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Motional States of Substitutional Species in Lattices*

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The general problem of the structure of the low-lying motional states of impurity species in crystals is approached by applying a group-theoretical reduction scheme to a basis set consisting of nearly isolated "pocket" states in a rigid lattice. The reduction is carried out for a number of possible symmetries. The concept of "barrier-lowering" perturbation is used within the framework of first-order perturbation theory to treat the ordering and splitting of motional states. The method is applied to Li^+, OH^-, and CN^- as impurity species in KCl, with particular emphasis on the analysis of dielectric measurements. It is concluded, in particular, that motion of OH^- involves both rotational and translational modes.

I. INTRODUCTION

THE subject of impurity motion in ionic or molecular lattices has attracted considerable attention; techniques for the theoretical analysis of the motion of, e. g., large monatomic impurities in ionic lattices[1] are well established. Recently, interest has been increasing in spectroscopic, thermodynamic, and dielectric properties associated with *polyatomic* impurities in lattices. Examples of such systems include OH^-,[2–4] CN^-,[5,6] and NO_2^- [7] as substitutional impurities in alkali-halide crystals, and HCl and other diatomic molecules in inert gas crystals.[8,9] In order to deal with such systems, it is clearly necessary to consider types of impurity motion not present in monatomic species. One such type of motion corresponds to internal modes of vibration of the impurity species which are in general relatively little perturbed by immersion in the lattice. A second type, however, which we shall, for simplicity, call "rotational," will be very much altered in the lattice. These modes correspond roughly to the rotational modes of the impurity species in vacuum, and, in general, cannot be clearly separated from motion involving displacement of the center of mass of an impurity when situated in the nonspherically symmetric environment of a lattice site. The object of this paper is to discuss the theoretical foundation for the description of such rotational motion in light of the available data on impurity species in alkali halides. Our discussion, however, is limited to certain special cases of the general problem. In particular, we concentrate on the analysis of the low-lying motional states of species subject to potential barriers large enough to impose an essentially librational character on these states. We note that the opposite case of small barriers and motion which is best described as weakly perturbed free rotation, is well described by the theory of Devonshire[10] and subsequent extensions of it.[7,8] To implement our discussion, we put forward below a unified and general scheme for the calssification of motional states of complex impurity species in rigid lattices, and indicate how the relevant energy splittings between low-lying motional states of the type described above may be computed using a simple and convenient perturbation procedure. This classification has relevance to both the thermodynamic and dielectric properties of such systems at low temperatures as well as to such nonequilibrium properties as dielectric relaxation; as we have recently indicated,[11] a proper assignment of low-lying motional states may be of crucial importance for the qualitative interpretation of such properties.

In addition to the systems mentioned above, we also apply our considerations to the case of the monatomic substituent Li^+ in KCl. This species appears to possess a set of "off-center" potential minima around its lattice site and can, therefore, in principle exhibit motional properties somewhat akin to those in the polyatomic cases.[12,13]

In Sec. II, below, we define our model and approach, and obtain a classification of the low-lying levels of impurity species in various lattice symmetries by application of group-theoretical arguments to a basis set of "localized pocket" states. The computational method based on the notion of *barrier-lowering perturbations* is described in Sec. III. In Sec. IV, we indicate the results of this analysis when applied to the physical cases of current interest and discuss the interpretation of motional state ordering in terms of "translational" and

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[1] See, for example, A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Solid State Physics* (Academic Press Inc., New York, 1963), Suppl. 3.

[2] W. Kanzig, H. R. Hart, and S. Roberts, Phys. Rev. Letters **13**, 453 (1964).

[3] U. Kuhn and F. Luty, Solid State Commun. **2**, 281 (1964).

[4] I. Shepherd and G. Feher, Phys. Rev. Letters **15**, 194 (1965).

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[6] W. D. Seward and V. Narayanamurti, Phys. Rev. **148**, 463 (1966).

[7] V. Narayanamurti, W. D. Seward, and R. O. Pohl, Phys. Rev. **148**, 481 (1966).

[8] W. H. Flygare, J. Chem. Phys. **39**, 2263 (1963).

[9] R. L. Armstrong, J. Chem. Phys. **44**, 530 (1966).

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[11] M. E. Baur and W. R. Salzman, Phys. Rev. Letters, **16**, 701 (1966).

[12] G. Lombardo and R. O. Pohl, Phys. Rev. Letters **15**, 291 (1965).

[13] G. J. Dienes *et al.*, Phys. Rev. Letters **16**, 25 (1966); J. A. D. Matthew, Solid State Commun. **3**, 365 (1965).

"rotational" motion. Section V contains a summary of the results obtained here and a brief discussion of a number of questions not touched on extensively in the body of the work.

II. CLASSIFICATION OF MOTIONAL STATES

In this section, we set forth a classification scheme based on group-theoretical arguments for the low-lying motional states of impurity species of the type described in the Introduction. In order to motivate the point of view which we adopt here and throughout the paper, a survey of the current state of the field is in order.

The original theoretical work by Devonshire on the problem of the rotational motion of trapped polyatomic impurities[10] was based on the choice of free rotor wave functions as a zero-order basis set. The predictions of this theory have been compared extensively with recent spectroscopic data on CN^- in KCl [6] and on HCl and related diatomic molecules in inert gas lattices.[8,9,14] In both these cases, reasonable agreement with Devonshire theory has been obtained; it should, however, be noted that the character of motion of the impurity species differs strongly between them. It seems now well established that HCl in inert gas matrices is best considered as a weakly perturbed rotor, whereas CN^- in KCl is best described as executing torsional oscillations insofar as its low-lying states are concerned. The applicability of the Devonshire model to CN^- in KCl is not entirely surprising in view of the dimensions of this species. Addition of covalent bond radii yields a value for the long-axis length of the CN^- ion nearly equal to the mean diameter, about 3.2 Å, of the cavity in which the ion resides in KCl. In addition, the center of mass of CN^- very nearly coincides with the midpoint of the C–N axis, so that the center of rotation is essentially the center of mass. It is therefore reasonable to suppose that motion of the CN^- ion in KCl will be angular in character.

The description employed so far for motional states of such species as Li^+ or OH^- in KCl has been rather different from that set out in the Devonshire theory. In these cases, motion of the center of mass must certainly be considered in analyzing the motional states, and the treatment of such motion lies outside the framework of the Devonshire model. In particular, the motion of the Li^+ impurity ion in a substitutional site in KCl has been discussed in terms of tunneling between potential minima located along the crystalline [100] directions,[10] and this point of view is supported by a recent calculation of the positions of the minima in the electrostatic potential due to a rigid lattice of octahedral symmetry surrounding such an ion.[13] In most of the work to date on the dielectric and thermodynamic properties of OH^- in KCl, the model employed has been that of a sixfold degenerate ground state, corresponding to the existence of six minima in the cavity potential, with the OH^- oriented along the [100] axes of the crystal.[3,4] The degeneracy is, in this picture, lifted by application of either an external strain or electric field. A classical model of this type omits the important feature of zero-field splitting. No sixfold degeneracy can rigorously be present in the motional states of an impurity at a lattice site of O_h symmetry, as obtains in unstrained KCl.[15] We may summarize the physical picture underlying the sixfold degenerate model by saying that it corresponds to a situation in which potential barriers between the potential minima in the cavity are sufficiently high to make the time required for spreading of a wave packet, initially localized near such a minimum, long compared with experimental time scales. Since characteristic motional times in OH^-–KCl are short, as evidenced by the existence of an electrocaloric effect,[4] the barriers to OH^- motion must be finite and the sixfold degeneracy is lifted.

