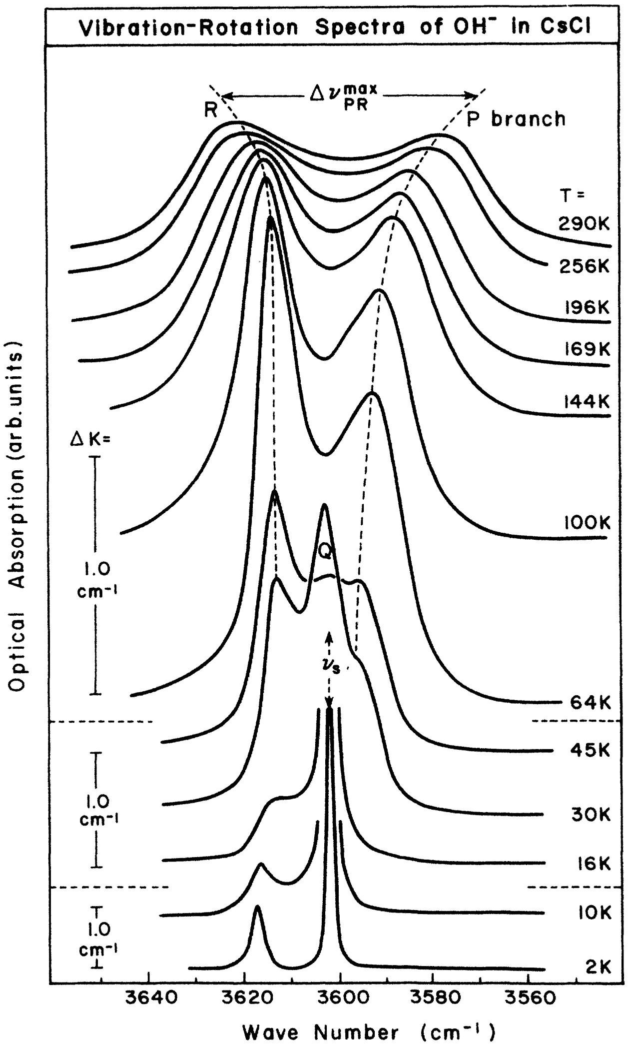

FIG. 1. Vibration-rotation absorption spectrum of OH^- in CsCl between 2 and 290 K. The fundamental vibrational absorption at $\nu_s=3602$ cm^{-1} and its rotational sideband, observed below 20 K, evolves above 40 K into a vibration-rotation spectrum with R and P branches separated by $\Delta\nu_{RP}$. For a convenient illustration, the vertical absorption scale is changed in three temperature ranges, as indicated on the left-hand side.

In order to test the isotope effect on this OH^- vibration-rotation spectrum, the same absorption measurements were repeated with CsCl doped with OD^-. Figure 2 shows spectral data at five selected temperatures, with two essential results.

(a) As expected, the stretching band of OD^- is shifted to lower energies by a factor of 1.356 compared to the corresponding OH^- band.

(b) Quite surprisingly, neither the close sideband separation of 16 cm^{-1} nor the P-R splitting is changed in any noticeable way by the OH^--OD^- isotope substitution.

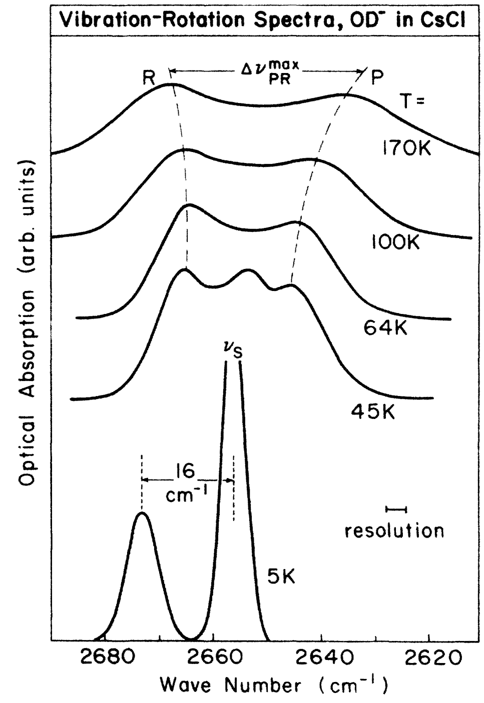

FIG. 2. Vibration-rotation absorption spectrum of OD^- in CsCl between 5 and 170 k.

Beyond the close 16 cm^{-1} rotational sideband, combination bands with larger splitting from the ν_s stretching band are observed for both OH^- and OD^- defects. The results for CsCl:OH^- (Fig. 3) show the existence of two small bands at 249 and 412 cm^{-1} separation from the ν_s band, a slightly stronger one at 96 cm^{-1}, and a much stronger absorption around 275 cm^{-1} which is split into a double band and reveals more substructure at low temperatures. Towards high temperature, the double structure and substructure of this band becomes washed out and a strong shift to higher energies of the envelope band occurs. Opposite to this, the small 96- and 249-cm^{-1} bands become less broadened and shift to lower and higher energies, respectively, under a temperature increase.

