

Rotronic Jahn-Teller effect for diatomic molecular impurities at cubic sites in ionic crystals

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(Received 7 November 1983)

The theory of hindered rotation of diatomic molecular impurities at cubic sites in ionic crystals is generalized to account for the orbital degeneracy of the molecule, with use of a crystal-field approach. This theory explains the observed $\langle 110 \rangle$ orientations of the molecular axis, the orientations of the π orbitals along either $\langle 110 \rangle$ or $\langle 100 \rangle$ axes, and the dominance of 90° tunneling in some cases, even using only the lowest-order term in the octahedral crystal field ($l=4$). It is shown that the coupling of the degenerate orbital to the rotation in the crystal field generates an instability if the molecular axis is parallel to a $\langle 111 \rangle$ direction, leading to a Jahn-Teller effect resulting from rotational-electronic (rotronic) coupling. Analytic expressions for the lowest branch of the adiabatic potential energy as a function of the orientation of the molecular axis are calculated for Σ , Π , and Δ states, and the orbital wave functions are determined for Π -state molecules. The case of a diatomic molecular impurity at a site of tetrahedral symmetry is discussed.

I. INTRODUCTION

The hindered rotation of molecular impurities in crystals has been studied for many decades. A considerable amount of experimental information is available on several diatomic molecular impurities in ionic crystals (for a review see Ref. 1).

In a crystal, molecular impurities are not free to rotate, but are constrained by the interactions with the crystal to librate about one of a set of equivalent orientations which correspond to minima of a multiwell potential energy. The eigenstates (which have the symmetry of the site) are a linear combination of the librational states for these minima or, correspondingly, they are eigenstates of a hindered rotator. Reorientation generally occurs via thermally stimulated transitions between the librational states.

Many theoretical studies^{1,2} have been published since the pioneering works of Hund³ (who calculated oscillatory states in a one-dimensional double-well harmonic potential) and of Pauling⁴ (who investigated how the planar rotational states of a free molecule are modified by a periodic potential). Devonshire⁵ presented a more complete approach, extending Pauling's model to the three-dimensional case of a rotator hindered by a crystal potential of octahedral symmetry. This model considers only the terms in the potential with the lowest-order angular dependence (i.e., up to fourth-order spherical harmonics), and predicts two possible inequivalent equilibrium orientations for the molecular axis of a diatomic molecular impurity (depending on the sign of the fourth-order term), namely, along the $\langle 100 \rangle$ and $\langle 111 \rangle$ axes of the lattice. This model, which neglects any possible degeneracy of the molecular orbital, is quite useful in the interpretation of experimental data using molecular impurities in a nondegenerate orbital state (Σ state). Indeed, the observed equilibrium orientation of the molecular axis for these impurities is mostly parallel to a $\langle 100 \rangle$ direction of the crystal, such as for OH^- ,⁶⁻⁹ OD^- ,⁸ or CN^- (Refs. 8 and 10) in the alkali halides. In the case of SH^- in KCl , KBr ,

and KI ,¹¹ $\langle 111 \rangle$ orientations have been reported. However, Devonshire's model is unable to explain the $\langle 110 \rangle$ orientations of OH^- in KI and NaBr ,¹² and of CN^- in RbCl .¹³

Beyeler¹⁴ extended Devonshire's model by including the second-lowest-order nontrivial term in the potential energy, i.e., up to spherical harmonics with $l=6$, thus using two adjustable parameters. As will be discussed in Sec. III, this model still predicts $\langle 100 \rangle$ and $\langle 111 \rangle$ orientations in most cases, but $\langle 110 \rangle$ orientations may occur for a range of parameters. Thus this description seems to provide a consistent basis for the interpretation of the experimental data on Σ -state molecules. However, when the molecular impurity has a degenerate orbital state (a Π state in all cases experimentally studied) the results are strikingly different. Känzig¹⁵ first identified O_2^- molecules substituting at a halide site in alkali halides, and showed that the molecular axes were along the $\langle 110 \rangle$ directions of the lattice. This proved to be the case for the electronic ${}^2\Pi_g$ ground state of O_2^- ,¹⁵⁻¹⁹ S_2^- ,¹⁹⁻²³ Se_2^- ,^{24,25} SSe_2^- ,^{24,25} and N_2^- (Refs. 26 and 27) in the alkali halides. Molecular axis orientations along the $\langle 110 \rangle$ directions were also found for O_2^- in SrO .²⁸ No observation of any Π -state molecular impurity in the electronic ground state with an equilibrium orientation other than $\langle 110 \rangle$ has ever been reported.

In the ${}^2\Pi_u$ excited state, $\langle 110 \rangle$ orientations have been observed for O_2^- , S_2^- , and Se_2^- in the alkali halides.²⁹⁻³¹ Only a few cases of molecular axis orientations other than $\langle 110 \rangle$ for diatomic molecules in the excited ${}^2\Pi_u$ state are known, in particular $\langle 111 \rangle$ orientations for O_2^- in NaCl and KBr .²⁹ In the case of CsBr containing O_2^- ,³⁰ the equilibrium orientation is $\langle 100 \rangle$. In Beyeler's model, $\langle 110 \rangle$ orientations are due to rather large values of the sixth-order term with respect to the fourth-order term in spherical harmonics (see Sec. III). Since the higher-order terms in the potential are thought to be small, they appear to be an unlikely cause of the almost universal observation of $\langle 110 \rangle$ equilibrium orientations for the Π -state mole-

cules O_2^- , S_2^- , Se_2^- , SSe_2^- and N_2^- in the alkali halides and SrO.¹⁵⁻³¹ This strongly suggests that the coupling of the degenerate orbital to the crystal must also be considered, and this is the goal of our paper.