The localized wave packet model, summarized in the preceding paragraph, does, however, provide a useful point of departure for a quantum-mechanical discussion of low-lying motional states which seems well adapted to the situation in such species as Li^+ and OH^- in KCl. One may adopt the sixfold degenerate manifold of states obtained for an octahedral cavity with infinite potential barriers as a zero-order basis set in place of the rotational wave functions employed in the Devonshire approach, and approach the problem of the ordering and splitting of correctly symmetrized linear combinations of them in terms of perturbation theory. From this point of view, which we follow in the rest of this work, it is the lowering of the potential barriers between potential minima in the cavity which permits tunneling and is responsible for the existence of nonvanishing zero-field splittings.[16] It is clear that this approach is well suited only to cases in which the barriers between minima are high enough so that the lowest motional state within a potential well lies at an energy well below the top of the lowest barrier. This lowest motional state is then well represented as having harmonic-oscillator character. In the case of a species like CN^- in KCl, the motion is better referred to as a harmonic torsional oscillation, or libration. In a system like HCl in argon,[14] such a picture is not at all applicable, and the basis set chosen in the Devonshire approach is preferable. Hence, we shall not attempt to apply the methods presented below to this case.

To proceed, we now give a more precise prescription of the zero-order basis set. We remark that we adopt

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[14] M. T. Bowers and W. H. Flygare, J. Chem. Phys. 44, 1389 (1966).

[15] See, for example, H. Eyring, J. Walter, and G. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1964), Chap. 10.

[16] It should be noted that the tunneling splitting under discussion is equivalent in character to the splitting of the ammonia inversion doublet; see, for example, C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), Chap. 12.

throughout a rigid lattice model for the host crystal, since the question of phonon interactions is of no concern here. We shall also leave open the precise symmetry of the crystal at this point, but merely suppose it to be high enough so that several equivalent potential minima (4, 6, or 8) exist for an impurity at a lattice site. We assume that the potential near each minimum can be regarded as that of a three-dimensional harmonic oscillator, and that the impurity species has at least one state lying well below the top of each potential well. Such a localized state will be called a *pocket state*, and will always be represented here by a wave function of harmonic-oscillator type. In particular, if we consider a case like Li^+ in KCl, the lowest pocket state wave function will be taken as $N\exp(-\beta r^2/2)$, where N is the normalization constant, r is the distance of the Li^+ ion from the minimum (*not* from the center of the cavity), and $\beta=(mK/\hbar^2)^{1/2}$, with m the mass of the ion and K the force constant. In principle, one could treat the harmonic-oscillator well as antisotropic. For the case of a species like CN^- in KCl, the lowest pocket state wave function would be of form $N\exp(-\gamma\Omega^2/2)$, where now Ω is an *angular* displacement of the axis of the molecule from its equilibrium orientation, and $\gamma=(Ik/\hbar^2)^{1/2}$ with I the moment of inertia of the molecule and k the force constant for libration (with units of energy).

In accordance with the remarks above, the set of pocket states will not be rigorously orthogonal but will overlap in view of the finite height of the potential barriers surrounding the minima. In consequence of this interaction of the pocket states, their degeneracy will be lifted. The set of correctly symmetrized states derived from the original set of pocket ground states, and split by the interaction, will be called the *ground* or *lowest manifold*. In principle, we can also discuss the first excited, and higher, manifolds, by applying our prescriptions to a zero-order set in which one excited pocket state is introduced, but these higher manifolds will not concern us in this paper. In the next section, we discuss the application of perturbation theory to the calculation of splittings within the lowest manifold; in the remainder of this section, we demonstrate the process of symmetrization of the pocket states for various impurity site symmetries.[17]

We carry through the symmetrization in detail for the case of a site with O_h symmetry and six potential minima displaced from the cavity center along the $\langle 100\rangle$ axes. The six pocket states are denoted $\psi_{\pm x}$, $\psi_{\pm y}$, $\psi_{\pm z}$, where the significance of the subscripts is self-evident. These states form a basis for a reducible representation of O_h, whose character under each operation of the group is readily calculated. In this way it is found that the representation decomposes according to $A_{1g}+T_{1u}+E_g$. In terms of symmetry properties, but of course not of detailed form, states belonging to these latter representations are analogous to s, $(p_{x,y,z})$, and (d_{z^2,x^2-y^2}) states for a purely spherical cavity. Now we introduce the linear combinations

$$\begin{aligned}\psi_{xg}&=a_+(2)^{-1/2}(\psi_{+x}+\psi_{-x})\,,\\ \psi_{xu}&=a_-(2)^{-1/2}(\psi_{+x}-\psi_{-x})\,,\end{aligned}\tag{1}$$

with similar definitions for ψ_{yg}, etc. In constructing these functions, we have inserted the factor $a_\pm=(1\pm S)^{-1/2}$, where S is the overlap integral

$$S=\langle\psi_{+x}|\psi_{-x}\rangle=\langle\psi_{+y}|\psi_{-y}\rangle=\langle\psi_{+z}|\psi_{-z}\rangle\,,\tag{2}$$

insuring that the new g and u functions are orthonormal. Now, ψ_{xu}, ψ_{yu}, ψ_{zu} transform like coordinates x, y, z under operations of O_h, while ψ_{xg}, ψ_{yg}, ψ_{zg} transform like x^2, y^2, z^2. Comparing with the transformation properties of the coordinates and their squares under O_h, we find at once that the properly symmetrized orthonormal states Φ are

$$\begin{aligned}\Phi(A)&=(3)^{-1/2}b_1(\psi_{xg}+\psi_{yg}+\psi_{zg})\,,\\ \Phi(E)_{x^2-y^2}&=(2)^{-1/2}b_2(\psi_{xg}-\psi_{yg})\,,\\ \Phi(E)_{z^2}&=(6)^{-1/2}b_3(2\psi_{zg}-\psi_{xg}-\psi_{yg})\,;\end{aligned}\tag{3a}$$

$$\begin{aligned}\Phi(T)_x&=\psi_{xu}\,,\\ \Phi(T)_y&=\psi_{yu}\,,\\ \Phi(T)_z&=\psi_{zu}\,.\end{aligned}\tag{3b}$$

In Eqs. (3a), we have introduced the normalization factors

$$\begin{aligned}b_1&=(1+4Ta_+{}^2)^{-1/2}\,,\\ b_2&=(1-4Ta_+{}^2)^{-1/2}\,,\\ b_3&=(1-4Ta_+{}^2)^{-1/2}\,,\end{aligned}\tag{4}$$

with

$$T=\langle\psi_{+x}|\psi_{+y}\rangle=\langle\psi_{+x}|\psi_{-y}\rangle=\cdots\,.\tag{5}$$