Due to its considerably lower oscillator strength and the limited Beckmann Instrument resolution, only two sidebands (separated by 94 and 207 cm^{-1} from the stretching band) were observable for OD^- in CsCl without any resolved substructure. The band at 94 cm^{-1} shows under temperature increase a low-energy shift similar to the 96-cm^{-1} band of OH^-, and if both bands are related, they indicate only a minute isotope effect. The 207-cm^{-1} band, on the other hand, broadens strongly and shifts to higher energies with a temperature similar to the 275-cm^{-1} band of OH^-. An isotope ratio of 1.33 results for the peak positions when the same transition is assigned to these two bands.

We were able to observe the weak second-harmonic transition of the OH^- stretchband in CsCl and CsBr. Table I summaries the peak positions and oscillator strengths for the fundamental and second-harmonic together with anharmonic model parameters derived and discussed in Sec. III. The oscillator strengths[18] were determined by comparison of the integrated absorption and chemically determined concentration of OH^- and OD^- and are correct to within a 50% error margin. The oscillator strengths for the 2656- and 2643-cm^{-1} OD^- stretch bands in CsCl and CsBr are 7×10^{-3} and 4×10^{-3}, respectively.

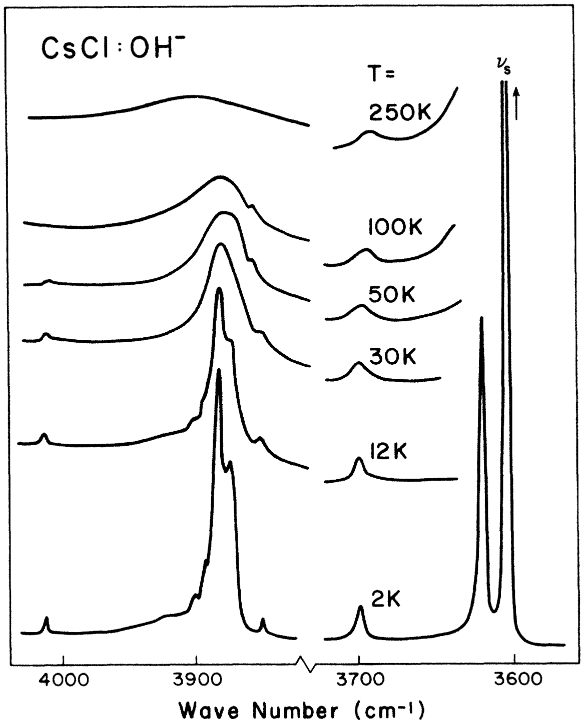

FIG. 3. Librational sidebands of OH^- in CsCl measured between 2 and 250 K. Besides the 16-cm^{-1} rotational sideband at 3618 cm^{-1}, two main combination bands at 3698 and 3877 cm^{-1} are observed.

B. CsBr

Figure 4 shows the absorption spectra of CsBr:OH^- for the temperature range of 12 to 200 K. At 12 K we observe the stretch band at 3580.4 cm^{-1} and the main librational sideband with a splitting of 288.5 cm^{-1} shifted to higher energies. The stretch band broadens with temperature but is still well detectable up to room temperature [full width at half maximum (FWHM) of 15 and 35

TABLE I. Fundamental and second-harmonic stretching frequency with respective oscillator strengths for OH^- molecules in CsCl and CsBr. Also shown are the derived anharmonic and Morse potential parameters.

Host material	CsCl	CsBr
Fundamental ν_1 (cm^{-1})	3601.5	3580.4
Oscillator strength f_1	1.1×10^{-2}	6×10^{-3}
Second harmonic ν_2 (cm^{-1})	7032	6987
Oscillator strength ratio f_1/f_2	2200	300
Harmonic frequency ν_e (cm^{-1})	3772	3755
Anharmonicity parameter $\nu_e x_e$ (cm^{-1})	85.4	87.1
Morse potential parameters V_D (eV)	5.6	5.0
β	2.09	2.13

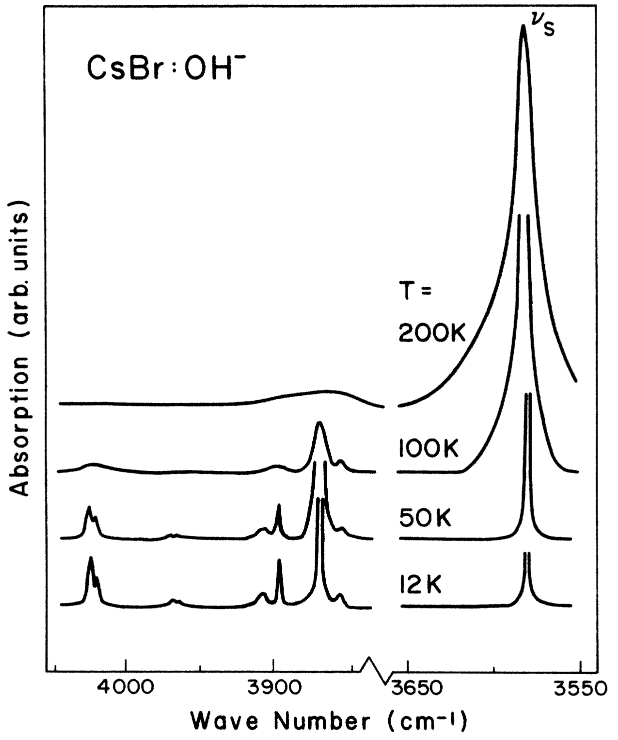

FIG. 4. Vibrational ν_s and vibrational sideband absorption in CsBr at four temperatures between 12 and 200 K.

