A line-shape formula has then been derived to take account of the effects caused by the exchange interaction. An analysis of the observed optical spectra of NaBr based on that formula supports our theory of the interference. The most striking feature in the spectra is a possible antiresonance on the low energy side, which is in general expected from the positive sign of the exchange energy. It has also been found that the interchannel interaction through the electron-phonon interaction is important, so the author hopes to do a theoretical study on the interference of a discrete exciton state with a continuum absorption caused by electron-phonon interaction.

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Theory for the Non-Devonshire Lines Observed in the Hydroxyl-Ion-Doped Alkali Halide Matrices

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The isotope effect of the non-Devonshire lines can be well understood if one takes the origin of these as transitions corresponding to the quantized translational motion of the impurity in the matrix cage and considers the various perturbing mechanisms. The present model in which rotation-translation coupling and coupling through the anisotropic part of crystalline field are considered as the chief perturbing mechanisms proves to be good in explaining the isotope effect of the near-infrared lines in the KCl and KBr matrices. It provides a good explanation of the multiplet line structure observed in the KCl-OH^- system and absence of such a structure in the KCl-OD^- system. The more complex case of the NaCl matrix is also explained in a satisfactory way. There has not been an attempt to explain the RbCl-OH^- system because of the lack of sufficient experimental data.

I. INTRODUCTION

Recent experiments on the near-[1-3] and far-infrared spectroscopy[4] and the thermal-conductivity measurements[5] on the hydroxyl-ion-doped alkali halide systems have established the presence of a 30–35 cm^{-1} energy level for this impurity. This level could not be explained by the Devonshire model, and hence was named the non-Devonshire level. Different workers tried to explain the origin of this level, but without significant success. In the KCl matrix, the OH^- to OD^- frequency ratio for the non-Devonshire line has been found to be very close to the square root of the moments of inertia of the two ions. This is the expected isotope effect for the energy levels associated with the torsional-harmonic-oscillation model of the impurity.[1] However, the simple torsional-harmonic-oscillator

model does not explain the observed isotope effect in the KBr matrix.

Baur and Salzman[6] tried to explain these non-Devonshire lines by assuming that the OH^- impurity sees potential minima along four axes making an angle of 40° with the ⟨100⟩ directions and not along the ⟨100⟩ directions themselves. The potential barrier between these new minima orientations and the ⟨100⟩ orientation is taken to be about 100 cm^{-1} to explain the 32-cm^{-1} level as originating because of the fast tunneling among the four new potential minima. Gomez *et al.*[7] and later Bron and Dreyfus[8] have discussed in detail the tunneling states of a dipolar impurity in a fcc lattice. Although, the formulations have been done for the ⟨100⟩, ⟨111⟩, and ⟨110⟩ equilibrium orientations alone, we can extract the important conclusion that the tunneling matrix element is directly proportional to the displacement parameter a, the square root of the mass of the impurity, and also to e^{-Ka^2}. Hence, if a tunneling-model assignment of the non-Devonshire line is correct, it should satisfy an isotope effect as follows:

$$\left(\frac{\omega_{OH}}{\omega_{OD}}\right)=\left(\frac{m_{OH}}{m_{OD}}\right)^{1/2}\left(\frac{a_{OH}}{a_{OD}}\right)\exp[-K(a_{OH}^2-a_{OD}^2)]$$

$$=\left(\frac{17}{18}\right)^{1/2}\left(\frac{a}{a+0.0509}\right)e^{+0.1018Ka}\ .$$

This comes out to be 0.219 for the KCl matrix and 0.254 for the KBr matrix (whereas the experimental values are 1.391 and 1.071 for these systems). In the above equation, the factor 0.0509 comes from the assumption that the same point of the impurity is pinned to the normal lattice site in the OH^- and the OD^- impurities. Under such an assumption, the difference in the off-c.m. positions of the two impurities will only be due to the different positions of their c.m. Such an assumption has recently been seen to be a good approximation in understanding the isotope effect of the librational lines of these impurity systems.[9,10]

More recently Scott and Flygare[11] have explained these non-Devonshire lines as occurring because of the transition between the lowest six and the next-higher six energy levels, which are obtained by adding a large V_6 term to the Devonshire potential. The Devonshire model considered only the first angle-dependent term (V_4) in the expansion of the potential energy in an octahedral lattice. The presence of such a large V_6 term has been demonstrated elsewhere[12] to give rise to a ⟨110⟩ minimum-energy configuration in the impurity. There is, on the other hand, overwhelming evidence for the ⟨100⟩ equilibrium orientation of the OH^- impurity in the alkali halide[13–15] matrices.

Very recently Keller and Kneubühl[16] have presented a simple model for the non-Devonshire lines. However, they did not make any quantitative interpretation of the existing experimental data, but only proposed that the non-Devonshire lines can be understood in terms of the oscillations of the impurity c.m. The model uses a two-dimensional potential and treats the problem classically. Probably, the introduction of a realistic three-dimensional potential and quantum-mechanical support is essential for the model before it could be put to a rigorous quantitative test.