The extension of this procedure to other possible symmetry groups need not be given in detail, and we content ourselves with presenting the results. In the case of O_h symmetry with eight minima along the $\langle 111\rangle$ axes, we introduce the pocket states ψ_{111}, $\psi_{11\bar{1}}$, $\psi_{1\bar{1}1}$, $\psi_{\bar{1}11}$, etc. Decomposition of the reducible representation formed by these eight states yields $A_{1g}+T_{2g}+T_{1u}+A_{2u}$. We then find easily

$$\begin{aligned}\Phi(A_{1g})&=(2)^{-1}c_1(\psi_{g111}+\psi_{g\bar{1}11}+\psi_{g1\bar{1}1}+\psi_{g11\bar{1}})\,,\\ \Phi(T_{1u})_x&=(2)^{-1}c_2(\psi_{u111}-\psi_{u\bar{1}11}+\psi_{u1\bar{1}1}+\psi_{u11\bar{1}})\,,\\ \Phi(T_{1u})_y&=(2)^{-1}c_2(\psi_{u111}+\psi_{u\bar{1}11}-\psi_{u1\bar{1}1}+\psi_{u11\bar{1}})\,,\\ \Phi(T_{1u})_z&=(2)^{-1}c_2(\psi_{u111}+\psi_{u\bar{1}11}+\psi_{u1\bar{1}1}-\psi_{u11\bar{1}})\,,\\ \Phi(T_{2g})_{xy}&=(2)^{-1}c_3(\psi_{g111}+\psi_{g11\bar{1}}-\psi_{g\bar{1}11}-\psi_{g1\bar{1}1})\,,\\ \Phi(T_{2g})_{xz}&=(2)^{-1}c_3(\psi_{g111}+\psi_{g1\bar{1}1}-\psi_{g\bar{1}11}-\psi_{g11\bar{1}})\,,\\ \Phi(T_{2g})_{yz}&=(2)^{-1}c_3(\psi_{g111}+\psi_{g\bar{1}11}-\psi_{g1\bar{1}1}-\psi_{g11\bar{1}})\,,\\ \Phi(A_{2u})&=(2)^{-1}c_4(\psi_{u111}-\psi_{u\bar{1}11}-\psi_{u1\bar{1}1}-\psi_{u112})\,,\end{aligned}\tag{6}$$

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[17] Basis sets corresponding, in essence, to the pocket state basis used here have recently been introduced independently in discussions of paraelectric resonance in OH^-–KCl by G. Feher, I. Shepherd, and B. Shore, Phys. Rev. Letters 16, 500 (1966), and L. Vredevoe (to be published).

where

$$\begin{aligned} \psi_{g111} &= (2)^{-1/2}a_+(\psi_{111}+\psi_{\bar{1}\bar{1}\bar{1}}) , \\ \psi_{u111} &= (2)^{-1/2}a_-(\psi_{111}-\psi_{\bar{1}\bar{1}\bar{1}}) , \\ \psi_{g11\bar{1}} &= (2)^{-1/2}a_+(\psi_{11\bar{1}}+\psi_{\bar{1}\bar{1}1}) , \text{ etc.} \end{aligned} \tag{7}$$

In these equations, the $a_\pm$ factor is defined in analogy with that for the six minima case, and the factors c are analogous to the factors b for the latter case.

In the case of O_h symmetry, tegragonally distorted in the z direction, and with six minima in the potential, the relevant group is D_{4h}.[18] The ground manifold decomposes according to $2A_{1g}+B_{1g}+E_u+A_{2u}$, and the correspondance with the O_h case is given by

$$\begin{aligned} A_{1g}(O_h) &= A_{1g}(D_{4h}) , \\ (E_g)_{x^2-y^2}(O_h) &= B_{1g}(D_{4h}) , \\ (E_g)_{z^2}(O_h) &= A_{1g}(D_{4h}) , \\ (T_{1u})_x+(T_{1u})_y(O_h) &= E_u(D_{4h}) , \\ (T_{1u})_z(O_h) &= A_{2u}(D_{4h}) . \end{aligned} \tag{8}$$

The decomposition of the states in D_{4h} symmetry in terms of pocket states can then be taken over from Eqs. (3).

Finally, it may be relevant for application to, e.g., an interstitial impurity, to consider a species in a cavity with tetrahedral fourfold minima. The four pocket states form a reducible representation which decomposes according to A_1+T_1, and, labeling the pockets 1–4, we find

$$\begin{aligned} \Phi(A_1) &= (2)^{-1}d_1(\psi_1+\psi_2+\psi_3+\psi_4) , \\ \Phi(T_1)_1 &= (2)^{-1}d_2(\psi_1+\psi_2-\psi_3-\psi_4) , \\ \Phi(T_1)_2 &= (2)^{-1}d_2(\psi_1-\psi_2+\psi_3-\psi_4) , \\ \Phi(T_1)_3 &= (2)^{-1}d_2(\psi_1-\psi_2-\psi_3+\psi_4) , \end{aligned} \tag{9}$$

where

$$d_1(1+3S)^{-1/2}, \quad d_2=(1-S)^{-1/2},$$

and

$$S=\langle\psi_i|\psi_j\rangle \quad i,j=1\text{–}4, \quad i\neq j.$$

It is clearly possible to obtain appropriate prescriptions along these lines for other symmetry groups, if required for physical applications.

III. BARRIER-LOWERING PERTURBATION THEORY

With procedures for the classification of symmetrized states in terms of a basis of pocket states in hand, it remains to formulate a method for the calculation of the ordering and splitting of states within the ground manifold in terms of perturbation theory. As indicated in Sec. II, the essential physical feature in this problem is that the barriers between minima in the cavity potential are of finite height. Were it not for this, all pocket states, and their symmetrized linear combinations, would be rigorously degenerate in energy. The problem of incorporating this feature into a perturbation calculation is somewhat delicate. One might expect that the energy calculation could be formulated in a way strictly analogous to the molecular-orbital calculation of bonding and antibonding energies in, e.g., the H_2^+ molecular ion.[19] Indeed, we shall reduce the general problem to one involving perturbations acting between single pairs of pocket states, so that one can cast the discussion in terms of a simple double minimum problem, that is, essentially the problem of the inversion doublet of ammonia.[16] To this extent, a parallel with the molecular problem exists, since, in that case, potential minima are present at the positions of the two nuclei. In the latter case, the splitting between bonding and antibonding levels is given by the so-called resonance integral $\langle\psi_1|H|\psi_2\rangle$, where H is the Hamiltonian and ψ_1 and ψ_2 are atomic wave functions centered on nucleus 1 and nucleus 2, respectively. In the molecular case, this integral is negative and in consequence the lower (bonding) combination of ψ_1 and ψ_2 is *symmetric*. In the case of overlapping harmonic-oscillator well potentials, however, the potential is everywhere positive, and the resonance integral is therefore also positive if the two wave functions are taken to be harmonic-oscillator ground-state functions. It follows that the lowest state is an antisymmetric combination of the latter functions. This contradicts the known situation in ammonia, for example, in which the lower state is the symmetric combination. Most simply stated, the difficulty is that a linear combination of two Coulomb potentials on different centers adds up to give a new potential which is not of Coulomb form, but a linear combination of two harmonic potentials with identical values of curvature parameter merely gives a new harmonic potential with lower curvature. Thus, the eigenstates which one computes by applying the molecular-orbital viewpoint to a potential which is the superposition of two harmonic-oscillator wells must be approximations to the exact eigenstates of merely a third, broader, well. By inspection, one sees that the symmetric combination of two harmonic-oscillator ground-state functions on different centers possesses three extrema and therefore must be an approximation to the second excited state of the combined potential. On the other hand, the antisymmetric combination has two extrema and is in approximation to the first excited state, hence lies lowest in energy. The situation is helped only quantitatively if the harmonic potentials are cut off at their point of contact; in any case, the ordering of states remains as indicated above. This result, of course, would not be incorrect if the potential barrier were correctly represented by a sum of harmonic-oscillator potentials, a situation indicated in Fig. 1 as the "unperturbed" case. In any real barrier problem, however, such a representation is probably unrealistic.