cm^{-1} at 200 and 300 K, respectively] and shows only a small shift of 4 cm^{-1} to higher energies. The main librational sideband with 288.5 cm^{-1} splitting broadens rapidly so that no peak position or half-width could be determined above 100 K. Up to that temperature there was no detectable shift of the peak position. In addition, we observe a variety of smaller sidebands. To investigate the question of isotope shifts absorption data were taken on a CsBr crystal doped with 5×10^{-5} mol ratio of OD$^-$. Table II contains these results together with the spectroscopic data for all fundamental and librational sidebands observed in CsCl doped with OH$^-$ and OD$^-$ and in CsI:OH. The isotope effects of the stretch band and the main librational sideband splitting yield values of 1.355 and 1.36, respectively.

C. CsI

The absorption spectra we obtained with a crystal of CsI doped with 3×10^{-3} mol ratio of OH$^-$ are given in Fig. 5 for the temperature range from 12 to 270 K with the 12-K peak positions and oscillator strengths ratio given in Table II. Similar to the CsBr host lattice there is only very limited temperature broadening of the stretch band up to room temperature (300-K half-width = 3 cm^{-1}), accompanied by a small shift of 3 cm^{-1} to higher energies. The librational sideband could be detected up to a temperature of 170 K. Due to the low segregation coefficient and oscillator strength of OH$^-$ in CsI, it is very difficult to achieve sizable optical densities of vibrational absorption in this host material. Therefore it is possible that the sideband broadens only moderately up to much higher temperatures than 170 K. For the same reason no attempt was made to grow a CsI crystal doped with OD$^-$ which would have been an interesting addition to the data presented here. At high concentrations of OH$^-$ in CsI a different vibrational band at 3562 cm^{-1} and three librational sidebands at 4143, 4235, and 4710 cm^{-1} are observed at 12 K. Upon heating of the crystal to 500 °C and rapid quenching to room temperature, these bands disappear. Since these highly OH$^-$-doped CsI crystals are optically opaque, we assign these bands to clusters of OH$^-$.

III. DISCUSSION

A. Fundamental and second-harmonic stretching absorption

The fundamental stretch bands of OH$^-$ in the three host materials show a frequency shift to lower energies with increasing lattice parameter as expected and observed in hosts with NaCl structure.[5] The value for free OH$^-$ radicals without any lattice surrounding thus has to be smaller than the 3571 cm^{-1} observed for CsI in agreement with photodetachment data of free OH$^-$ by Owrutsky.[19]

Our measurement of the second-harmonic absorption in CsCl and CsBr allows a direct determination of the purely harmonic frequency ν_e and anharmonicity parameter $\nu_e x_e$. The fundamental and second-harmonic frequency labeled ν_1 ($=\nu_s$) and ν_2 define the anharmonicity parameter[20] as

$$2\nu_1-\nu_2=2\nu_e x_e \;, \qquad (1)$$

with $\nu_1=\nu_e-2\nu_e x_e$ and $\nu_2=2\nu_e-6\nu_e x_e$. This yields $\nu_e x_e$ and the harmonic frequency ν_e with values given in Table I.

The observed OH$^-$-to-OD$^-$ isotope ratios of the stretch bands of 1.356 in CsCl and 1.355 in CsBr are close to the one of $(\mu_{\mathrm{OD}}/\mu_{\mathrm{OH}})^{1/2}=1.375$ (μ is the reduced mass) expected for a purely harmonic oscillator. For an anharmonic oscillator the vibrational frequencies are predicted at $\nu_1=\rho\nu_e-2\rho^2\nu_e x_e$ with $\rho=1$ for OH$^-$ and $\rho=1/1.375$ for OD$^-$. When the measured anharmonicities from Table I are used, the predicted isotope effect becomes 1.358 for CsCl and 1.357 for CsBr in excellent agreement with the experimental results.