In addition to the equilibrium orientation, much is known about reorientation processes. The electron paramagnetic resonance (EPR) spectrum of O_2^- in alkali halides³² consists of six spectra corresponding to the six $\langle 110 \rangle$ axes. Application of uniaxial stress partially lifts the sixfold orientational degeneracy and the population changes are observed by monitoring the intensities of the EPR spectra. For a diatomic molecular impurity at a site of octahedral symmetry and oriented along a $\langle 110 \rangle$ axis, there are two possible reorientations between equivalent $\langle 110 \rangle$ orientations, 60° and 90° reorientations, which can proceed by phonon-assisted tunneling at low temperatures and over-the-barrier hopping at high temperatures. The relative tunneling matrix elements can be estimated by measuring the reorientation times τ_{60° and τ_{90° at low temperatures after removal of uniaxial stress. In the case of O_2^- in KCl,³¹⁻³⁴ and S_2^- in KCl, KBr, KI, RbI, and NaBr,^{21,35} it is found that $\tau_{60^\circ} \ll \tau_{90^\circ}$ indicating that the matrix element for 60° reorientation is larger than for 90° reorientation. However, experiment shows that $\tau_{60^\circ} \simeq \tau_{90^\circ}$ for O_2^- in KI,^{32,33,35,36} and $\tau_{90^\circ} \ll \tau_{60^\circ}$ in RbI: O_2^- .³⁷

Dominant 90° reorientation is not compatible with Beyeler's model, which predicts in all cases easier 60° reorientation, but can be understood when the degeneracy of the π orbital is taken into account.

In addition to molecular axis orientations and reorientation times, the orientation of the π orbital could be determined experimentally in a number of cases. The orbitals were found to be parallel either to a $\langle 110 \rangle$ (Refs. 17-20) or to a $\langle 100 \rangle$ (Refs. 17-20, 24, 25, and 38) direction, both directions being orthogonal to the $\langle 110 \rangle$ orientation of the molecular axis. This feature can also be understood within a theory which includes the orbital degeneracy of the Π state.

In this work, we propose a theory of the adiabatic potential energy for the hindered rotation of an orbitally degenerate diatomic molecular impurity in a static crystal field of cubic symmetry. The adiabatic potential energy is calculated from the crystal field as a function of the orientation of the molecular axis. The theory takes into account explicitly the orbital degeneracy of the molecule. For example, in the case of a Π state, the theory predicts that $\langle 110 \rangle$ equilibrium orientations occur readily, even when only the lowest-order nontrivial term in the crystal field is considered. There exists a coupling between the rotation in the crystal field and the degenerate orbital state. This coupling renders the $\langle 111 \rangle$ equilibrium orientations unstable against a tipping away from $\langle 111 \rangle$ towards $\langle 110 \rangle$, thereby lifting the degeneracy in a very similar way to vibronic coupling in usual Jahn-Teller systems. This rotational-electronic, or rotronic, coupling is responsible for the $\langle 110 \rangle$ orientations of the Π -state molecular impurities. [In a previous reference,⁴⁶ the effect has been named "rotonic" (rotational-electronic). However, because of a possible confusion with the word "roton" (elementary vortex ring in superfluid He), we renamed it "rotronic" (rotational-electronic)].

The outline of the paper is as follows. In Sec. II, the expression for the static crystal-field potential at a site of octahedral symmetry is obtained and used to calculate general expressions for the orientation-dependent adiabatic potential energy of a diatomic molecular impurity in terms of the quantum number Λ —the orbital angular momentum about the molecular axis. In Sec. III the theory is first applied to the case of a Σ state ($\Lambda=0$) and the results—which coincide with those of Devonshire⁵ and Beyeler¹⁴—are discussed. Then, we consider a Π -state ($\Lambda=1$) molecule and study in detail the predictions of the theory (adiabatic potential energy, orientation of the molecular axis, reorientation rates for 60° and 90° reorientations, and orientation of the π_g orbital). The section ends with a brief discussion of the predictions of the theory when applied to Δ -state ($\Lambda=2$) and to Φ -state ($\Lambda=3$) molecules. The application of the theory to other possible cubic symmetries is contained in Sec. IV and the results discussed for Σ - and Π -state molecules. In Sec. V we conclude with a comparison of the results obtained in Secs. II-IV to experiment. The main mathematical equations needed to obtain the adiabatic potential energy in the general case are given in the Appendix.

II. GENERAL THEORY

The usual approach^{5,14} to the study of hindered rotation of molecules in crystals is to treat the motion of the molecular impurity as that of a free rotator perturbed by the static crystalline surroundings. In crystal-field theory, the ions of the crystal are treated as sources of an electrostatic potential which acts on the electrons of the defect. Therefore, overlap effects such as covalent bonding are not included. However, since many predictions are simply a consequence of symmetry, the results predicted by crystal-field theory are more general than their physical basis. We will treat the hindering of the molecular rotation as if it were the result of such a static crystal field. In the absence of overlap and thus of covalency, the electrostatic potential obeys Laplace's equation in the region of the molecular impurity, hence it can be expanded in spherical harmonics. It is more convenient to replace the complex spherical harmonics by the real axial harmonics (sometimes referred to as "tesseral" or "zonal" harmonics) defined by³⁹

$$Z_{l0} = Y_{l0}, \quad (1a)$$

$$Z_{lm}^c = \frac{1}{\sqrt{2}} [(-1)^m Y_{lm} + Y_{l,-m}], \quad (1b)$$

and

$$Z_{lm}^s = \frac{-i}{\sqrt{2}} [(-1)^m Y_{lm} - Y_{l,-m}], \quad (1c)$$

where m goes from 1 to l . The superscript $c(s)$ indicates a φ dependence as $\cos(m\varphi)$ [$\sin(m\varphi)$]. The general form of the electrostatic potential in the region of the impurity can be written as

$$V(\vec{r}) = \sum_{l=0}^{\infty} r^l \left\{ B_{l0} Z_{l0}(\theta) + \sum_{m=1}^l [B_{lm}^c Z_{lm}^c(\theta, \varphi) + B_{lm}^s Z_{lm}^s(\theta, \varphi)] \right\}, \quad (2)$$

and each term of the sum is real. The B_{lm} are constants which depend on the positions of the ions in the crystal.

Since the static potential is required to be an invariant under all point-group operations of the molecular site considered, only invariant combinations of the Z_{lm} can be included in Eq. (2). This is equivalent to saying that, for fixed l , the Z_{lm} may be used as a basis for a reducible representation of the point group. If the representation contains Γ_1 (or Γ_1^+), then the corresponding combination of the Z_{lm} is an invariant term in V . For $l=0$, the term proportional to $Z_{00}=(4\pi)^{-1/2}$ is always present. This constant term produces a uniform shift of all levels, and therefore can be ignored.