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[18] The group is C_{4v} if the distorting field is included.

[19] See, for example, C. A. Coulson, *Valence* (Oxford University Press, New York, 1961), 2nd ed.

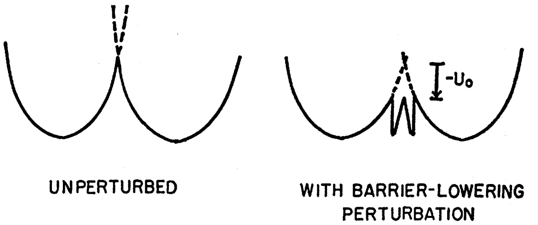

FIG. 1. Illustration of barrier-lowering perturbation.

In the case of ammonia, for example, one may easily fit parabolic forms to the double minima of the potential curve and find that the point of contact of the parabolas is at a potential of about 4000 cm^{-1} or twice the actual barrier height. Since the splitting of ground manifold states is very dependent on this height, application of the overlapping oscillator potential picture without modification to the case of ammonia would give a splitting which is too small by about 10^3, as well as an incorrect level ordering.

In light of these observations, we choose to consider the fundamental quantity responsible for the ordering of levels in a barrier problem, and for the magnitude of the splittings between them, to be the *energy of lowering of the barrier below what it would be on the simple overlapping harmonic-oscillator-well model.* We emphasize that we introduce this quantity simply as a device to permit a proper representation of the form of the potential within a theory founded on the use of harmonic-oscillator basis states. If the central barrier is lowered by a perturbation $-U_0$, it can easily be seen that the ordering of states in, e.g., ammonia, imposed by this perturbation is correct. In the remainder of this article we adhere to this point of view, and calculate ordering and splitting of states within the ground manifold by applying first-order perturbation theory to pocket states of harmonic-oscillator character, with the barrier-lowering energy as perturbation. We neglect the small splitting which would be present in the absence of the barrier-lowering perturbation.

We leave explicit application of the method sketched above to the following section, and continue this section with a discussion of the form to be taken for the perturbation $-U_0$. In order to reproduce the exact form of the potential barrier between two minima, this quantity would have to be taken as a rather complicated function of the variable (either r or Ω) in terms of which displacement from a potential minimum is measured. However, it is sufficient for our purposes to take the perturbation as merely a negative constant for the whole range of the displacement variable. It must be remembered that the perturbation correction to the energies of the symmetrized basis set enters in the form of integrals

$$\langle\psi_{+x}|U_0|\psi_{-x}\rangle, \text{ etc.}$$

These integrals are conveniently extended over all space in order to simplify integration over Gaussian factors, but contain significant contributions only from the region where the overlap of ψ_{+x} and ψ_{-x} is considerable, that is, near the barrier maximum. To be entirely consistent, we should also take into account diagonal matrix elements of $-U_0$; the result of such a calculation would of course be only an equal downward shift of all levels in the ground manifold with no splitting. Therefore, we ignore the diagonal elements of the perturbation. In light of the above remarks, we have by this technique in effect achieved the goal of inserting a perturbation only near the barrier maximum, which will produce splittings within the ground manifold. More elaborate specifications of the barrier perturbation can be introduced, should the experimental situation warrant such refinement in future. With the model and form of the perturbation so defined, we have in essence a two-parameter theory involving $-U_0$ and the curvature at the potential minima. The width of the barrier is a function of the curvature parameter and the distance d between potential minima, whereas the height of the barrier involves mainly $-U_0$. The form of the perturbed potential within our approximation of a constant $-U_0$ is sketched in Fig. 1. One further point needs to be noted. In general, we must expect the barrier perturbation to differ depending on whether the overlapping pocket states are neighboring, like ψ_{+x}, ψ_{+y} in O_h symmetry, or opposed, like ψ_{+x}, ψ_{-x} in O_h. Thus, in a case involving six minima in O_h symmetry, there will be two barrier-lowering parameters; with eight minima in O_h, there will be three, with six minima in D_{4h} there will be four, and with four minima in T_d, there will be one. Accordingly, to conclude this section, we set out the general formulas for splittings induced by the barrier-lowering perturbation in each of these cases.

For the case of O_h with sixfold minima along the $\langle 100\rangle$ axes, we represent the perturbation formally by terms $-M$ and $-E$. $-M$ lowers the potential at the cavity center and, therefore, provides an enhanced coupling between opposed states ψ_{+x} and ψ_{-x}, ψ_{+y} and ψ_{-y}, and ψ_{+z} and ψ_{-z}. $-E$ lowers the potential along the cavity [111] axes and provides an enhanced coupling between neighboring states, ψ_{+x} and ψ_{+y}, etc. In specific cases in the next section, we give numerical estimates for these perturbations. Let the matrix element of M between two opposed states be m and that of E between two neighbor states be e. Taking the diagonal elements of $-M$ and $-E$ with the properly symmetrized states for O_h symmetry given in Eqs. (3) and dropping all matrix elements diagonal in the pocket state basis as discussed above, we find immediately for the shifts in energy W under the perturbation:

$$\begin{aligned} W(A_{1g}) &= -m-4e, \\ W(E_g) &= 2e-m, \\ W(T_{1u}) &= +m. \end{aligned} \tag{10}$$

The sum $W(A_{1g})+2W(E_g)+3W(T_{1u})$ is 0, as must be the case. The nondegenerate state A_{1g} thus always lies lowest in energy, and the ordering of E_g and T_{1u} states depends on the details of the potential. There are two characteristic splitting parameters, $\Delta_1 = W(E_g) - W(A_{1g}) = 6e$, and $\Delta_2 = W(T_{1u}) - W(A_{1g}) = 2m+4e$. It must be remembered that large values of e or m mean *small* barriers.