A translational-harmonic-oscillator model with a given spring constant encounters the following difficulty. The isotope effect for this model is given by

$$\left(\frac{\omega_{OH}}{\omega_{OD}}\right)=\left(\frac{M_{OD}}{M_{OH}}\right)^{1/2}\ ,$$

where M is the total mass of the impurity. This explains well the results in the KBr matrix, but fails completely in the case of the KCl matrix. Table I summarizes the different situations.

In this paper we present the conviction that the origin of the non-Devonshire line is the quantized translational motion of the impurity. Any departure from the simple translational-harmonic-oscillator isotope effect is proposed to be due to the fact that this motion is not free but is coupled to the system and also to the other types of motions of the impurity via some mechanisms. Various authors[3,17,18] have calculated the change in the simple harmonic-oscillator isotope effect of an atomic impurity due to the coupling of its translational motion to the lattice via short-range forces. These calculations provide too small a change in the isotope effect to explain the results in the present systems. For the dipolar impurities, it is observed that there are two more mechanisms by which the translational motion is coupled. First, when the impurity in the matrix has an angular motion about a point [the impurity center of interaction (c.i.)] other than the c.m., the translational motion is coupled to the angular motion of the impurity. Second, the angular motion of the impurity induces localized vibrations in the nearest-neighbor atoms, which get coupled to the translational motion of the impurity. Owing to this mechanism, therefore, the translational motion gets coupled to the lattice via its angular motion. In the present paper, we have examined these two coupling terms in detail and have worked out their effect on the translational frequency of the impurity. It has been observed that the rotation-translation coupling term presents negligible modification to the translational frequency, whereas the coupling through the propagation of the localized lattice waves gives an important contribution to this.

TABLE I. Isotope effect of the non-Devonshire lines as expected from different models.

System	Torsional-harmonic-oscillator model[a]	Fast-tunneling model[b]	Translational-harmonic-oscillator model with the same spring constant	Experimental
KCl	1.369	0.219	1.029	1.391[c]
KBr	1.369	0.254	1.029	1.071[c]
NaCl	1.369	0.178	1.029	...
RbCl	1.369	0.104	1.029	...

[a]Reference 1.
[b]Reference 6.
[c]References 1–4.

II. THEORY

The Hamiltonian governing the rotational and the translational motions of the electronically unexcited molecules in a crystal matrix can be written in the form

$$H=\sum_{\alpha l}\frac{P_\alpha^2(l)}{2M(l)}+\sum_{\alpha l}\frac{J_\alpha^2(l)}{2I_{\alpha\alpha}}+V_v(r_G^N,\Omega^N)\ . \tag{1}$$

Here v designates the intramolecular vibrational quantum number. In cases where the concentration of the solute molecule in the matrix is very small, the problem reduces to one of an isolated molecule trapped in an infinite lattice. In such a case, v becomes the vibrational quantum state of the dipolar impurity and Ω^N reduces to the orientational angles of the impurity molecule. As has been pointed out elsewhere,[19] the dependence of the potential energy on v affects only the frequency of the band center, in which we are not interested at the present moment. It is therefore sufficient to write V in the form

$$V=V(r_G^N,\Omega)\ . \tag{2}$$

At the substitutional site of an fcc lattice, the angular dependence of V will have octahedral symmetry. To a first approximation, we assume that the position dependence and angle dependence of V can be separated out, i.e., we can write in the form

$$V=V(r_G^N)+V_c(\Omega)\ . \tag{3}$$

The angular motion of the molecule is coupled to the lattice vibrations via two mechanisms. First, when the molecule in the matrix makes angular motion about a point (the c.i.) other than the c.m., the angular motion is coupled to the translational motion of the impurity, which is thus also coupled to the vibrations of the entire lattice.[20] Second, the angular motion is also governed by the V_c part of the potential energy, i.e., the anisotropic part of the crystalline field. The relative displacement of the impurity nearest-neighbor atoms modifies the crystalline field and thus affects the rotational motion.[21] We shall calculate these two coupling terms separately.

III. RTC TERM

Expanding the potential $V(r_G^N)$ in powers of the displacements of the molecular c.i. from their equilibrium positions and retaining only the dominant quadratic term, one has

$$V(r_G^N)=\frac{1}{2}\sum_{\substack{ll'\\ \alpha\beta}}A_{\alpha\beta}(l,l')u_\alpha^{\text{c.i.}}(l)u_\beta^{\text{c.i.}}\ . \tag{4}$$

Here the coefficients

$$A_{\alpha\beta}(l,l')=\frac{\partial^2V(r_G^N)}{\partial u_\alpha^{\text{c.i.}}(l)\,\partial u_\beta^{\text{c.i.}}(l')} \tag{5}$$

denote the force constants, the index $\alpha=x,y,z$ gives the direction of the displacement, and l indicates the position of the lattice points in the crystal. The crystal is assumed to be a fcc one, in which the impurity molecule occupies a substitutional lattice site labeled $l=0$.