For O and O_h point-group symmetry, the invariant terms up to $l=8$ are⁴⁰

$$V_4(\theta, \varphi) = \frac{1}{2\sqrt{3}} [\sqrt{7}Z_{40}(\theta) + \sqrt{5}Z_{44}^c(\theta, \varphi)], \quad (3)$$

$$V_6(\theta, \varphi) = \frac{1}{2\sqrt{2}} [Z_{60}(\theta) - \sqrt{7}Z_{64}^c(\theta, \varphi)], \quad (4)$$

and

$$V_8(\theta, \varphi) = \frac{1}{8\sqrt{3}} [3\sqrt{11}Z_{80}(\theta) + 2\sqrt{7}Z_{84}^c(\theta, \varphi) + \sqrt{65}Z_{88}^c(\theta, \varphi)]. \quad (5)$$

Now, the potential (2) for octahedral symmetry takes the general form

$$V(\vec{r}) = \sum_{l=4,6,8,\dots} B_l r^l V_l(\theta, \varphi). \quad (6)$$

We consider a diatomic molecular impurity in such a crystal field. The expectation value of the electrostatic potential integrated over the nonspherical charge distribution of the molecule gives a potential energy which depends upon the orientation of the molecular axis. Thus, in order to obtain the desired potential energies (which are adiabatic potential energies in the sense used for other descriptions of the Jahn-Teller effect), one must calculate matrix elements of the crystal-field potential within the degenerate orbital states and diagonalize the matrix. The difficulty lies in the fact that simple expressions for the crystal field are obtained in a coordinate system fixed in the lattice (the cubic axes in all of the cases considered here), but the wave functions of the orbitally degenerate state are relatively simple only in a coordinate system fixed in the molecule.

The main steps of this calculation are performed in the Appendix. Upon transforming from the coordinate system fixed in the crystal, in which the terms appearing in the crystal field are given by Eq. (6) in terms of the $V_l(\theta, \varphi)$ [see Eqs. (3)–(5)], to a coordinate system fixed in the molecule, it can be shown that the terms which may give nonzero matrix elements are those with $m=0$ and $m=2\Lambda$ [see Eq. (A6)],

$$V_{l0}(\theta_0, \varphi_0) Z_{l0}(\theta', \varphi') + V_{l,2\Lambda}^c(\theta_0, \varphi_0) Z_{l,2\Lambda}^c(\theta', \varphi') + V_{l,2\Lambda}^s(\theta_0, \varphi_0) Z_{l,2\Lambda}^s(\theta', \varphi'), \quad (7)$$

where θ', φ' are the spherical polar angles in the reference

frame fixed in the molecule, and θ_0, φ_0 specify the orientation of the molecular axis in the crystal. All other terms in V_l give matrix elements equal to 0 because of their dependence on φ' . Explicit expressions for V_{l0} , $V_{l,2\Lambda}^c$ and $V_{l,2\Lambda}^s$ are given in the Appendix for $l=4, 6$, and 8 , as functions of the rotation matrices [see Eqs. (A7)–(A9)]. As mentioned earlier, the quantum number Λ is the orbital angular momentum about the molecular axis. It is equal to 0 for a Σ state, 1 for a Π state, 2 for a Δ state, etc. For simplicity, and because it makes no difference in the form of the final expressions, we consider the degenerate state as arising from an electron in a single degenerate orbital. The wave functions for the degenerate orbital are denoted by $\psi_\Lambda^c(r, \theta', \varphi')$, proportional to $\cos(\Lambda\varphi')$ and $\psi_\Lambda^s(r, \theta', \varphi')$, proportional to $\sin(\Lambda\varphi')$. We need to calculate all matrix elements of the kind

$$\langle \psi_\Lambda^i | r^l Z_{lm}^j(\theta', \varphi') | \psi_\Lambda^k \rangle,$$

where the indices i, j, k stand for s or c . Since Z_{lm}^c and Z_{lm}^s depend on φ' as $\cos(m\varphi')$ and $\sin(m\varphi')$ respectively, it is straightforward to see that there are only two kinds of nonzero matrix elements, namely

$$\mathcal{J}_{l0} = \langle \psi_\Lambda^c | r^l Z_{l0} | \psi_\Lambda^c \rangle = \langle \psi_\Lambda^s | r^l Z_{l0} | \psi_\Lambda^s \rangle \quad (8)$$

and

$$\begin{aligned} \mathcal{J}_{l,2\Lambda} &= \langle \psi_\Lambda^c | r^l Z_{l,2\Lambda}^c | \psi_\Lambda^c \rangle = -\langle \psi_\Lambda^s | r^l Z_{l,2\Lambda}^c | \psi_\Lambda^s \rangle \\ &= \langle \psi_\Lambda^s | r^l Z_{l,2\Lambda}^s | \psi_\Lambda^s \rangle = \langle \psi_\Lambda^c | r^l Z_{l,2\Lambda}^s | \psi_\Lambda^c \rangle. \end{aligned} \quad (9)$$

Thus the matrix for the crystal-field potential takes the simple form

$$V = \begin{bmatrix} A+B & C \\ C & A-B \end{bmatrix}, \quad (10)$$

where the first row (column) corresponds to the index c . The eigenvalues of V give the adiabatic potential energies as functions of the orientation of the molecule with respect to the cubic axes of the crystal

$$E_\pm = A \pm (B^2 + C^2)^{1/2}, \quad (11)$$

with

$$A = \sum_{l=4,6,8,\dots} B_l \mathcal{J}_{l0} V_{l0}, \quad (12)$$

$$B = \sum_{l=4,6,8,\dots} B_l \mathcal{J}_{l,2\Lambda} V_{l,2\Lambda}^c, \quad (13)$$

and

$$C = \sum_{l=4,6,8,\dots} B_l \mathcal{J}_{l,2\Lambda} V_{l,2\Lambda}^s. \quad (14)$$

The quantity A [Eq. (12)] will also contain an additional term corresponding to the energy of the symmetric charge distribution from the core electrons (those other than the π orbital) and from the nuclei, which can be written as $\sum_l S_l V_{l0}$ with S_l proportional to B_l .