Perturbation theory links the anharmonicity of the stretching potential to the intensity of the second-harmonic transition.[21] Using the anharmonicity parameters calculated from the second-harmonic positions, the mechanical anharmonicity can be accounted for by fitting a Morse potential[20]

$$V(\zeta)=V_D(1-\exp\beta\zeta)^2 \qquad (2)$$

to the data. Here $\zeta=(r-r_e)/r_e$ denotes the relative change of the O—H interatomic distance around its equilibrium position $r_e=0.96$ Å, β is a dimensionless scaling parameter, and V_D denotes the dissociation energy. The resulting parameters together with the spectroscopic data are shown in Table I. The dissociation energies are in reasonable agreement with the theoretical value of 5.1 eV calculated by Rosenfeld[22] using the self-consistent-field molecular-orbital approximation. With only mechanical anharmonicity present in the OH^- molecule as described above the predicted intensity ratios between fundamental and second harmonic are $f_2/f_1 = x_e + x_e^2$ to lowest order. This yields ratios of 1/43 and 1/42 for CsCl and CsBr, respectively, using the values given in Table I. Poor agreement with the observed ratios of 1/2200 and 1/300 suggests that electrical anharmonicity plays a significant role. Electrical anharmonicity results from a nonlinear dependence of the dipole moment on the O—H interatomic distance. Expanding the electric dipole moment to second order in the relative O—H separation ζ gives

$$p(\zeta) = p_e + p_e'\zeta + p_e''\frac{\zeta^2}{2} + \cdots \ . \tag{3}$$

From perturbation theory the ratio $\rho'' = (p_e''/p_e')$ is given to lowest order in the electric anharmonicity expansion as the solution to the equation[21]

$$\frac{f_2}{f_1} = x_e + x_e^2 - \frac{2x_e}{\beta}\rho'' + \frac{x_e + 4x_e^2}{\beta^2}\rho''^2 - \frac{5x_e^2}{\beta^3}\rho''^3 \ . \tag{4}$$

With the observed values for f_2/f_1, β, and x_e from Table I, and the experimental value for the equilibrium OH^- separation[19] $r_e = 0.96$ Å, Eq. (4) has only one real and positive solution, i.e., the same sign for p_e' and p_e''. The experimental values are $\rho'' = +15.7$ for CsCl and $\rho'' = +17.9$ for CsBr. The theoretical values determined graphically from the plot $p(\zeta)$ given in Cade's paper[23] after shifting to center-of-mass coordinates show the same sign (both negative) for p_e' and p_e'' in agreement with the experiment but a somewhat smaller value of $\rho \sim 5$. To the degree that the calculated slope and curvature of $p(\zeta)$ are reliable, the larger experimental values for ρ'' indicate strong electrical anharmonicity and suggest that higher contributions in the expansion $p(\zeta)$ may not be negligible.

The oscillator strength is related to the electronic charge e and the derivative of the dipole moment with respect to the displacement as

$$f = \frac{1}{3}\left[\frac{1}{e}\frac{dp}{dr}\right]^2 , \tag{5}$$

Comparison of the experimental f values given in Table I with the theoretical values for free OH molecules[5,23] of 6.8×10^{-3} for OH^- and 2.7×10^{-3} for OD^{-1} shows

TABLE II. Fundamental stretch band frequency ν_1, librational sideband shift $\nu_L - \nu_1$, FWHM, and oscillator strength ratio f_L/f_1 of OH^- and OD^- ir absorption transitions in CsCl, CsBr, and CsI, measured at 2 K* and 12 K.

Host	Impurity	Fundamental ν_1 (cm^{-1})	Sideband shift $\nu_L - \nu_1$	FHWM (cm^{-1})	Oscillator strength ratio f_L/f_1
CsCl	OH^-	3601.5*	0.0		1
			16.0*	2.6	1×10^{-1}
			96.2*	5.6	2×10^{-2}
			248.8*	3.6	3×10^{-3}
			270.9*	9	1×10^{-1}
			279.3*	10	2×10^{-1}
			290.9*	2	2×10^{-3}
			299.0*	3	3×10^{-3}
			411.7*	3	3×10^{-3}
	OD^-	2656*	0.0		1
			16*		1×10^{-1}
			94		1×10^{-1}
			207		1×10^{-1}
CsBr	OH^-	3580.4	0.0	3	1
			275.8	3	4×10^{-3}
			288.5	3	1×10^{-1}
			315.7	2	7×10^{-3}
			327.7	4	5×10^{-3}
			441.3	2	6×10^{-3}
			445.2	2	1×10^{-2}
			542.5	4	3×10^{-3}
	OD^-	2643	0.0		1
			212		1×10^{-1}
CsI	OH^-	3571.4	0.0		1
			347.9		1×10^{-1}

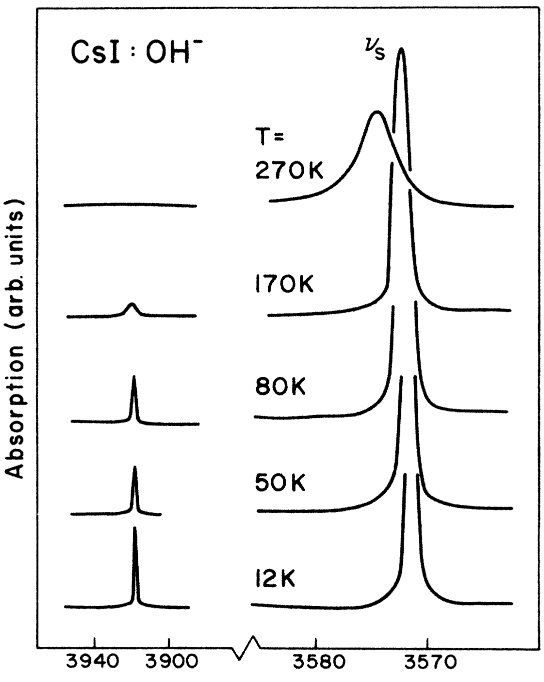

FIG. 5. Vibrational ν_s and sideband absorption of OH^- in CsI between 12 and 270 K.

reasonable agreement.