The displacement coordinates about the c.i. can be expressed in terms of the coordinates about the c.m. and the molecular orientational angles:

$$u_\alpha^{\text{c.i.}}(l)=u_\alpha^{\text{c.m.}}(l)+a\phi_{z\alpha}\,\delta_{l,0}\ . \tag{6}$$

Substitution of (6) into (4) gives

$$V(r_G^N)=\frac{1}{2}\sum_{\substack{ll'\\ \alpha\beta}}A_{\alpha\beta}(ll')u_\alpha(l)u_\beta(l')+a\sum_{1\alpha\beta}A_{\alpha\beta}(l,0)\,\phi_{z\alpha}u_\beta(l)\ . \tag{7}$$

In this, the first term is the usual harmonic quadratic term expressed about the c.m. whereas the second term provides the desired coupling between the lattice vibrations[22] and the angular motion of the molecule. The strength of this coupling is determined by the length a, i.e., by the separation between the molecular c.i. and c.m.

IV. COUPLING THROUGH ANISOTROPIC PART OF CRYSTALLINE FIELD

To obtain this, we will have to look for the anisotropic interaction between the trapped molecule and one of its surrounding neighbors. This is naturally between the multipole moments of the trapped molecule and the induced dipole moment in the atoms of the host lattice. The explicit expressions for these are well known.[23] These can be rearranged and written in terms of spherical harmonics as follows[24]:

$$V=\sum_{t=1}^{4}A_t(R(l))\,Y_0^t(\omega(l))\ . \tag{8}$$

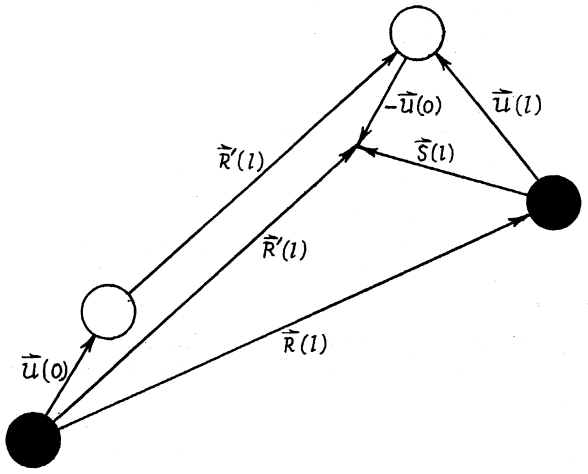

FIG. 1. Model for the displacement of the lattice points: ● normal position of the lattice atom; O displaced position of the lattice atom.

Here $\omega(l)$ denotes the orientation of the molecule relative to the "$R(l)$ frame"—a rectangular coordinate frame with the z axis along the internuclear vector $\vec{R}(l)$. To consider the dynamics of the lattice, we introduce a very simple model (Fig. 1). Let $\vec{u}(l)$ denote the displacement of the lattice point l from its equilibrium position $\vec{R}(l)$, and let $\vec{R}'(l) = \vec{R}(l) + \vec{S}(l)$ [where $\vec{S}(l) = \vec{u}(l) - \vec{u}(0)$] be the instantaneous value of the intermolecular axis between the central trapped molecule and the lth lattice atom. Then the interaction energy V' in the distorted configuration becomes

$$V' = \sum_t A_t(R'(l))\, Y_0^t(\omega'(l)) = \sum_t \sum_m Y_m^t(\omega(l))[A_t(R'(l))D_{m0}^t(\alpha'\beta'\gamma')]. \quad (9)$$

Here ω and ω' denote the orientation of the trapped molecule in the $\vec{R}(l)$ and $\vec{R}'(l)$ frames, respectively, and $(\alpha'\beta'\gamma')$ are the Euler angles of rotation carrying the $\vec{R}'(l)$ frame to the $\vec{R}(l)$ frame. Using the relations

$$R'\cos\beta' = R + S_0\,, \qquad R'\sin\beta' e^{\pm i\alpha'} = \mp\sqrt{2}\, S_{\pm 1}\,, \quad (10)$$

and

$$R' = R(1 + 2S_0R^{-1} + S^2R^{-2})^{1/2}, \quad (11)$$

and expanding in powers of the displacement parameter S, we get

$$V' = V + V_1 + \text{terms having higher powers of } S = V + \sum_{t,m} G_{tm}(R(l))\, Y_m^t(\omega(l))S_m(l)\,, \quad (12)$$

where

$$G_{t,0}(R(l)) = A_t'(R(l))\,,$$

and

$$G_{t,\pm 1}(R(l)) = -[\tfrac{1}{2}t(t+1)]^{1/2}[A_t(R(l))/R(l)]\,.$$

The prime on A_t stands for the differentiation with respect to $R(l)$. To get the total crystalline-field interaction, we will have to sum (12) over all the neighbors and far neighbors:

$$V_c' = \sum_l (V + V_1) = V_c + V_{c1}\,, \quad (13)$$

where

$$V_{c1} = \sum_{l,t,m} G_{tm}(R(l))\, Y_m^t(\omega(l))S_m(l)\,. \quad (14)$$

V_c is the crystalline field for the case of a static lattice for which the closed expression has been obtained elsewhere.[10,24] For performing summation over l in (14), we make the transformation from the $R(l)$ frame to the C frame (a rectangular coordinate system with the z axis along the symmetry axis of the lattice cage):

$$S_m = \sum_n D_{nm}'(\alpha_1\beta_1\gamma_1)s_n\,, \qquad Y_m^t(\omega(l)) = \sum_n D_{n,m}^t(\alpha_1\beta_1\gamma_1)\, Y_n^t(\Omega)\,. \quad (15)$$