It is important to point out that the relevant parameters

in our calculations are not the B_l but the quantities

$$C_l = B_l \mathcal{F}_{10} + S_l \quad (15)$$

and

$$D_l = B_l \mathcal{F}_{l,2\Lambda} . \quad (16)$$

$$E_{\pm}(\theta_0, \varphi_0) = C_4 V_{40} + C_6 V_{60} + \cdots \pm \{ D_4^2 [(V_{4,2\Lambda}^c)^2 + (V_{4,2\Lambda}^s)^2] + 2D_4 D_6 (V_{4,2\Lambda}^c V_{6,2\Lambda}^c + V_{4,2\Lambda}^s V_{6,2\Lambda}^s) + D_6^2 [(V_{6,2\Lambda}^c)^2 + (V_{6,2\Lambda}^s)^2] + 2D_4 D_8 (V_{4,2\Lambda}^c V_{8,2\Lambda}^c + V_{4,2\Lambda}^s V_{8,2\Lambda}^s) + \cdots \}^{1/2} . \quad (17)$$

In order to determine the minima of the lowest sheet of the adiabatic potential energy $E_{-}(\theta_0, \varphi_0)$, one must first calculate all invariant combinations of the V_{lm}^i appearing in Eq. (17) as functions of θ_0 and φ_0 for the particular value of Λ considered. Since very complicated functions of θ_0 and φ_0 already result for $l=4$, it is convenient to define the direction cosines of the molecular axis relative to the cubic axes as follows:

$$l = \sin\theta_0 \cos\varphi_0 , \quad (18a)$$

$$m = \sin\theta_0 \sin\varphi_0 , \quad (18b)$$

$$n = \cos\theta_0 . \quad (18c)$$

The notations can be further simplified by realizing that all functions of θ_0 and φ_0 invariant in octahedral symmetry can be written as combinations of the two functions

$$f_4 = m^2 n^2 + n^2 l^2 + l^2 m^2 , \quad (19a)$$

$$f_6 = l^2 m^2 n^2 . \quad (19b)$$

Examples are given in Sec. III.

In addition to adiabatic potential energies—the eigenvalues E_{\pm} of the matrix for V , Eq. (11)—the eigenfunctions (which are the associated electronic functions) can easily be calculated as linear combinations of the basis functions ψ_{Λ}^c and ψ_{Λ}^s . If we denote with ψ_{Λ}^{\pm} the eigenfunctions corresponding to the eigenvalues E_{\pm} , simple considerations lead to

$$\psi_{\Lambda}^{+} = \psi_{\Lambda}^c \sin\alpha - \psi_{\Lambda}^s \cos\alpha , \quad (20)$$

and

$$\psi_{\Lambda}^{-} = \psi_{\Lambda}^c \cos\alpha + \psi_{\Lambda}^s \sin\alpha , \quad (21)$$

where the angle α can be shown to be

$$\tan\alpha = -\frac{B + (B^2 + C^2)^{1/2}}{C} = \frac{C}{B - (B^2 + C^2)^{1/2}} . \quad (22)$$

B and C are given by Eqs. (13) and (14). Examples will be discussed in the next section.

III. APPLICATIONS OF THE THEORY

A. Nondegenerate orbital state

The theory developed in the previous section can easily be applied to the case of a Σ state ($\Lambda=0$). The matrix for

It can be shown that, although the parameters B_l do not form a rapidly decreasing sequence, the parameters C_l and D_l defined above do rapidly decrease as l increases as long as the spatial extension of the molecular-charge distribution is smaller than the nearest-neighbor distance. This justifies the truncation of the crystal-field potential [Eq. (6)] to its first few terms. The final form of the adiabatic potential energy is now, up to sixth order,

the crystal-field potential [Eq. (10)] reduces to a 1×1 matrix, the D_l are equal to 0 and the adiabatic potential energy is now given by [see Eq. (17)]

$$E(\theta_0, \varphi_0) = \sum_{l=4,6,8,\dots} C_l V_{l0}(\theta_0, \varphi_0) , \quad (23)$$

where the V_{l0} are given in Eqs. (A7)–(A9) for $l=4, 6$, and 8. With the use of the definitions of the rotation matrices (see the Appendix), one obtains

$$V_{40} = \frac{\sqrt{7}}{2\sqrt{3}} (1 - 5f_4) , \quad (24a)$$

$$V_{60} = \frac{1}{4\sqrt{2}} (2 - 21f_4 + 231f_6) , \quad (24b)$$

$$V_{80} = \frac{\sqrt{33}}{2^{14}} (1 - 18f_4 - 52f_6 + 65f_4^2) , \quad (24c)$$

where the V_{l0} are given in Eqs. (A7)–(A9) for $l=4, 6$, and 8. With the use of the definitions of the rotation matrices (see the Appendix), one obtains

$$E(\theta_0, \varphi_0) = \frac{\sqrt{7}}{2\sqrt{3}} C_4 (1 - 5f_4) + \frac{1}{4\sqrt{2}} C_6 (2 - 21f_4 + 231f_6) + \cdots . \quad (25)$$

It should be noted that this expression can be obtained directly from Eqs. (3)–(6). For $\Lambda=0$, it is indeed not necessary to rotate the potential V [Eq. (6)] and perform the integration since the resultant potential energy of the molecule, E (not just the crystal-field potential V), can be written as a series of invariant terms in $Z_{lm}(\theta_0, \varphi_0)$. The Devonshire model⁵ is obtained by neglecting all terms except for the first term in Eq. (25),

$$E = \frac{\sqrt{7}}{2\sqrt{3}} C_4 (1 - 5f_4) . \quad (26)$$

As mentioned in Sec. I, this function admits only two kinds of minima: along the $\langle 111 \rangle$ directions for $C_4 > 0$ [with $E = -(\sqrt{7}/3\sqrt{3})C_4$] and along the $\langle 100 \rangle$ directions for $C_4 < 0$ [with $E = (\sqrt{7}/2\sqrt{3})C_4$]. The $\langle 110 \rangle$ orientations correspond in all cases to saddle points. Beyeler¹⁴ considered both C_4 and C_6 in Eq. (25) and discussed the influence of the third term ($l=8$). The stationary points of such a potential energy were first studied in 1963 in conjunction with rare-earth ions.⁴¹ It is easy to