The observed half-widths of the main stretch bands in the three host materials at 12 K are limited by the instrumental resolution limit of about 1 cm^{-1}. The true low-temperature half-widths could be lower than indicated. The early onset of broadening in CsCl could be related to the presence of the hindered rotor state producing the sideband at 10–16 cm^{-1}. The details of this lifetime effect possibly produced by phonon scattering processes have been described elsewhere.[5] The onset of broadening only at higher temperatures in CsBr and CsI is consistent with the absence of close sidebands and thus broadening phonon scattering processes.

B. Rotational dynamics in the low-barrier systems CsCl:OH⁻(OD⁻)

1. *Quasifree rotor*

For thermal energies large compared to the reorientational barrier the angular eigenstates of the molecule must correspond closely to the ones of the free rotor. Vibration-rotation spectra for free molecules have been discussed in detail by Herzberg.[20] The eigenvalues are given by

$$E_{v,J}=h\nu(v+\tfrac{1}{2})+\frac{\hbar^2}{2I}J(J+1)\ , \qquad (6)$$

where v and J are the vibrational and rotational quantum numbers and I the moment of inertia. The transitions with $\Delta J=+1$ and $\Delta J=-1$ give rise to the R and P branches, respectively, while the transitions with $\Delta J=0$ are forbidden for free diatomic molecules. The strengths of the vibration-rotation transitions are determined by thermal population of the rotational levels in the vibrational ground state. For molecules in a crystal matrix the situation is similar but the rotational levels are not resolved. Thus an envelope function is observed with the shape of the vibration-rotation band determined by thermal population. The separation between the maxima of the P and R branches is given by

$$\Delta\tilde{\nu}_{PR}^{\max}=\left[\frac{8\tilde{B}kT}{hc}\right]^{1/2} . \qquad (7)$$

Here $\tilde{B}=(h/8\pi^2cI)$ is the rotational constant of the molecule in wave numbers and k, h, and c denote the Boltzman constant, Planck's constant, and the speed of light, respectively. Thus a measurement of the temperature dependence of the P-R separation allows the determination of the rotational constant and moment of inertia of the molecule. The measured P-R separations plotted as a function of $\sqrt{T}$ are given in Fig. 6 for OH^- and OD^-. Both sets of data seem to fit the $\sqrt{T}$ dependence rather well. For a totally free OH^- and OD^- rotor one would expect a rotational constant for the vibrationally excited state of $B_1=18.15$ and 9.60 cm^{-1}, respectively, when the measured O—H equilibrium distance[19] of 0.96 Å is used and corrections for the anharmonicity of the stretching potential are included.[24] The rotational constants obtained experimentally (Fig. 6) are $B=1.0\pm0.1$ cm^{-1} in both cases with no apparent isotope effect as could have been expected. Two different effects are favorable candidates to explain this strong increase in the moment of inertia of OH^- and OD^- in CsCl.

(a) Considering the "dressing effect," the basic model of a dipole moving in a static potential of octahedral symmetry is not really correct, because each dipole creates a distortion of the lattice surrounding it. The noncubic part of this distortion, e.g., of E_g and T_{2g} symmetry,

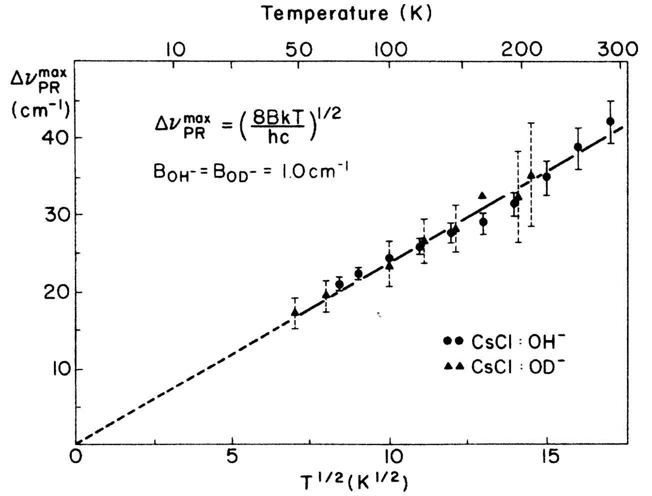

FIG. 6. Separation of the P and R branch maxima in CsCl doped with OH^- and OD^-. The $\sqrt{T}$ dependence of the P-R splitting confirms quasifree rotation of the molecule with the slope yielding for both OH^- and OD^- a rotational constant of $B=1.0\pm0.1$ cm^{-1} without apparent isotope effect.

mainly produced by displacements of the eight nearest-neighbor cesium ions, can largely increase the "effective moment of inertia" of the defect lattice system.[25] Due to the heavy cesium ions and their large distances from the pivot point, very small displacements are sufficient to completely overwhelm the OH^--OD^- isotope effect. This so-called dressing effect should be most effective at low rotational frequencies when the surrounding ions are able to respond readily. Small deviations of the more accurate CsCl:OH^- data from the exact $\sqrt{T}$ dependence could be produced by a temperature dependence of the dressing effect.