Here s_n and Ω refer to the lattice fixed C frame. This gives V_{c1} in the form

$$V_{c1} = \sum_\lambda{}' \sum_l \sum_{t,m,n} \sum_p \left(\frac{4\pi}{2p+1}\right)^{1/2} C(t,l,p;m,n) \times Y_{m+n}^p(\alpha_1\beta_1\gamma_1) f_{t,p}(R)\, Y_n^t(\Omega)s_n(l)\,. \quad (16)$$

The different summations can be performed and the Clebsch-Gordan coefficients evaluated to give V_{c1} in the form

$$V_{c1} = Q\{(P_1\cos\theta + S_1\cos^3\theta)u_z(0) + (P_2\cos\theta + S_2\cos^3\theta) \times [u_x(0)e^{i\phi} + u_y(0)e^{-i\phi}]\}, \quad (17)$$

where

$$P_1 = (3/\sqrt{\pi})(f_{10} - \tfrac{7}{4}f_{34})\,, \qquad S_1 = (35/4\sqrt{\pi})\, f_{34}\,, \qquad P_2 = (1/\pi)^{1/2}\{\tfrac{3}{2}f_{10} - \tfrac{7}{16}\sqrt{3}\,[(\tfrac{3}{2})^{1/2} + (\tfrac{5}{2})^{1/2}]f_{34}\}, \quad (18)$$

and

$$S_2 = \tfrac{35}{16}(3/\pi)^{1/2}[(\tfrac{3}{2})^{1/2} + (\tfrac{5}{2})^{1/2}]f_{34}\,.$$

f_{34} and f_{10} are given by[21]

$$f_{34} = (\tfrac{4}{7})^{1/2}(A_3' - 3A_3/R)\,, \qquad f_{10} = -(\tfrac{1}{3})^{1/2}(A_1' + 2A_1/R)\,,$$

and

$$Q=\sum_{\lambda}' \sin ka/ka \ . \tag{19}$$

The prime over the summation indicates that the summation is to be carried over half the Brillouin zone. This coupling of the angular motion and the lattice vibrations (in fact the vibrations of the impurity) depends upon the multipole moments of the impurity as well as on the matrix properties such as polarizability of its constituent atoms and the equilibrium lattice parameter.

V. EXCITATION OF LATTICE MODES

With all the coupling terms thus obtained, the total Hamiltonian can now be written as

$$H=H_{\text{lattice}}+H_{\text{imp}}+V_{\text{coup}}^{\text{RTC}}+V_{\text{coup}}^{\text{Cr.f.}} , \tag{20}$$

where

$$H_{\text{lattice}}=\sum_{\alpha l}\frac{P_{\alpha}^{2}(l)}{2M(l)}+\frac{1}{2}\sum_{\substack{ll'\\ \alpha\beta}}A_{\alpha\beta}(l,l')u_{\alpha}(l)u_{\beta}(l') , \tag{21}$$

$$H_{\text{imp}}=J^{2}/2I+V_{c}(\theta,\phi) , \tag{22}$$

and $V_{\text{coup}}^{\text{RTC}}$ and $V_{\text{coup}}^{\text{Cr.f.}}$ are as given by Eqs. (7) and (17), respectively.

When the coupling is small, one may assume that the dynamics of the system are essentially determined by H_{lattice} and H_{imp}. The molecular angular motion and lattice vibrations are then uncoupled. The evaluation of the eigenvalues of H_{lattice} depends upon the determination of the normal modes $d(f)$ which can be found by solving the equations of motion

$$M(l)\ddot{u}_{\alpha}(l)+\sum_{\beta l'}A_{\alpha\beta}(l,l')u_{\beta}(l')=0 . \tag{23}$$

The $3N$ normal modes can be written as

$$u_{\alpha}(l)=\sum_{f}\chi_{\alpha}(l,f)d(f)e^{i\omega(f)t} , \tag{24}$$

and the $d(f)$ can conveniently be expressed in terms of the creation and annihilation operators such as

$$d(f)=\left(\frac{h}{2\omega(f)}\right)^{1/2}[a(f)+a^{\dagger}(f)] . \tag{25}$$

Substitution of Eq. (23) into (7) gives

$$V_{\text{coup}}^{\text{RTC}}=a\sum_{\alpha f}M(0)\,\phi_{z\alpha}\,\omega^{2}(f)\chi_{\alpha}(0,f)d(f) . \tag{26}$$

The angular motion of the impurity can be of two types. In the first case, when the potential barrier hindering the angular motion is small, the motion can be treated as an approximately free rotation. The basis set for the eigenfunction is taken to be the normalized spherical harmonics and the energy eigenvalues are determined for the various irreducible representations of the O_h group. This has been done by Devonshire[25] and also by Sauer.[26] However, none of the authors have published either the dipolar transition probability or the eigenfunctions for the different levels. These are needed for the perturbation calculation of the lattice modes.