show that only three kinds of minima can occur, corresponding to orientations of the molecular axis along the $\langle 100 \rangle$, $\langle 110 \rangle$, or $\langle 111 \rangle$ directions. The stationary points corresponding to $\langle ll_n \rangle$ orientations are, in all cases, saddle points. A detailed study of the various minima of the adiabatic potential energy, Eq. (25), as a function of C_4 and C_6 , is contained in Fig. 1 and Table I. As shown in Fig. 1, $\langle 110 \rangle$ absolute minima can occur for a range of parameters. However, this requires a sufficiently large positive value of C_6 . In fact, since $\langle 100 \rangle$ minima are observed much more often than $\langle 111 \rangle$ minima for molecular-orbital singlets and hence C_4 is usually negative, it would appear necessary to have C_6 larger than $|C_4|$ if $\langle 110 \rangle$ minima were to occur because of the sixth-order term in the potential. But, since the values of the C_l should decrease with l , this does not seem to be a plausible explanation for the almost universal observation of $\langle 110 \rangle$ minima for orbitally degenerate ions. Furthermore, as has been mentioned in Sec. I, there exist two inequivalent types of reorientation between equivalent $\langle 110 \rangle$ orientations, corresponding to a reorientation of 90° (e.g., $[110] \rightarrow [1\bar{1}0]$) and of 60° (e.g., $[110] \rightarrow [101]$). The 60° reorientation dominates over virtually all the range of parameters for which $\langle 110 \rangle$ absolute minima occur. In region (3) of Fig. 1, the reorientation occurs via the subsidiary minima along $\langle 111 \rangle$. In regions (1) and (2), the reorientation occurs via the saddle point corresponding to $\langle ll_n \rangle$ orientations in the $\{110\}$ planes, and these planes link minima that are 60° apart much more effectively than

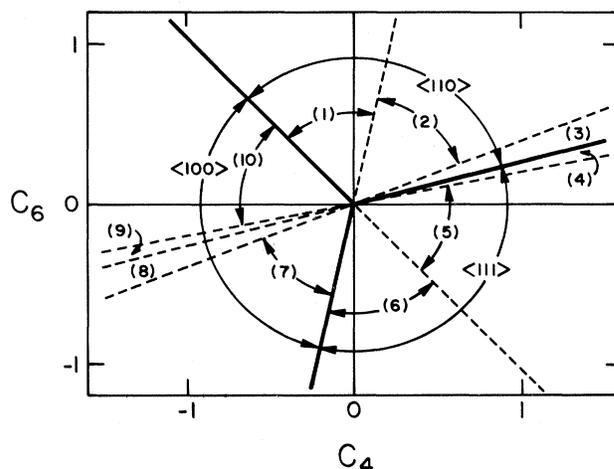


FIG. 1. Equilibrium orientations for a diatomic molecule having a nondegenerate orbital state in a crystal field of cubic symmetry as a function of the fourth- and sixth-order terms in the potential energy [Eq. (25)]. The boundaries of the regions are given in Table I. The solid lines separate the regions where $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ orientations correspond to absolute minima of the potential energy.

those that are 90° apart, until very near the boundary of region (1) with region (10), where C_6 is comparable to $|C_4|$ and C_4 is negative. Only in this limited region could 90° reorientation be comparable to 60° reorientation.

TABLE I. Types of stationary points and their corresponding molecular axis orientations for an orbital singlet in an octahedral crystal field of fourth and sixth order [Eq. (25)]. The regions are shown in Fig. 1. abs. max. (min.) stands for absolute maximum (minimum), max. (min.) for maximum (minimum), and SP for saddle point.

Region (see Fig. 1)	Stationary points			
	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$	$\langle ll_n \rangle$
(1) $\frac{1}{5} \frac{\sqrt{7}}{\sqrt{6}} \frac{C_4}{C_6} > -\frac{9}{10} \frac{\sqrt{7}}{\sqrt{6}}$, $C_6 > 0$	max.	abs. min.	abs. max.	SP
(2) $\frac{12}{5} \frac{\sqrt{7}}{\sqrt{6}} > \frac{C_4}{C_6} > \frac{1}{5} \frac{\sqrt{7}}{\sqrt{6}}$, $C_6 > 0$	abs. max.	abs. min.	max.	SP
(3) $\frac{7}{2} \frac{\sqrt{7}}{\sqrt{6}} > \frac{C_4}{C_6} > \frac{12}{5} \frac{\sqrt{7}}{\sqrt{6}}$, $C_6 > 0$	abs. max.	abs. min.	min.	SP
(4) $\frac{81}{20} \frac{\sqrt{7}}{\sqrt{6}} > \frac{C_4}{C_6} > \frac{7}{2} \frac{\sqrt{7}}{\sqrt{6}}$, $C_6 > 0$	abs. max.	min.	abs. min.	SP
(5) $\frac{20}{81} \frac{\sqrt{6}}{\sqrt{7}} > \frac{C_6}{C_4} > -\frac{10}{9} \frac{\sqrt{6}}{\sqrt{7}}$, $C_4 > 0$	abs. max.	SP	abs. min.	
(6) $\frac{1}{5} \frac{\sqrt{7}}{\sqrt{6}} > \frac{C_4}{ C_6 } > -\frac{9}{10} \frac{\sqrt{7}}{\sqrt{6}}$, $C_6 < 0$	min.	abs. max.	abs. min.	SP
(7) $\frac{12}{5} \frac{\sqrt{7}}{\sqrt{6}} > \frac{C_4}{ C_6 } > \frac{1}{5} \frac{\sqrt{7}}{\sqrt{6}}$, $C_6 < 0$	abs. min.	abs. max.	min.	SP
(8) $\frac{7}{2} \frac{\sqrt{7}}{\sqrt{6}} > \frac{C_4}{ C_6 } > \frac{12}{5} \frac{\sqrt{7}}{\sqrt{6}}$, $C_6 < 0$	abs. min.	abs. max.	max.	SP
(9) $\frac{81}{20} \frac{\sqrt{7}}{\sqrt{6}} > \frac{C_4}{ C_6 } > \frac{7}{2} \frac{\sqrt{7}}{\sqrt{6}}$, $C_6 < 0$	abs. min.	max.	abs. max.	SP
(10) $\frac{20}{81} \frac{\sqrt{6}}{\sqrt{7}} > \frac{C_6}{ C_4 } > -\frac{10}{9} \frac{\sqrt{6}}{\sqrt{7}}$, $C_4 < 0$	abs. min.	SP	abs. max.	