A few comments on these results are relevant. If the central barrier is small compared to the barriers between neighbors ($m \gg e$), then the states A_{1g} and E_g remain essentially degenerate, and the lowest manifold consists of two triplets. This is the case of "tunneling" across the cavity center, which it seems appropriate to call the *translational* case. The opposite limit, which probably applies in the case of CN^- in KCl, we shall call the rotational case. Here, there is essentially no possibility for reorientation of the impurity species through the cavity center (which would imply an inversion of the species), and reorientation must proceed via neighboring minima. It follows that $m \ll e$, so that the T_{1u} levels lie between A_{1g} and E_g, and Δ_1 equals $(\frac{3}{2})\Delta_2$. This latter result should correspond to the asymptotic limit of the Devonshire theory in the limit of large barriers, but unfortunately accurate numerical estimates of the large barrier limit of the Devonshire result are not available.[20] It should be emphasized that our model only applies if the potential minima are deep enough to possess at least one bound state below all barrier crests, and cannot be expected to reproduce the low barrier splittings given to reasonable numerical accuracy in Devonshire's work. We note that the treatment given here, furnishes a natural criterion for *rotational* or *translational* motion of the impurity species, in the sense introduced above. If T_{1u} is above E_g, the motion is of the latter character; if it is below E_g, the motion is of the former character. Because it is possible for T_{1u} and E_g to cross, intermediate cases also are possible; and, as discussed in Sec. IV below, OH^- seems to be one of these.

For T_d symmetry, with minima at the corners of a tetrahedron, there is a single barrier perturbation $-E$ with matrix element $-e$ between each pair of pocket states; and the shifts in energy are:

$$\begin{aligned} W(A_1) &= -3e, \\ W(T_1) &= +m. \end{aligned} \tag{11}$$

The single splitting parameter equals $4e$. In the case of a one-dimensional double minimum problem (ammonia) with barrier perturbation $-M$ and matrix element $-m$, we have:

$$\begin{aligned} W(+) &= -m, \\ W(-) &= +m, \end{aligned} \tag{12}$$

where (+) and (−) are the symmetric and antisymmetric combinations of pocket states. The single splitting parameter equals $2m$.

In the case of D_{4h} symmetry (octahedral lattice with a sixfold minimum in the presence of a homogeneous electric or strain field), we have barrier perturbations $-M$ between opposed pockets along a twofold axis, $-M'$ between opposed pockets along the fourfold axis, $-E$ between neighboring particles in a plane perpendicular to the fourfold axis, and $-E'$ between neighboring particles in a plane containing the fourfold axis. The energies of the states are then

$$\begin{aligned} W(A_{1g}) &= -\tfrac{1}{3}(2m+m'+4e+8e'), \\ W(A_{1g}) &= -\tfrac{1}{6}(2m+4m'-4e-16e'), \\ W(B_{1g}) &= -m+2e, \\ W(E_u) &= m, \\ W(A_{2u}) &= m'. \end{aligned} \tag{13}$$

In the case of nearly pure rotation, m and m' are zero, and the spectrum of states falls into a 1-3-1-1 arrangement. In the case of no rotation, e and e' are zero; and the spectrum remains 1-1-1-2-1.

Finally, in the case of O_h symmetry with an eightfold potential minimum, we have perturbations $-M$ along the main cube diagonal, $-E$ along cube edges, and $-C$ along face diagonals. The energies are

$$\begin{aligned} W(A_{1g}) &= -m-3e-3c, \\ W(T_{2g}) &= -m+e+c, \\ W(T_{1u}) &= m-e+c, \\ W(A_{2u}) &= m+3e-3c. \end{aligned} \tag{14}$$

The six splitting parameters are easily read off this list and we do not list them here. The case of rotational motion is obtained if m and c are zero, yielding a 1-3-3-1 pattern of levels with equal intervals $2e$ between them. The parameter c is always likely to be small since very large potential barriers are to be expected at the face centers.

IV. APPLICATIONS

A. Ammonia Inversion

The ammonia system is the most evident one on which to test the model described in the preceding sections. From the inversion potential given in the literature,[21] we have fitted the potential minima to two identical harmonic-oscillator curves with $K = 1.0 \times 10^5$ dynes/cm. The intercept of these curves is at 3820 cm^{-1}. The actual barrier height is 2070 cm^{-1} so that the barrier lowering perturbation is $-M = -1750$ cm^{-1}. The reduced mass for NH_3 is obtained in the usual fashion, and the separation between the minima is taken as 0.76 Å. Inserting these numbers into first-order perturbation theory, we obtain a splitting of 0.5 cm^{-1}

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[20] In his original numerical calculations (Ref. 10), Devonshire predicted an actual crossing of levels, with E_g *lower* than T_{1u} for extremely high values of the barrier potential. On our analysis, this cannot be correct, and reflects numerical inaccuracies in the calculation. It is clear that a more refined calculation of the Devonshire type would be of great value in clarifying this point.

[21] Reference 16, p. 301.

TABLE I. Computed values of barrier-lowering perturbation and splitting parameter for range of K values, case of Li^+.

$K(10^{-4}$ dyne/cm)	$M(cm^{-1})$	$2m(cm^{-1})$
1.7	200	1.0
1.8	240	1.0
1.9	240	1.0
1.9	280	0.9
2.0	320	0.8
2.1	360	0.8
2.2	400	0.8

between the inversion levels, with the ordering correctly predicted. The experimental value is 0.8 cm^{-1}. Hence the application of our prescription in its most unrefined form gives a value for the splitting here which is semiquantitatively correct.

B. Li^+ in KCl

In this case, we labor under the handicap of having no very precise idea of the form of the potential function. However, it seems well established[13] that there are potential minima on the $\langle 100\rangle$ axes at a distance of 0.38 Å from the cavity center with a central barrier equal to 400 cm^{-1}. This immediately enables us to set bounds on the value to be taken for K, the force constant for the harmonic well. If $K \geqslant 2.6\times10^5$ dyn/cm, the energy of the ground state in the well is greater than the central-barrier height. Also, if $K \leqslant 1.1\times10^4$ dyn/cm², the potential at the intercept of the harmonic potential curves is less than the known central-barrier height.[13] By analogy to the case of ammonia, we expect the potential at the intercept of the two harmonic potential curves to be between 1.5 and 2 times greater than the actual barrier height. Thus, K should be such as to make the potential at contact 600–800 cm^{-1}, giving K between 1.7×10^4 dyn/cm and 2.2×10^4 dyn/cm. With K in this range, we find the results set out in Table I for the magnitude of the barrier-lowering perturbation M and the splitting parameter $2m$ as functions of K. In order to complete the determination of the ground manifold spectrum, it is necessary to assign also the parameter e, reflecting the barrier-lowering perturbation between neighboring minima, and here the results of Ref. 13 give no help. However, it is possible to make an order of magnitude estimate of the barrier between neighboring minima on the basis of an electrostatic calculation using a point charge model for the fields arising from Cl^- ions surrounding the cavity. We find in this way that this barrier is on the order of 10^4 cm^{-1}, and that the parameter e is therefore negligibly small. It follows that the levels A_{1g} and E_g remain very nearly degenerate, with the levels T_{1u} at an energy Δ_1 equal to $2m$ or about 1.0 cm^{-1} above them. This interpretation is in accord with the original suggestion[12] that the motion of Li^+ in KCl is best regarded as a translational tunneling. Experimentally, a phonon resonance at 1.2 cm^{-1} has been observed in this system,[12] and it seems reasonable to attribute it to transitions occurring between the (A_{1g}, E_g) set and the T_{1u} set of impurity motional states. It should be noted that the value of K of about 2×10^4 dyne/cm obtained for Li^+ in KCl indicates that Li^+ ion moves in a rather broad, shallow well with respect to radial displacement from the cavity center. The well is certainly much steeper with respect to angular displacement from the minimum, so that the actual contours of constant potential energy are ellipsoidal in shape.