The second type of motion occurs when the potential barrier hindering the angular motion is large. In this case, the angular motion can best be thought of as oscillational (librational) about a stable equilibrium orientation. Gomez *et al.*[7] have constructed eigenstates in this approximation, with the harmonic-oscillator functions as the basis set. Localization is obtained by starting with very deep potential wells which restrict the harmonic oscillator to a particular axis. Correctly symmetrized eigenstates can then be obtained by allowing overlap between the wave functions of one well and the other wells. This has been provided in Appendix A of Ref. 7 which can be used for the calculation of the dipolar and the octupolar transition probabilities. These are needed in the calculation of the shift of the lattice-mode levels.

To zeroth order in V_{coup}, the energy eigenstates of the system (matrix impurity) are determined by

$$(H_{\text{lattice}}+H_{\text{imp}})|n_1\cdots n_f\cdots n_{3N};\psi_R\rangle = [\textstyle\sum_f(n_f+\frac{1}{2})\hbar\omega_f+E_R]\,|n_1\cdots n_{3N};\psi_R\rangle . \tag{27}$$

Here R stands for the different angular-motion states.

Let us now consider the lattice level corresponding to the translational motion of the impurity. We use a shorter notation $|n,R\rangle$ to denote the state n_f (corresponding to the translational motion of the impurity) equal to n, all other $n_i=0$, with the angular-motion state of the impurity given by ψ_R. The perturbation of the lattice levels by the discrete rotor levels can then be obtained as

$$E(n,R)=(n+\tfrac{1}{2})\hbar\omega+\sum_{n'R'}\left(\frac{h(n+1)}{8\pi^{2}\omega M}\,\delta_{n',n+1}+\frac{hn}{8\pi^{2}\omega M}\,\delta_{n',n-1}\right)\frac{|\chi(0,\omega)|^{2}[(P_1+aM\omega^{2})\langle R|\cos\theta|R'\rangle+S_1\langle R|\cos^{3}\theta|R'\rangle]}{(n-n_f')\hbar\omega+(E_R-E_{R'})} . \tag{28}$$

In the low-barrier approximation, the wave function ψ_R corresponding to a given level is not available in literature.[9] Naturally, the dipolar and the octupolar transition probabilities cannot be evaluated and hence the perturbation to the lattice modes in the low-barrier approximation cannot be evaluated.[27]

In the high-barrier case, the desired wave functions are available.[7] It is seen that the transition corresponding to the translational motion of the

impurity is obtained as a quartet with the frequencies given below:

$$\begin{aligned}
(1A_{1g} \rightarrow 0\,T_{1u}) &= \hbar\omega + [3\Delta B_1^2/(\hbar\omega)^2]M|\chi(0,\omega)|^2 ,\\
(1\,T_{1u} \rightarrow 0E_g) &= \hbar\omega + [\Delta B_1^2/2(\hbar\omega)^2]\,M\,|\chi(0,\omega)|^2 ,\\
(1\,T_{1u} \rightarrow 0A_{1g}) &= \hbar\omega - [\Delta B_1^2/(\hbar\omega)^2]\,M\,|\chi(0,\omega)|^2 ,\\
(1E_g \rightarrow 0\,T_{1u}) &= \hbar\omega - \tfrac{3}{2}[\Delta B_1^2/(\hbar\omega)^2]\,M\,|\chi(0,\omega)|^2 ,
\end{aligned} \tag{29}$$

where Δ is the tunnel-splitting parameter and

$$B_1 = (h/8\pi^2\omega Mc)^{1/2}[(P_1 + aM\omega^2)\langle A_{1g}|\cos\theta|T_{1u}\rangle + S_1\langle A_{1g}|\cos^3\theta|T_{1u}\rangle]Q . \tag{30}$$

$\chi(0,\omega)$ is the amplitude of vibration of the zeroth-site atom (i.e., the impurity) corresponding to a mode of frequency ω. The dipolar and octupolar transition probabilities can be evaluated by using the wave functions given in Ref. 7. These are obtained as

$$\begin{aligned}
\langle A_{1g}|\cos\theta|T_{1u}\rangle &= \frac{1}{\sqrt{3}}\,\frac{1+2S}{(1+4S)^{1/2}} ,\\
\langle A_{1g}|\cos^3\theta|T_{1u}\rangle &= \left(\frac{1}{12}\right)^{1/2}\frac{(2+3/\alpha a^2)+(1+6/\alpha a^2)S}{(1+4S)^{1/2}} ,\\
\langle T_{1u}|\cos\theta|E_g\rangle &= \left(\frac{2}{3}\right)^{1/2}\frac{S-1}{(1-2S)^{1/2}} ,
\end{aligned} \tag{31}$$

and

$$\langle T_{1u}|\cos^3\theta|E_g\rangle = \left(\frac{1}{24}\right)^{1/2}\frac{S(1+6/\alpha a^2)-(4+6/\alpha a^2)}{(1-2S)^{1/2}} .$$

Here $S = e^{-\alpha a^2/2}$ is the overlap integral between the two adjacent minima. In arriving at the above expression we have made two assumptions. One, the overlap integral $S' \ll S$, so that S' can be neglected. This has been justified by a number of workers for the system OH^--ion alkali halide matrix.[28] Second, the tunnel-splitting parameter Δ is assumed to be small in comparison to the translational frequency ($\hbar\omega$) of the impurity. This is justified for the system KCl-OH^- ($\Delta = 0.18\ cm^{-1}$,[8] $\hbar\omega \simeq 30\ cm^{-1}$) and also for the KBr-$OH^-$ system (see Sec. VI).