B. $\Lambda=1$: Π state

All orbitally-degenerate diatomic molecular impurities studied experimentally in octahedral sites in cubic crystals (O_2^- , S_2^- , Se_2^- , SSe^- , and N_2^-) have a ground state with $\Lambda=1$, i.e., a Π state. The invariant terms in Eq. (17) now include V_{40} , V_{60} , V_{80} [defined in Eq. (24)], as well as terms within the square root. It is possible to show that the invariant terms within the square root, up to twelfth order (i.e., up to sixth order after taking the square root) are

$$(V_{42}^c)^2 + (V_{42}^s)^2 = \frac{35}{3}(-3f_6 + f_4^2), \quad (27)$$

$$V_{42}^c V_{62}^c + V_{42}^s V_{62}^s = \frac{35}{8}(14f_6 - f_4^2 - 33f_4 f_6), \quad (28)$$

$$(V_{62}^c)^2 + (V_{62}^s)^2 = \frac{105}{64}(96f_6 + f_4^2 - 418f_4 f_6 + 1089f_6^2), \quad (29)$$

$$V_{42}^c V_{82}^c + V_{42}^s V_{82}^s = \frac{35\sqrt{11}}{6\sqrt{2}}(-9f_6 + 3f_4^2 + 39f_4 f_6 - 13f_4^3). \quad (30)$$

Substituting these results into Eq. (17) yields an expression for the adiabatic potential energy which is valid up to fourth, fifth, or sixth order.

1. Lowest-order terms

If one neglects all but fourth-order terms, the adiabatic potential energy is

$$E_{\pm}(\theta_0, \varphi_0) = \frac{\sqrt{7}}{2\sqrt{3}} C_4 (1 - 5f_4) \pm \frac{\sqrt{35}}{\sqrt{3}} |D_4| (-3f_6 + f_4^2)^{1/2}. \quad (31)$$

The constant $|D_4|$ results from the crystal-field matrix elements of the Π state. For a singlet, D_4 is 0. The orientations of the molecular axis corresponding to minima of

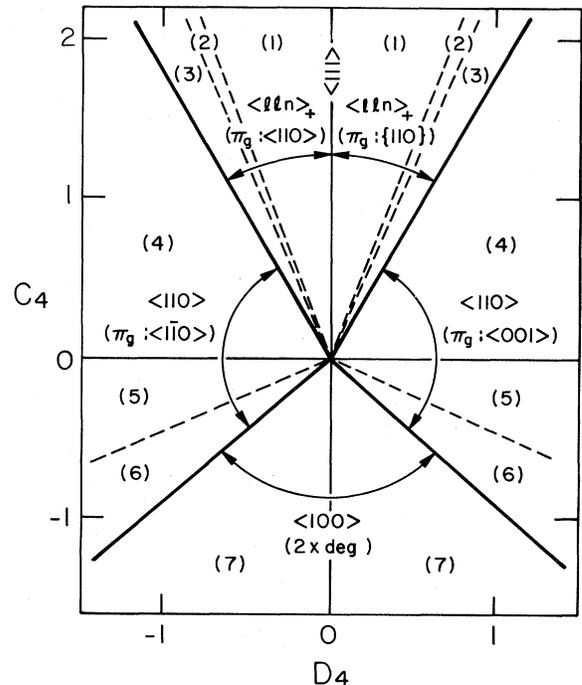


FIG. 2. Equilibrium orientations for a diatomic molecule in a Π state if only the lowest-order nontrivial term (fourth order) in the octahedral field is considered [Eq. (31)]. $\langle 111 \rangle$ minima occur only if $C_4 > 0$ and $D_4 = 0$. The boundaries of the regions and the various kinds of stationary points are discussed in Table II. The orientation of the π_g orbital is given in each region (see Sec. III B 3).

the lowest branch of the adiabatic potential energy, E_- , are shown in Fig. 2, and described in detail in Table II. In regard to only absolute minima, the situation can be summarized as follows.

If $C_4 \leq -(2/\sqrt{5})|D_4|$ the minimum of E is given by

TABLE II. Types of stationary points and their corresponding molecular axis orientations for an orbital Π state in an octahedral crystal field of fourth order [see Eq. (31)]. The regions are shown in Fig. 2. The abbreviations are the same as those used in Table I. In regions (1)–(3), the superscripts indicate the order in energy of the various stationary points.

Region (see Fig. 2)		$\langle 100 \rangle$	$\langle 110 \rangle$	Stationary points		$\langle ll n \rangle_+$	$\langle ll n \rangle_-$
				$\langle 111 \rangle$			
(1)	$\frac{ D_4 }{C_4} < \frac{\sqrt{5}}{6}$, $C_4 > 0$	abs. max. ⁵	SP ⁴	max. ³		abs. min. ¹	SP ²
(2)	$\frac{\sqrt{5}}{6} < \frac{ D_4 }{C_4} < \frac{\sqrt{5}}{4}(\sqrt{3}-1)$, $C_4 > 0$	abs. max. ⁵	SP ³	max. ⁴		abs. min. ¹	SP ²
(3)	$\frac{\sqrt{5}}{4}(\sqrt{3}-1) < \frac{ D_4 }{C_4} < \frac{\sqrt{5}}{4}$, $C_4 > 0$	abs. max. ⁵	SP ²	max. ⁴		abs. min. ¹	SP ³
(4)	$\frac{ D_4 }{C_4} > \frac{\sqrt{5}}{4}$, $C_4 > 0$	abs. max.	abs. min.	max.			SP
(5)	$\frac{ D_4 }{C_4} > \sqrt{5}$, $C_4 < 0$	max.	abs. min.	abs. max.			SP
(6)	$\frac{\sqrt{5}}{2} < \frac{ D_4 }{C_4} < \sqrt{5}$, $C_4 < 0$	SP	abs. min.	abs. max.			
(7)	$\frac{ D_4 }{C_4} < \frac{\sqrt{5}}{2}$, $C_4 < 0$	abs. min.	SP	abs. max.			

$$E_+ = E_- = E_{\langle 100 \rangle} = \frac{\sqrt{7}}{2\sqrt{3}} C_4, \quad (32)$$

which corresponds to $\langle 100 \rangle$ orientations, and the energy is still doubly degenerate. In real systems, however, this degeneracy would be removed by the vibronic Jahn-Teller effect, which has not been included in our treatment.