(b) Another possibility is an *off-center rotation of the whole molecule.* The equilibrium configuration of the impurity in the matrix is determined by the charge distributions and repulsive interaction of the molecule and the neighboring ions of the host lattice. Consequently the lattice site of the vacancy does not necessarily have to correspond with the center of mass of the defect. If we consider only an off-center displacement to account for the observed rotational constants, we obtain the pivot point to be within 0.07 Å of the H or D and within 1.03 Å of the O positions. This suggests oxygen to be very strongly off center and H and D to be only slightly off center. We also have to allow for the case where both effects, dressing and off-center motion, contribute to the large moment of inertia leading to a smaller off-center displacement. The rotational constant derived from the *P-R* separation is nearly independent of temperature. This precludes a temperature-induced off-center to on-center change as observed[26] in other off-center systems like RbCl:Ag^+. More insight into the problem an be gained if we look at the different libration bands.

2. *Librational sidebands*

At 2 K the strongest librational sidebands of OH^- (OD^-) in CsCl form three groups distinguished by their separation from the main band of 16 (16), 96 (94), and 275 (207) cm^{-1} with respective isotope effects of ~1, 1.02, and 1.33.

The 16-cm^{-1} sidebands are only resolved up to ~40 K. Above that temperature thermal population of rotational levels with increasing degeneracy causes this sideband to decrease together with the *Q* branch. The small separation from the stretch band places these sidebands into a frequency range where acoustic phonons are readily available to produce dressing effects.

Two aspects of the close sidebands need more consideration; the 16-cm-to-10-cm^{-1} shift of the high-energy sideband between 2 and 30 K and the weakness and small strength increase with temperature of the 10 cm^{-1} low-energy sideband. The decreasing high-energy sideband frequency can be explained as a softening of the hindering potential or temperature-dependent dressing effect between 2 and 30 K. The 10-cm^{-1} separation of both the low- and high-energy sidebands indicates similar angular hindering potentials in the vibrational ground and excited state at 30 K. The weakness of the low-energy sideband is paralleled by results for CN^- in KCl (Ref. 27) and can be explained with different oscillator strengths to the transitions at high and low energies. For equal high- and low-energy oscillator strengths, one expects a ratio of $\exp(-h\nu/kT)$ between the zero. There is no simple model to predict strengths for the two transitions different from this.

In summary, the absence of any isotope effect and small separation of the 16-cm^{-1} sidebands suggest that they belong to a hindered rotational motion of a strongly dressed or largely off-center OH^- or OD^- molecule in analogy to the quasi-free-rotor motion. The onset of quasifree rotation above ~45 K yields a barrier height of ~30 cm^{-1} above the zero-point energy of the hindered rotational ground state.

The two groups of OH^- (OD^-) sidebands with 275 (207) and 96 (94) cm^{-1} splitting from the main band broaden with increasing temperature but stay well defined above the onset of the free rotation at 45 K. Thus the modes associated with these bands can be simultaneously excited with both the free-rotor motion and the low-frequency hindered rotation of the molecule. The half-width of the 275-cm^{-1} double sideband in CsCl broadens as $\sim T^{1/2}$ above 12 K and saturates at 16 cm^{-1} at low temperature as shown in Fig. 7. Comparison with the slightly smaller "half-width" of the vibration-rotation spectra around the stretch band shows that this mode is mainly excited in conjunction with a vibration-rotation transition, i.e., a change in the rotational quantum number. We therefore expect the angular motion associated with the 275 (207)-cm^{-1} mode to fall in the plane of rotation. The strong shift of the 275-cm^{-1} sideband to higher energies with increasing temperature similar to the *R* branch suggests that $\Delta J = +1$ transitions are favored over $\Delta J = -1$ transitions. A simple two-dimensional torsional harmonic oscillator model[6] predicts an isotope shift for center of mass libration of

$$\nu_{OH}/\nu_{OD} = (I_{OD}/I_{OH})^{1/2} = 1.375 \ .$$

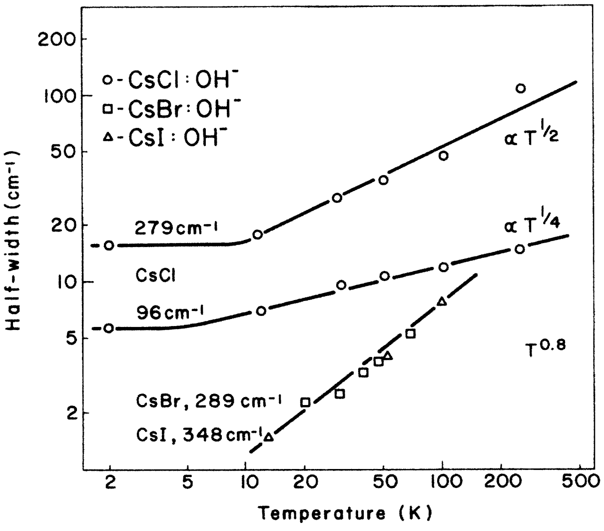

FIG. 7. Half-width (FWHM) of various librational sidebands of the OH^- stretch band in CsCl, CsBr, and CsI, plotted in double logarithmic scale as a function of temperature.