We must now calculate $|\chi(0,\omega)|^2$ as a function of ω. The introduction of a defect such as OH^- in KCl- and KBr-type matrices produces changes in the force constants as well as in the mass. For simplicity, we consider only the change in forces to the nearest neighbors. We are then left with a cluster of seven atoms and hence only 21 degrees of freedom to consider. The frequencies of the impure lattice are, therefore, obtained as the solutions of the following equation[29]:

$$\left|\sum_{\beta l''} g_{\alpha\beta}(l,l'')C_{\beta\gamma}(l'',l') - \delta_{\alpha\gamma}\delta(l,l')\right| = 0 . \tag{32}$$

The summation is only over the cluster and $g_{\alpha\beta}(l,l'')$ is the lattice Green's function. The block diagonalization of the 21 dimensional matrices has been carried out elsewhere[29] and it has been shown that the mode in which the impurity molecule moves is the F_{1u} mode. For this mode Mannheim[30] has shown that the frequencies are given as the solution of

$$-M\omega^2[g_{xx}(0,0)]^2 - 1 = \left[\frac{M}{M'} - 1 + \frac{2\omega^2}{\omega_{max}^2}\left(1 - \frac{A_{xx}^{00}}{A_{xx}^{00'}}\right)\right]^{-1} .$$

An expression for $|\chi(0,\omega)|^2$ has also been provided for the case $\omega \leq \omega_{max}$[30]:

$$|\chi(0,\omega)|^2 = \frac{1}{MN}\{(M'/M)^2[1+\rho(\omega)S(\omega)]^2 + (M'/M)^2[\tfrac{1}{2}\pi\omega g_0(\omega)\rho(\omega)]^2\}^{-1} , \tag{33}$$

where

$$S(\omega) = P\int \frac{\omega' g_0(\omega')\,d\omega'^2}{\omega'^2 - \omega^2} \tag{34}$$

and

$$\rho(\omega) = \frac{M}{M'} - 1 + \frac{2\omega^2}{\omega_{max}^2}\left(1 - \frac{A_{xx}^{00}}{A_{xx}^{00'}}\right) . \tag{35}$$

For the force constants, we assume that the forces are derivable from a Born-Mayer potential

$$\phi(r) = -e^2/r + Ae^{-r/\rho} .$$

For the changes in the force constants, we regard the OH^- ion in a first approximation as a distorted F^- ion and then adjust the force-constant parameters within $\pm 20\%$ to get the best results. This may be a poor approximation, but in the absence of any data about the Born-Mayer potential parameters for the OH^--impurity alkali atoms there is no other better choice.

VI. RESULTS AND DISCUSSIONS

A. KCl-OH^- and KCl-OD^- Systems

From Eq. (29) it can be seen that the transition corresponding to the translational motion of an impurity embedded in an octahedrally symmetric lattice site appears as a quartet. If $\langle 1A_{1g} - 0T_{1u}\rangle$ is assigned to be the 32-cm^{-1} line in this matrix, then

$$32 = \omega_{tr}(OH^-) + \frac{3\Delta_{OH}B_1^2}{\omega_{tr}^2}M_{OH^-}|\chi(0,\omega)|^2 . \tag{36}$$

Similarly,

$$23 = \omega_{tr}(OD^-) + \frac{3\Delta_{OD}B_1^2}{\omega_{tr}^2}M_{OD^-}|\chi(0,\omega)|^2 . \tag{37}$$

Equation (36) when solved gives $\omega_{tr}(OH) = 21.4\ cm^{-1}$. Table II summarizes the constants used in all these calculations. The same calculation for OD^- presents some difficulty, because the tunneling

TABLE II. Constants used in the calculations.

	KCl	KBr	NaCl	RbCl	OH^-
R (Å)[a]	3.12	3.25	2.80	3.26	•••
α^+ (Å^3)[b]	3.29	3.29	1.57	4.56	•••
α^- (Å^3)[b]	4.98	6.44	4.98	4.98	•••
B (cm^{-1})[c]	•••	•••	•••	•••	18.9 10.0[d]
μ (D)[e]	•••	•••	•••	•••	4.59
Θ (D Å)[e]	•••	•••	•••	•••	9.15
Ω (D Å^2)[e]	•••	•••	•••	•••	2.556
Φ (D Å^3)[e]	•••	•••	•••	•••	0.25
Bond length (Å)[f]	•••	•••	•••	•••	0.974

[a]N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon, New York, 1940).

[b]S. Robertz, Phys. Rev. 81, 865 (1951).

[c]C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).

[d]Values for OD^- impurity.

[e]Reference 10.