If

$$-\frac{2}{\sqrt{5}} |D_4| \leq C_4 \leq \frac{4}{\sqrt{5}} |D_4|,$$

$\langle 110 \rangle$ directions correspond to equilibrium orientations for the molecular axis. The degeneracy is lifted and

$$E_- = E_{\langle 110 \rangle} = -\frac{\sqrt{7}}{8\sqrt{3}} C_4 - \frac{\sqrt{35}}{4\sqrt{3}} |D_4|. \quad (33)$$

For $C_4 \geq (4/\sqrt{5}) |D_4|$, the lowest branch of the adiabatic potential energy corresponds to orientations of the molecular axis which vary continuously from $\langle 111 \rangle$ towards $\langle 110 \rangle$ as $|D_4|/C_4$ varies. For $D_4=0$, the energy is degenerate and

$$E_+ = E_- = E_{\langle 111 \rangle} = -\frac{\sqrt{7}}{3\sqrt{3}} C_4. \quad (34)$$

As $|D_4|$ increases, $\langle 111 \rangle$ orientations become maxima of E_- , the degeneracy is lifted, the molecular axis is tilted away from $\langle 111 \rangle$ orientations towards $\langle 110 \rangle$ in a $\{110\}$ plane, and the minimum of the adiabatic potential energy is given by [for $|D_4| < (\sqrt{5}/4)C_4$]

$$E_- = E_{\langle ll n \rangle_+} = -\frac{\sqrt{7}}{3\sqrt{3}} C_4 - \frac{\sqrt{35}}{6\sqrt{3}} \frac{D_4^2}{\sqrt{5}C_4 - 2|D_4|}. \quad (35)$$

The corresponding orientation of the molecular axis is now denoted by $\langle ll n \rangle_+$ (see Table II), where

$$l^2 = \frac{1}{3} \left[1 + \frac{|D_4|}{\sqrt{5}C_4 - 2|D_4|} \right], \quad (36a)$$

and

$$n^2 = \frac{1}{3} \left[1 - \frac{2|D_4|}{\sqrt{5}C_4 - 2|D_4|} \right]. \quad (36b)$$

Another similar stationary point, denoted by $\langle ll n \rangle_-$ in Table II, occurs in the regions (1)–(5) in Fig. 2. The corresponding orientations are given by Eqs. (36) with the opposite first sign inside the parentheses. It is, however, always a saddle point and corresponds to a tilting away from $\langle 111 \rangle$ towards $\langle 100 \rangle$. Clearly, if the coupling to the Π state is comparable to or larger than the coupling to the average molecular-charge distribution, $\langle 110 \rangle$ minima result even from the lowest-order terms in the potential (fourth order). The tilting from $\langle 111 \rangle$ towards $\langle 110 \rangle$ is illustrated in Fig. 3, which shows constant potential-energy contours for one octant of the sphere projected on the $\{111\}$ plane normal to the $\langle 111 \rangle$ axis through this octant. The values of C_4 and D_4 correspond to region (1) in Fig. 2.

As discussed in the previous sections, $\langle 110 \rangle$ minima for a Σ -state molecule could arise only from sixth- (or higher-) order terms in the potential. In addition, 90° reorientation between equivalent $\langle 110 \rangle$ orientations is

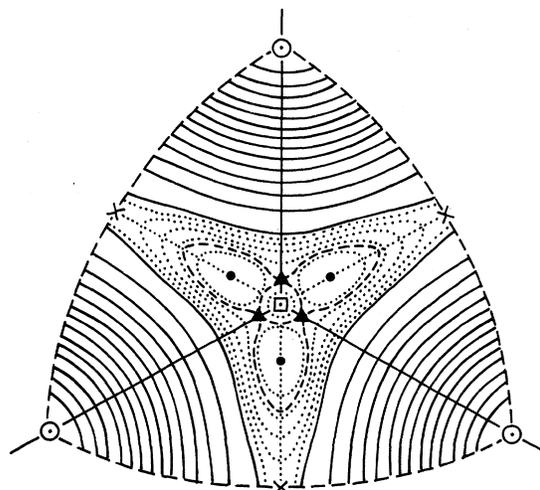


FIG. 3. Constant potential-energy contours for a Π state in the cubic field given by Eq. (31) with $|D_4|/C_4 = \frac{7}{20}$ [region (1) in Fig. 2]. Three absolute minima (full circles) correspond to the $\langle ll n \rangle_+$ orientations [see Eq. (35)], three saddle points (crosses) to the $\langle 110 \rangle$ orientations, three absolute maxima (circles) to the $\langle 100 \rangle$ orientations, and the local maximum (square) is the $\langle 111 \rangle$ orientation. The three triangles show the $\langle ll n \rangle_-$ orientations (see Table II) and correspond to saddle points. The energy difference between two solid lines is given by $(E_{\langle 100 \rangle} - E_{\langle ll n \rangle_+})/15$, and between two dotted lines is by $(E_{\langle 100 \rangle} - E_{\langle ll n \rangle_+})/90$.

comparable to 60° reorientation only in a very small region of the parameter plane, where C_6 needs to be negative and comparable to $|C_4|$.

The case of Π states is different: $\langle 110 \rangle$ minima readily occur, already when only fourth-order terms in the crystal field are included. In addition, 90° reorientation is comparable to or greater than 60° reorientation for

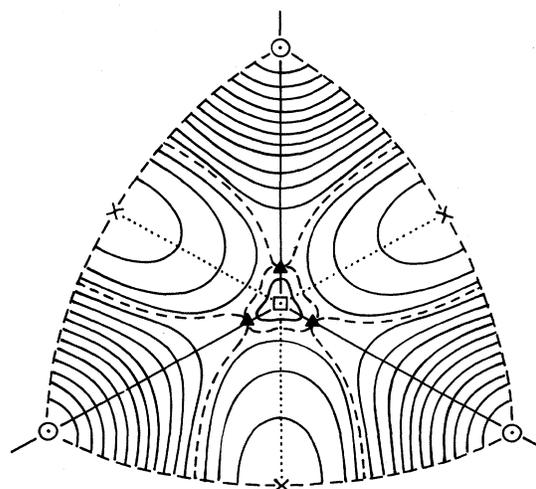


FIG. 4. Constant potential-energy contours for a Π state in the cubic field given by Eq. (31) with $|D_4|/C_4 = 1$ [region (4) in Fig. 2]. Reorientation by 60° dominates via the saddle points (triangles) corresponding to the $\langle ll n \rangle$ orientations (see the text) over 90° reorientation. The energy difference between two solid lines is given by $(E_{\langle 100 \rangle} - E_{\langle 110 \rangle})/15$.