The observed value between the 275-cm^{-1} double band and the 207-cm^{-1} band of 1.33 is in good agreement thus indicating torsional oscillation about the center of mass with the full rotational constants of $B_1 = 18.15$ for OH^- and $B_1 = 9.60$ for OD^-. The slightly *smaller* isotope shift cannot originate from dressing effects since the lattice does not allow the phonons ($\omega_{\mathrm{LO}} = 162\ \mathrm{cm}^{-1}$) to follow the libration. A dressing effect on OD^- only would increase the isotope effect. The small discrepancy may be explained with a two-dimensional mechanical model. Allowing for off-center position and coupling between center-of-mass oscillation and libration, Keller and Kneubühl[14] calculated an isotope shift of 1.30. The splitting of the 275-cm^{-1} sideband into two bands at 279.3 and 270.9 cm^{-1} below 12 K cannot be explained with the harmonic-librator model. The 96.2 (94)-cm^{-1} sidebands broaden to a much lesser degree than the vibrational-rotation spectrum. Figure 7 shows the temperature dependence of the half-width of the 96-cm^{-1} band with a slope of $T^{1/4}$. Thus this mode cannot be excited in conjunction with a change of the rotational quantum number. The isotope effect of 1.02 fits well with the one predicted by the harmonic-oscillator model for an oscillation of the whole molecule:

$$\omega_{\mathrm{OH}}/\omega_{\mathrm{OD}} = (18/17)^{1/2} = 1.03 \ .$$

Another possible explanation for the small isotope effect is a strongly dressed angular motion perpendicular to the plane of rotation to account for the absence of rotational broadening. This, however, would require an angular potential minimum of C_2 symmetry to produce the 275- and 96-cm^{-1} sidebands which is only possible for a $\langle 110 \rangle$ equilibrium orientation of the molecule.

In addition, we observe weaker sidebands with splittings of 249 and 412 cm^{-1}. As all the 96-, 249-, and 412-cm^{-1} transitions remain *sharper* under temperature increase than the vibration-rotation spectrum, only three possibilities exist.

(a) They occur only from the lowest (nonrotational) $v = 0$ state. As a necessary consequence, their absorption strength must thermally decay due to rapid thermal depopulation of this lowest state.

(b) They occur with different selection rules (e.g., $\Delta J = 0$).

(c) They originate from unknown defect-associated (aligned) OH^- defects without close-lying rotational states.

Possibility (c) was checked by intentional doping with the most likely cationic impurities K^+ and Rb^+. The absorption spectra at 2 K show new sharp stretching bands on the low-energy side of ν_1 and a new high-energy sideband with 314-cm^{-1} splitting from the 3596-cm^{-1} stretch band both attributed to K^+ associated OH^- defects, but no increase of the 96-, 249-, or 412-cm^{-1} bands. For (c) one would also expect large isotope effects in disagreement to the one observed for the 96/94-cm^{-1} bands. Thus, the weak sidebands with 249 and 412-cm^{-1} splitting are likely transitions to higher hindered rotor states as qualitatively suggested by the Devonshire model. For a detailed fit, this model, however, is too crude, particularly when the OH^- equilibrium orientation is not known. The decreasing oscillator strength predicted by (a) could not be observed, thus leaving (b) as a possible choice.

In an extension of the model given by Keller and Kneubühl,[14] the following mechanical double-librator model explains—at least qualitatively—all aspects of the stretch band and three strongest sidebands for OH^- and OD^- in CsCl. The molecule sites in a shallow off-center potential with the H or D ion close to the lattice site. There are three modes, two librational modes and one corresponding to a radial oscillation of the molecule. The low-frequency 16-cm^{-1} modes are assigned to an angular off-center oscillation of the oxygen ion about the lattice site. There is no isotope effect for this mode because the H (D) ion does not participate in the mode. At temperatures above 45 K states become thermally populated for which libration becomes delocalized and quasifree rotation takes place in the off-center potential. In addition to this mode, a high-frequency libration of the molecule about its center of mass corresponding to the 275- and 207-cm^{-1} bands can be excited. This oscillation about the radius vector connecting the lattice site with the O ion shows nearly the full isotope effect of 1.33. The third mode is assumed to be a radial oscillation of the whole molecule in the off-center potential, which shows only a minute isotope effect of $\sqrt{18/17} = 1.03$ thus accounting for the 96- and 94-cm^{-1} sidebands. This mode is also present over the whole temperature range investigated. Electric-field-induced or stress dichroism experiments will have to be conducted to give the equilibrium orientation of the molecule and the directions of the transition dipole moment of the different vibration-libration combination bands. If our model is correct, we would expect the moments to be perpendicular to the axis of the molecule for the 16- and the 275-cm^{-1} sidebands, and parallel for the 96-cm^{-1} band.