[f]Obtained from the known value of the rotational constant.

frequency for this isotopically substituted impurity is not known. However, our calculations on this impurity have revealed that for the tunneling frequency (here, frequency is expressed in wave-number units cm^{-1}) of OD^- in KCl between 0 and 0.05 cm^{-1}, $\omega_{tr}(OD)$ lies between 23 and 20.5 cm^{-1}. If the latter value is nearer to correctness, the translational-frequency isotope effect becomes $21.4/20.5 = 1.04$, which is very close to the ideal value of 1.029. For the tunneling frequency of OD^-, the only thing which can be said is that the isotope effect of the librational frequencies of these same impurities in the KCl matrix suggests that[9,10]

$$a_{OD} = (a_{OH} + 0.0509)\ \text{Å}\ .$$

With this value of a for OD^- and the experimental value of the librational frequency, the tunneling frequency can be estimated from Eq. (17) of Ref. 8. This actually comes out to be 0.05 cm^{-1}. The calculated positions of the other three lines in the quartet are obtained at $\simeq 23.2$, 17.9, and 16.1 cm^{-1}, respectively, for the KCl-OH^- case. A line at $\simeq 25$ cm^{-1} does appear for the KCl-OH^- case. The detailed weak structure at frequencies below this is not available, but from the first curve of Fig. 2 of Ref. 4, the possibility of a weak shoulder at about 21 cm^{-1} cannot be ruled out. For KCl-OD^- the other three lines of the quartet come out to be at $\simeq 20.9$, 19.7, and 19.3 cm^{-1}, respectively. It is quite likely that these structures would not have been resolved owing to insufficient resolution of the spectrograph (1.0 cm^{-1} in Ref. 4). The reason can also be ascribed to the phonon scattering from these levels of the impurity, which broadens the lines and ultimately makes the resolution still more difficult. This is in agreement with the observations of Wedding and Klein, who have failed to resolve a side-band line analogous to the 25-cm^{-1} OH^- side-band line in KCl, and have just observed one single *broad* line at about 23 cm^{-1} in the KCl-OD^- case.

B. KBr-OH^- and KBr-OD^- Systems

For this system, we have to discuss the results under the handicap of no definite information about the tunneling frequencies. As is clear from the KCl matrix case, this plays an important role in understanding the isotope effect of the non-Devonshire lines. An estimate for the tunneling frequency of OH^- and OD^- dipoles in the KBr matrix can be made from the dielectric relaxation measurements of Knop *et al.*[31] It has been observed in the above reference that

$$\tau_0 = K/\Delta^2 T\ ,$$

where K is a constant and τ_0 is the relaxation time of the dipole. From this it can be concluded that

$$\frac{(\tau_0)_{KCl}}{(\tau_0)_{KBr}} = \frac{\Delta^2_{KBr}\, T_{KBr}}{\Delta^2_{KCl}\, T_{KCl}}\ .$$

This relation, therefore, can be used to estimate the tunneling frequency of OH^- in KBr matrix. This comes out to be 0.038 cm^{-1}. The values of $(\tau_0)_{KCl}$, $(\tau_0)_{KBr}$, etc. have been used from Refs. 31–33. Similarly, the tunnel splitting for KBr-OD^- is estimated as 0.026 cm^{-1}. These values are believed to be good to within an order of magnitude.

When an equation like (36) is solved for the KBr matrix, it is seen that for Δ(KBr-OH^-) lying between 0.0 and 0.1 cm^{-1}, $\omega_{tr}(OH)$ comes out to lie between 37.0 and 36.2 cm^{-1}. Similarly for Δ(KBr-OD^-) lying between 0.0 and 0.1 cm^{-1}, $\omega_{tr}(OD^-)$ is obtained to lie between 35.5 and 34.5 cm^{-1}. The isotope effect for the translational frequency thus becomes 1.071 ± 0.045, which is in agreement with the ideal value of 1.029.

The other lines of the quartet come out to be at 36.3, 36.0, and 35.9 cm^{-1} for the KBr-OH^- case. Naturally, these structures will not be resolved. Similarly for the case of KBr-OD^-, the other lines of the quartet cannot be resolved, because they all appear at a separation of $\simeq 1$ cm^{-1} from the 35.5-cm^{-1} line. In this case, therefore, our model does not throw any light on the 30-cm^{-1} line in KBr-OH^- or the 23-cm^{-1} line in KBr-OD^-. It may be mentioned here that these lines have not been observed in the far-infrared measurements of Bosomworth.[1]

C. NaCl Matrix

The near- and far-infrared measurements on OH^--doped NaCl reveal complicated results in the sense that the non-Devonshire line appears with a

complicated structure. Absorption peaks have been found at about 9.2, 10.3, 12.2, 15.6, and 22.0 cm^{-1}. Kirby *et al.*[2,3] and Wedding and Klein[4] have made a detailed study of these lines at various temperatures. Wedding and Klein[4] have performed electric-field-induced dichroism experiments also on the main stretching band. These two authors, however, present tentative assignments of these absorption lines. More recently Scott and Flygare[9] have explained this complex cluster of lines as occurring because of transition between the lowest six and the next-higher six energy levels which are obtained on the basis of a V_4+large V_6+C_{4v} shape of the potential function. We now proceed to show that the salient features of these absorption lines can also be understood in terms of the present model. If one assigns the 22-cm^{-1} line to $(0T_{1u} \rightarrow 1A_{1g})$ transition, then the frequencies of the other lines in the quartet come out to be as follows:

$$(0T_{1u} \rightarrow 1A_{1g}),\quad 22\ cm^{-1}$$
$$(0E_g \rightarrow 1T_{1u}),\quad 15.7\ cm^{-1}$$
$$(0A_{1g} \rightarrow 1T_{1u}),\quad 11.9\ cm^{-1}$$
$$(0T_{1u} \rightarrow 1E_g),\quad 10.6\ cm^{-1}\ .$$