With the above assignment of K, we find the pocket ground state to have an energy of 108 cm^{-1}. The energy of the first excited pocket state is 324 cm^{-1}, sufficiently close to the central barrier maximum to make application of our perturbation method to the first excited manifold for Li^+ in KCl of dubious value. Nevertheless, it is interesting to note that at least some of the states of this manifold will lie at energies below the top of the central barrier.

Some experimental information is available on the dielectric properties of Li^+-KCl[12]; from measurements of the electrocaloric effect, it has been inferred that the effective dipole moment, μ_{eff}, of the Li^+ impurity in its cavity is 2.54 D. It is of some interest therefore to discuss the significance of μ_{eff} in terms of the analysis given here. Consider an electric field $\mathbf{E}$ in the z direction applied to a Li^+ ion in KCl. None of the properly symmetrized motional states for the impurity possess a nonvanishing diagonal dipole moment matrix element; but in the presence of the field, off-diagonal coupling of the states occurs. This produces both an alteration in the pattern of impurity energy levels and a polarization of the ion cavity system.[22] The states $(T_{1u})_{x,y}$ and $E_{x^2-y^2}$ remain unshifted under the field perturbation, but $(T_{1u})_z$, E_{z^2} and A_{1g} mix. The matrix elements coupling them are

$$\begin{aligned} \mu_1 E &\equiv \langle \Phi(A_{1g}) | \boldsymbol{\mu}\cdot\mathbf{E} | \Phi(T_{1u})_z \rangle, \\ \mu_2 E &\equiv \langle \Phi(E_g)_{z^2} | \boldsymbol{\mu}\cdot\mathbf{E} | \Phi(T_{1u})_z \rangle. \end{aligned} \tag{15}$$

Accordingly, with the assumption that Δ_2 is zero, the new energy levels of the system are given by the roots of

$$\begin{vmatrix} 0-\lambda & 0 & +\mu_1 E \\ 0 & 0-\lambda & +\mu_2 E \\ +\mu_1 E & +\mu_2 E & \Delta-\lambda \end{vmatrix} = 0, \tag{16}$$

where $\Delta_1 \equiv \Delta$. Solving, we obtain

$$\begin{aligned} \lambda &= 0, \\ \lambda &= \Delta/2 \pm [\Delta^2/4 + E^2(\mu_1^2+\mu_2^2)]^{1/2}. \end{aligned} \tag{17}$$

Thus, four levels remain at the same energy as in the absence of a field; one is shifted to higher energy and one to lower. The result is a 1–2–2–1 pattern of levels with splittings $[\Delta^2/4+E^2(\mu_1^2+\mu_2^2)]^{1/2}-\Delta/2$, Δ, and $[\Delta^2/4+E^2(\mu_1^2+\mu_2^2)]^{1/2}-\Delta/2$, respectively. In the limit of high fields, when $E^2(\mu_1^2+\mu_2^2) \gg \Delta^2/4$, the level

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[22] We ignore actual electrostatic distortion of the cavity, although this must certainly be present to some extent.

arrangement is essentially the 1–4–1 predicted on the basis of the classical model in which the Li^+ ion is taken as localized in one of six pockets, with the degeneracy of two of the pockets removed by the field. In this limit, which applies in the experiments reported in Ref. 12, the splitting between the shifted levels and central quartet becomes $E(\mu_1^2+\mu_2^2)^{1/2}$. It is instructive to write out the matrix elements μ_1 and μ_2 in terms of integrals over the pocket state basis functions. We have:

$$\begin{aligned}\mu_1 &= (3)^{-1/2}b_1[\langle\psi_{xg}|\mu\cos\theta|\psi_{zu}\rangle \\ &\quad +\langle\psi_{yg}|\mu\cos\theta|\psi_{zu}\rangle+\langle\psi_{zg}|\mu\cos\theta|\psi_{zu}\rangle], \\ &\cong(3)^{-1/2}b_1\langle\psi_{zg}|\mu\cos\theta|\psi_{zu}\rangle, \\ &\cong a_+a_-b_1(12)^{-1/2}[\langle\psi_{+z}|\mu\cos\theta|\psi_{+z}\rangle \\ &\quad -\langle\psi_z|\mu\cos\theta|\psi_{-z}\rangle],\end{aligned} \tag{18}$$

where we have used Eqs. (1) and (3). In writing (18) in its approximate form, we have neglected contributions to the dipole moment matrix element from overlap terms of the form

$$\langle\psi_{+x}|\mu\cos\theta|\psi_{+z}\rangle,\quad \text{etc.},$$

and have retained only terms diagonal in the pocket state basis set. This is reasonable since the barrier between neighboring pocket states (ψ_{+x} and ψ_{+z}, etc.) is large and the amplitude of the pocket functions will be small near the barrier maximum, leading to very small values for the overlap terms. Now we introduce the assumption that $\cos\theta$ is $+1$ for a particle localized in the $+z$ pocket and -1 for a particle localized in the $-z$ pocket,[23] and let μ_g be the geometrical dipole moment for a configuration in which the particle is placed exactly at the minimum of a potential well. Using Eq. (18), we then have

$$\mu_1\cong a_+a_-b_1(\tfrac{1}{3})^{1/2}\mu_g. \tag{19a}$$

Carrying out the same procedure for μ_2, we obtain

$$\mu_2=a_+a_-b_3(\tfrac{2}{3})^{1/2}\mu_g=(b_3/b_1)(2)^{1/2}\mu_1. \tag{19b}$$

From our discussion above of the ground manifold splittings in the high-field limit, it is evident that the effective dipole moment measured in high-field experiments[12] is

$$\mu_{\text{eff}}=(\mu_1^2+\mu_2^2)^{1/2}. \tag{20}$$

Therefore, using Eqs. (19), we obtain at once

$$\mu_{\text{eff}}\cong\mu_g,$$

where we have neglected deviations from unity of the normalization factors. Thus, the high-field case corresponds to the classical limit with respect to both the form of the level spectrum and the magnitude of the measured dipole moment. The geometrical dipole moment, available from the results of Ref. 13, is 2.00 D, in reasonable agreement with the high-field effective dipole moment of Ref. 12.

As has been pointed out,[11] the level pattern of the ground-state manifold of an ion in a cavity with O_h symmetry and a sixfold minimum may permit an interesting departure from conventional dielectric behavior at low-field strengths. If the condition

$$\mu_2/\mu_1>2(\Delta_2/\Delta_1-1)^{1/2} \tag{21}$$

is satisfied, the dielectric constant will exhibit a maximum as a function of temperature, even in the absence of interactions between impurity ions. This condition is certainly not satisfied in Li^+ in KCl according to the above analysis, but it would nevertheless be of interest to measure the low-field, low-temperature dielectric constant of this system, in order to check the value of Δ_1.