C. High rotational barrier systems
$\mathrm{CsBr{:}OH^-(OD^{-1})}$, $\mathrm{CsI{:}OH^-}$

The librational sidebands observed in CsBr with 289-cm^{-1} and 212-cm^{-1} splittings from the fundamental for OH^- and OD^- show an isotope effect of 1.36. The fact that this is close to the expected value of 1.375 suggests a deep and nearly harmonic potential well for this host material. The barrier height predicted by the Devonshire model for the known $\langle 111 \rangle$ equilibrium orientation is $V_0 = 970\ \mathrm{cm}^{-1}$ when the libration band is assigned to the T_{1u}-E_g transition based on selection rules given elsewhere.[6] The 289-cm^{-1} band together with a number of smaller sidebands has also been observed as a direct librational transition by Harrison and Lüty.[3] The pure librational frequency and the sideband splitting are determined in the harmonic librator model by the rotational constants for the vibrational ground state B_0 and for the first excited state B_1, respectively. The negligible difference between the two sets of frequencies calls for a deep well with small anharmonicity in agreement with our above estimate of the barrier height. Similar to the situation in CsCl the weaker sidebands observed in

CsBr:OH^- cannot be fit to Devonshire models even in their extended version.[28] Due to the low concentrations of cationic impurities (≤ 10 ppm), we believe that these transitions are higher hindered rotor excitations of OH^- as predicted qualitatively by the Devonshire model. However, since CsBr crystals were not explicitly doped with K^+ or Rb^+ impurities this still needs to be confirmed. The weak sideband with 542.5-cm^{-1} splitting could possibly be a second harmonic of the 288.5-cm^{-1} librational sideband. Since the angular barrier is of comparable magnitude, the hindering potential is expected to be highly anharmonic.

In CsI:OH^- the observed main sideband splitting of 347.9 cm^{-1} is even larger than in CsBr or CsCl and suggests the largest barrier for reorientation of the OH^- molecule. The predicted large barrier heights in both host materials are in good agreement with the absence of rotational broadening up to room temperature.

The most puzzling question arising from the results in all three crystals is the following: Why does OH^- display quasifree rotational behavior in the host with the smallest lattice constant and encounter increasingly higher angular barriers in CsBr and CsI? A possible explanation for this unexpected behavior could be an off-center position of OH^- increasing from CsCl to CsI, which would likely be due to the large-ion size mismatch, the OH^- being much smaller than the anion it replaces. Similar to CsCl one would expect to see a high-energy sideband and negligible isotope effect corresponding to the angular oscillation of the whole OH or OD molecule. No such bands could be resolved possibly due to low optical density or oscillator strength. The off-center potential heights V_0 could dramatically increase from CsCl$\rightarrow$CSBr$\rightarrow$CsI; i.e., the expected sidebands should be more shifted from ν_s and become weaker. Another possibility is a different equilibrium orientation (possibly $\langle 100 \rangle$ or $\langle 110 \rangle$) for OH^- in CsCl, that leads to a low angular hindering potential.

Klein has predicted ratios of the oscillator strength of the librational sideband and the main stretch band of 0.12 and 0.079 for OH^- and OD^-, respectively.[6] Comparison with the experimental data shows agreement within the error limit.

We plotted the half-widths of the main librational sidebands as a function of temperature with the result shown in Fig. 7. In all three host materials the temperature dependence follows approximately power laws above ~ 30 k with onset of broadening at 12 K and ~ 20 K in CsCl and CsBr, respectively. For CsI we did not observe a limiting linewidth above the resolution limit. The temperature broadening of the two narrow sidebands in CsBr and CsI seems to be proportional to $T^{0.8}$. A T^1 dependence would suggest a one-phonon scattering process to limit the lifetime. There is no simple model for the observed temperature dependence. Comparing with Harrison data[3] on the direct libration band in CsBr suggests that the half-width of the fundamental stretch band the direct excitation libration band add to produce the half-width of the combination bands.

IV. SUMMARY AND CONCLUSION

We have presented infrared absorption data of OH^-- and OD^--doped CsCl, CSBr, and CsI crystals. Vibration-rotation spectra observed in CsCl above 45 K constitute the first direct evidence of quasifree rotation of the OH^- molecule in ionic solids. The greatly increased moment of inertia together with absence of an isotope effect indicates an off-center position or a strong dressing effect on the angular motion. Higher-frequency modes are found to superimpose on the rotational motion. The results can be explained in terms of an extended double-librator model with a low-frequency off-center libration below 45 K and rotation of the whole molecule above 45 K. Two superimposed modes correspond respectively to a high-frequency libration about the center of mass and a high-frequency radial oscillation of the whole OH^- molecule present over the entire temperature range investigated. The systems CsBr:OH^-(OD^-) and CsI:OH^- are rotationally localized with high angular barriers and isotope shifts close to predictions by the harmonic torsional oscillator model. In order to understand the interesting host lattice variation of the rotational behavior and distinguish between various models, equilibrium orientation and off-center displacement data of OH^- are needed. Experiments for this are planned and will yield more insight into the interesting dynamics of OH^- and OD^- in cesium halides.

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