These are in reasonably good agreement with the experimentally observed positions of the peaks.[1-4] The small difference in the calculated and observed peak positions of the $(0A_{1g} \rightarrow 1T_{1u})$ and $(0T_{1u} \rightarrow 1E_g)$ transitions may be assigned to the anharmonicity effects. This has been shown elsewhere to shift the positions of the absorption peaks by a small amount.[34] A word can also be said about the temperature dependence of the absorption peaks. The 10.6-cm^{-1} line results from a transition, the lower level of which occurs above the ground state. The intensity of this line should therefore decrease with the temperature. The line at 10.3 cm^{-1} does disappear below 4 °K. The lower level of the transition (11.9 cm^{-1}) is the ground-state level. Hence, on lowering the temperature, its intensity should increase. The line at ~12 cm^{-1} observed by Klein and Wedding does grow up when the temperature is decreased below from 10 to 1.4 °K (left-hand portion of the absorption peaks of Fig. 9 in Ref. 4). This temperature dependence is, however, opposite to that observed by Kirby *et al.*[2] Similarly, the peak at 22 cm^{-1} should decrease in intensity with decreasing temperature. This is also in confirmation to the experimentally observed results (Fig. 1 of Ref. 2; Fig. 10 of Ref. 4). The fifth observed peak is inexplicable in terms of the model in its present form. This may be due to the lowering of the lattice symmetry from octahedral to tetragonal, which may result in the splitting of the lines. The presence of such lowered lattice symmetries has recently been suggested by Pompi and Narayanamurti[35] for the RbCl-CN^- system and by Scott and Flygare[11] for the present system. The isotope effect of the absorption peaks has not been attempted because no data on the NaCl-OD^- system are available. We also do not attempt to apply the present formulation to the RbCl-OH^- system because the tunneling frequency of this system is not available and the isotope effect of the absorption peaks has not been studied.

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Tunneling through a Barrier Containing a Pair of Interaction Impurities*

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A theoretical study of the tunneling phenomenon through a metal-insulator-metal junction containing paramagnetic impurities is made. The impurity spins are assumed to be interacting weakly with each other through a general indirect-exchange interaction. Expressions for conductance are obtained by perturbation theory up to third order treating the impurity-electron–conduction-electron interaction as a perturbation. The voltage and temperature dependence of the resulting expression of conductance is analyzed and compared with the recent experimental results on the type of junction considered here. Agreement between the experimental and theoretical results is satisfactory.

I. INTRODUCTION

The use of tunneling phenomena is one of the most powerful methods of investigating electronic states in metals, semimetals, and semiconductors. Electron tunneling is also useful in investigating the interaction between electrons and internal excitations of magnetic impurities in the insulating barriers. A complete account of tunneling in solids has been given by Duke.[1] While investigating tunneling through metal-insulator-metal junctions, Wyatt[2] found that these junctions exhibit anomalous behavior in the conductance as a function of the applied bias. In particular, he found that the conductance had a logarithmic voltage dependence and that the zero-bias conductance increased logarithmically with the decrease in temperature.

There have been various theoretical attempts to explain the zero-bias anomalies, notable are those of Kim,[3] Anderson,[4] Appelbaum,[5] Solyom and Zawadowski.[6] Perhaps the most successful theory is that of Anderson and Appelbaum who have considered the interaction of a single magnetic impurity with the conduction electrons. Like Kondo,[7] they used the second Born approximation in considering the s-d exchange interaction. Recently, Beal Monod[8] investigated the effect of a pair of interacting magnetic impurities on the conductivity of a simple metal. He showed that coefficient of $\ln|k_BT/2\epsilon_F|$ remains negative, as it was for a single impurity, but its absolute value decreases.

In what follows, the tunneling phenomenon is investigated, taking into account the weak interaction between a pair of magnetic impurities. We shall perform the calculation of the scattering amplitude by perturbation theory up to third order. The interaction between the impurity electrons and conduction electrons is described by the s-d exchange interaction, and for simplicity, each impurity is supposed to have total spin $\frac{1}{2}$. We assume the two spins $\vec{S}_1$ and $\vec{S}_2$ to be coupled by a general interaction W. The interaction W may be due to the Ruderman-Kittel-Kasuya-Yosida (RKKY)[9] interaction between the impurities via the conduction electrons, direct interaction, or indirect exchange interaction.

The tunneling Hamiltonian method, first used by Cohen, Phillips, and Falicov,[10] is followed in the present work. In Sec. II, we shall formulate the Hamiltonian of the problem. In Secs. III and