Note added in proof. Recent sound-velocity measurements on Li^+ in KCl show conclusively that the potential minima for the Li^+ ion are on the [111] axes [N. E. Byer and H. S. Sack, Phys. Rev. Letters **17**, 72 (1966)]. Presumably the minima on the [100] axes originally proposed in Ref. 12 and discussed quantitatively in Ref. 13 are also present, but are shallower than the [111] minima; it is likely that they are in fact saddle points in the cavity potential. The appropriate level scheme for Li^+ in KCl is therefore that given in Eq. (14) above for the case of an eightfold minimum. Since the face diagonal of the cube whose corners are situated at the [111] minima passes through the [100] axis, on which the potential is known to be lower than at the cavity center, it is clear that the barrier-lowering term $-M$ (main cube diagonal) must be smaller than the term $-C$ (face diagonal). Hence the parameter m is smaller than c. Further, the distance along a cube edge between two neighboring minima is smaller than that along a face diagonal, and the edge potential barrier height would be expected to be lower than the face-diagonal potential barrier height, since overlap with neighboring Cl^- ions is smaller along an edge. It follows that $-C$ and c are small compared to $-E$ and e. On the basis of these remarks, it seems a reasonable approximation to set m and c equal to zero. The level sequence in the gound manifold of Li^+ in KCl then becomes A_{1g}, T_{1u}, T_{2g}, A_{2u} in order of increasing energy, with an energy splitting $2e$ between each adjacent pair in this sequence. The dipole-moment operator has symmetry-allowed matrix elements between the pairs (A_{1g},T_{1u}), (T_{1u},T_{2g}), and (T_{2g},A_{2u}). The phonon resonance energy, 1.2 cm^{-1}, is presumably equal to $2e$, rather than $2m$ as inferred in the body of this article. The analysis given above for barrier parameters for Li^+ in KCl could evidently be modified to apply to the eightfold minimum case, if a calculation on the order of Ref. 13 were available for the [111] positions. It is of interest to note that, on the revised picture, tunneling

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[23] We use the physical definition of dipole moment, in which the direction of the dipole is taken from negative charge to positive charge.

of the Li^+ ion through the cavity center is of minor importance; the ion can perhaps best be regarded as orbiting around the cavity center.

C. CN^- in KCl

The considerable body of spectroscopic data on this species[6] indicates that the lowest manifold consists of A_{1g}, T_{1u}, E_g as expected for O_h symmetry with a sixfold minimum. The ratio Δ_2/Δ_1, is found to be 1.7, in reasonable agreement with the result predicted here for a pure rotational case. Since a thorough application of the Devonshire theory to this species has been carried out,[6] with particular attention being given to the question of the barrier height, we omit a detailed treatment using our approach.

D. OH^- in KCl

The motion of OH^- in KCl is more complex. By analogy with CN^- in KCl, a ground manifold composed of $A_{1g}+T_{1u}+E_g$ would be anticipated, but the impurity is sufficiently small (radius about 1.5 Å) so that center-of-mass displacement within the cavity appears possible. Indeed, one must expect a cavity potential with a large number of minima as a function of center-of-mass position and angular orientation of the impurity. It has been suggested[24] that an important factor in this connection is the formation of hydrogen bonds between O and second-nearest neighbor Cl^- ions with the O atom off center in the cavity. However, it is well established that hydrogen bond formation demands a linear arrangement of O, H, and Cl;[25] and linearity in the present case would require that the O atom be at the cavity center. This model would then predict an eightfold minimum in the potential since there are eight second-nearest neighbor Cl^- ions. There is some experimental evidence bearing on this point. As we have seen above in the discussion of Li^+ in KCl, application of a large electric field to a dipolar impurity species in a crystal will bring the motional spectrum into the same form as would be predicted on the classical localized state model. High-field experiments on OH^- in KCl have been carried out; the optical,[3] dielectric,[4] and thermodynamic[4] properties of the system in large fields conform well to predictions made on the basis of the classical model with six equivalent minima along the [100] axes. This is strong evidence for the contention that the fundamental qualitative feature of the cavity potential is a sixfold minimum. Superposed upon this fundamental structure there will probably be smaller ripples in the potential with a large set of shallow minima and maxima; but it is improbable that the zero-point energy of the impurity in one of the main sixfold wells is so small that these minor variations are of critical importance for the motional spectrum. On this picture, absolute minima in the potential energy are achieved when the OH^- ion is aligned along a [100] axis, and it is further reasonable to surmise that the O atom will be somewhat off center to minimize the interaction of H with neighboring K^+ ions.

On the basis of these remarks, we interpret the pocket states for a case involving both center-of-mass motion and rotation of the impurity species about its own axis of inertia as follows: Specification of the position of an impurity within a pocket (e.g., choice of the argument of a pocket state wave function) means a specification of the position of the center of mass of the species. For each position of the center of mass (except perhaps when it is on a symmetry axis of the cavity) there will be a unique angular orientation of minimum energy of the impurity. Both the center of mass and the angular orientation of the impurity can, therefore, to an approximation, be regarded as specified by the single argument of the wave function. We further assume that as the impurity moves from one absolute minimum to another the only angular orientations which need to be considered are those which correspond to potential minima for the given position of the center of mass. In other words, we assume a saddle-point model for impurity motion, in which barrier penetration occurs via the position of minimum energy on the barrier and the angular orientation of the species is determined by the position of the center of mass. In the case of OH^- in KCl, the pocket states correspond to configurations in which the position of the center of mass of OH^- is off center and close to a [100] axis, and the orientation of the O-H bond is close to that of the axis.

If now the center of mass is moved far from the [100] axis, the angular orientation of lowest energy may alter radically. If the center of mass is off center on the [110] axis, for example, it seems unlikely that the orientation of the O-H bond is along this axis. Such an orientation would bring O close to a second-nearest neighbor Cl^-. The precise specification of the orientation of minimum energy for general position of the center of mass lies outside the scope of this work, and we merely remark that the problem of fundamental importance for the calculation of splittings in the ground manifold of OH^- in KCl, assuming the model described above, is that of the location and energy of the saddle points in the barriers between the sixfold absolute minima.

Some indirect evidence on the character of the motion of this species is available from low-field, low-temperature dielectric data.[2] A maximum in the dielectric constant of OH^- in KCl as a function of temperature has been found, and this feature may have its source in the nature of the splittings in the ground manifold of motional states.[11] Applying this notion, we have estimated values for Δ_1, Δ_2, μ_1, and μ_2 for OH^- in KCl in previous work[11] based on the data of Ref. 2; these quantities have the same significance here as in the case

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[24] R. O. Pohl (private communication).

[25] G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (W. H. Freeman and Company, San Francisco, 1960).

of Li^+ in KCl. In our discussion of the latter above, we found that $\mu_2/\mu_1=(2)^{1/2}$, within the approximation of neglect of overlap terms. However, analysis of the experimental data for OH^- in KCl indicated that this ratio was about 4 in that case.[11] Furthermore, the ratio Δ_2/Δ_1 for OH^- in KCl was found to be about 1.2 in Ref. 11, indicating that the motion of OH^- in KCl is of mainly rotational character, with some contribution from center of mass displacement. Therefore, the barrier-lowering perturbation $-E$ in our terminology is significant and we must expect the overlap of neighbor pocket state basis functions to be more important than in Li^+ in KCl. Retaining the overlap terms modifies Eqs. (19); introducing the notation μ_{10}, μ_{20} for dipole moment matrix elements obtained from the approximate form of Eqs. (19), we find

$$\mu_1=\mu_{10}+a_+a_-b_1(12)^{-1/2}(8\langle\psi_{+x}|\mu\cos\theta^+\psi_{+z}\rangle)), \quad (22a)$$

$$\mu_2=\mu_{20}-a_+a_-b_3(24)^{-1/2}(8\langle\psi_{+x}|\mu\cos\theta|\psi_{+z}\rangle)). \quad (22b)$$

The observed increase in the μ_2/μ_1 ratio over the no-overlap value of $(2)^{1/2}$ must, therefore, mean that the matrix element $\langle\psi_{+x}|\mu\cos\theta|\psi_{-z}\rangle$ is *negative* or that, in the region near the barrier maximum, the orientation of the net dipole moment has reversed relative to that obtaining at a potential minimum. Since the total dipole moment is the sum of a dipole moment from O to the cavity center and one from O to H, there are two distinct mechanisms by which this reorientation may be effected in principle. Either the OH may perform a "planetary" motion, with center of mass turning around the cavity center at a constant distance from it while the ion simultaneously rotates around its own principal axis, or the center of mass may be displaced past the cavity center. In the first case, the dipole from O to H is reversed while that from O to the cavity center merely rotates through a small angle; in the second case, the dipole from O to the cavity center is reversed while that from O to H rotates by a small amount. The actual motion is likely to be a combination of these two modes which means that it is to be regarded as a mixture of rotation governed by a barrier-lowering perturbation $-E$ and center-of-mass translation governed by a barrier-lowering perturbation $-M$. A rough numerical analysis can be given using Eqs. (4), taking a_+^2 to be of order unity, and T to be of order 0.1 to obtain the estimates $b_1=(1.4)^{-1/2}$, $b_3=(0.8)^{-1/2}$. Then, since $a_+a_-\cong1$, we have

$$(2)^{1/2}(b_1/b_3)\mu_2+\mu_1=\mu_{20}+\mu_{10}=(1+(2)^{1/2})\mu_{10},$$

or using the experimentally determined values of μ_1 and μ_2

$$\begin{aligned}\mu_{10}&=0.96\text{ Debye},\\ \mu_{20}&=1.36\text{ Debye}.\end{aligned} \quad (23)$$

From this, we easily find

$$\langle\psi_{+x}|\mu\cos\theta|\psi_{+z}\rangle=-0.40\text{ Debye}. \quad (24)$$

The geometrical dipole μ_g can be estimated using the relation previously derived for Li^+; this will, however, be a lower limit, since the considerable orientational freedom of OH^- in a pocket, will result in an average over the pocket somewhat less than the actual dipole moment for OH^- in its position of minimum energy. Accordingly,

$$\mu_g\geqslant(3^{1/2}/b_1)\mu_1=2.0\text{ Debye}.$$

Since the actual dipole moment of the OH^- ion is about 1.5 Debye[3], the remaining contribution to μ_g must arise from displacement of the ion from the cavity center. It follows that this displacement is at least 0.1 Å.

V. SUMMARY

We have presented a classification based on group-theoretical arguments for the lowest manifold of motional states of substitutional impurity species in crystal lattices with particular attention being given to ionic impurities in the KCl lattice. We have chosen as a basis set for this classification, nearly isolated "pocket states" which form a reducible representation for the symmetry groups of interest. This seems to be a natural and reasonable approach for systems in which barriers impeding impurity motion in a cavity are larger than the zero-point energy of any single pocket, i.e., in the high-barrier limit which appears to obtain in the cases considered. We have shown how a simple, reasonably accurate, perturbation scheme can be applied to calculate splittings between the states of the lowest manifold if sufficient information concerning the form of the potential in the cavity is available. The critical element in this discussion was the concept of "barrier-lowering perturbation," which seems new to this work and may have a wider application than has been attempted here. In the case of Li^+-KCl, it is possible to carry the analysis reasonably far; and the predicted features of the motional spectrum are in agreement with presently available experimental data. It would be of value to obtain low-temperature, low-field dielectric constant data for this system in order to obtain further information on lowest manifold splittings and dipole moment matrix elements. Of particular interest is the question of the ratio μ_2/μ_1, predicted to be $(2)^{1/2}$ on the assumption of neglect of overlap between neighboring pockets.

The case of OH^- is more complicated, but we have been able to establish certain qualitative features governing the motion of the ion. In particular, the motion in this case appears to combine both rotation and translation, as indicated by departure of the dipole moment matrix element ratio from the value $(2)^{1/2}$.

We have not attempted to consider the effects expected upon isotopic substitution, but this can easily be done within the framework of the barrier-lowering perturbation method. In general, increase in mass or

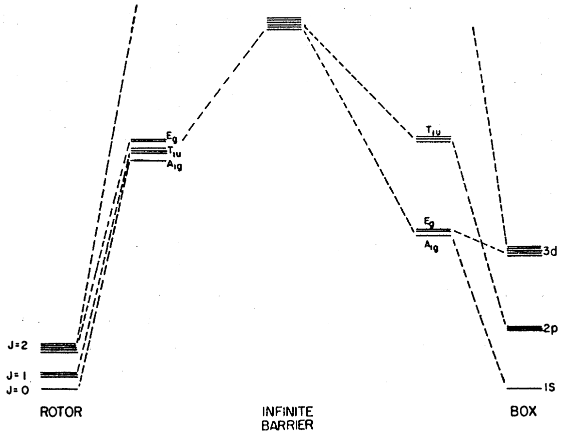

FIG. 2. Shift of motional states with barrier height.

moment of inertia will decrease the lowest manifold splittings.

We have restricted our discussions here entirely to the case of a rigid lattice, neglecting the perturbations caused by lattice motion on the manifold of impurity motional states. This precludes any discussion of phonon-induced transitions between motional states, but the classification of the latter given here should serve as a point of departure for consideration of the former. We have also neglected the possibility of static distortion of the neighborhood of the impurity due to its presence; this is intimately connected with the general question of phonon interactions. Although we have not considered distortion of the lattice in a strong electric field, lowering the lattice symmetry from O_h, say, to D_{4h}, it can easily be verified that all of our principal qualitative conclusions remain unchanged even if small effects of this sort are taken into account.

From a qualitative standpoint, it is of interest to relate the low-lying motional manifolds of impurity ions in cavities with a many-valley potential to the situation when no internal barriers at all are present. We show this schematically in Fig. 2, which indicates how the lowest states of (1) a rigid dumbbell rotor, and (2) a particle in a box shift when barriers between neighboring, and opposed pockets, respectively, are introduced. For infinite barriers, reduction to a degenerate sixfold level occurs, and intermediate barriers give level patterns as discussed above. Not shown on this figure is the pattern for a mixed rotational-translational case. The spacings in the level patterns have been chosen to correspond to a situation in which the moment of inertia I of the rotor is given by mR^2, where m is the mass of the particle in a box, and R is the radius of the (spherical) box; the ground states of rotor and box have been chosen to have the same energy. In this work, we have chosen the set of infinite-barrier states, in essence, as the fundamental basis set on which to construct an analysis. In the case of very small barriers, our approach is quantitatively inadequate, but it should be noted that qualitative features of the level pattern remain the same.

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