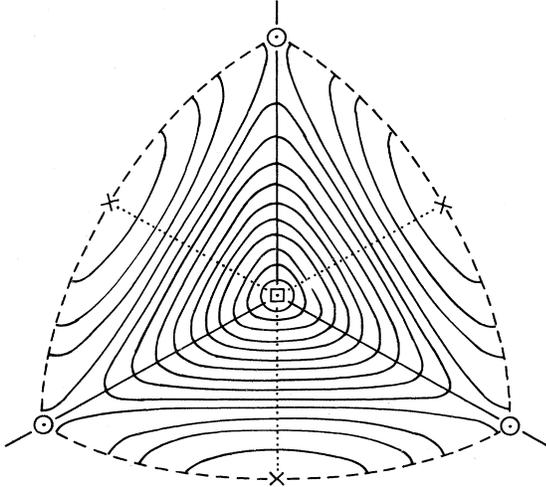


FIG. 5. Constant potential-energy contours for a Π state in the cubic field given by Eq. (31) with $|D_4|/C_4 = -\frac{5}{3}$ [region (6) in Fig. 2]. Reorientation between two $\langle 110 \rangle$ orientations (crosses) occurs via the saddle points corresponding to the $\langle 100 \rangle$ orientations (circles), whether it is for 60° or 90° reorientation. The energy difference between two solid lines is given by $(E_{\langle 111 \rangle} - E_{\langle 110 \rangle})/15$.

$-\sqrt{5} \leq |D_4|/C_4 \leq -\sqrt{5}/2$ and near but less than the value of $-\sqrt{5}$ [region (6) in Fig. 2]. Examples are shown in Figs. 4 and 5. Figure 4 corresponds to $|D_4|/C_4 = 1$, a value such that 60° reorientation dominates. In Fig. 5 on the other hand, $|D_4|/C_4$ is equal to $-\frac{5}{3}$, and 90° reorientation dominates.

As mentioned in Sec. I, there is experimental evidence for 90° reorientation times shorter than 60° for molecular Π states [$\text{RbI}:\text{O}_2^-$ (Ref. 37)].

2. Contribution of higher-order terms

The inclusion of higher-order terms in Eq. (31) adds considerable complexity. Explicit expressions for the energy can be written with the use of Eqs. (17) and (27)–(30), and a few qualitative conclusions can still be extracted. In particular, it can be shown that the effect of sixth-order terms is to change the region of the (C_4, D_4) plane in which $\langle 110 \rangle$ absolute minima occur. However, the terms proportional to C_6 and D_6 contribute with opposite signs in the inequality determining the boundaries of this region. Thus, as long as the sixth-order terms are relatively small, their inclusion does not significantly modify the earlier results.

3. Wave functions

If only the fourth-order term in the potential is considered, the expression determining the electronic eigenfunctions [Eq. (22)] is

$$\begin{aligned} \tan \alpha &= -\frac{V_{42}^c + (D_4/|D_4|)[(V_{42}^c)^2 + (V_{42}^s)^2]^{1/2}}{V_{42}^s} \\ &= \frac{V_{42}^s}{V_{42}^c - (D_4/|D_4|)[(V_{42}^c)^2 + (V_{42}^s)^2]^{1/2}}. \end{aligned} \quad (37)$$

Since the minima all lie in $\{110\}$ planes, we are only interested in Eq. (37) for direction cosines $l = m \neq n$. Evaluating V_{42}^s and V_{42}^c in these planes yields

$$\begin{aligned} V_{42}^s &= 0, \\ V_{42}^c &= \frac{\sqrt{35}}{\sqrt{3}} l^2 (n^2 - l^2), \end{aligned} \quad (38)$$

so that Eq. (37) becomes

$$\begin{aligned} \tan \alpha &= \frac{\sqrt{35}}{\sqrt{3}} [-l^2(n^2 - l^2) - (D_4/|D_4|)l^2|n^2 - l^2|] / 0 \\ &= \frac{\sqrt{3}}{\sqrt{35}} 0 / [l^2(n^2 - l^2) - (D_4/|D_4|)l^2|n^2 - l^2|]. \end{aligned} \quad (39)$$

Thus, $\tan \alpha$ is either 0 or ∞ depending on the signs of D_4 and $n^2 - l^2$.

For a $\langle 100 \rangle$ minimum, the double degeneracy remains and this is manifest in Eq. (39) by an indeterminate expression, $0/0$, for $\tan \alpha$. For either $\langle 110 \rangle$ minima or those tilted in a $\{110\}$ plane, $n^2 - l^2$ is negative. Thus, for D_4 positive (negative), the value of $\tan \alpha$ is 0 (∞). Hence we can write $\psi_1^- = \psi_1^c$ if $D_4 > 0$, and $\psi_1^- = \psi_1^s$ if $D_4 < 0$ [see Eq. (21)].

Because of the notation used to obtain the crystal field in the molecular reference frame, ψ_1^s is a π orbital oriented along the $\langle 110 \rangle$ axis perpendicular to the $\{110\}$ plane containing the minimum. Consequently, ψ_1^c is a π orbital in the $\{110\}$ plane. Thus if $D_4 > 0$, the π orbital is in the $\{110\}$ plane, whereas if $D_4 < 0$, it is oriented along the $\langle 110 \rangle$ direction (see Fig. 2).

C. $\Lambda > 1$: Δ and Φ states

1. $\Lambda = 2$: Δ state

If one considers only the lowest-order term in the crystal field ($l = 4$), the adiabatic potential energy for a Δ state is given by

$$\begin{aligned} E_{\pm}(\theta_0, \varphi_0) &= \frac{\sqrt{7}}{2\sqrt{3}} C_4 (1 - 5f_4) \\ &\quad \pm \frac{\sqrt{5}}{2\sqrt{3}} |D_4| [(1 - f_4)^2 - 12f_6]^{1/2}. \end{aligned} \quad (40)$$

The essential difference with the corresponding function for a Π state [Eq. (31)] is that the degeneracy is also lifted for $\langle 100 \rangle$ orientations.

The lower sheet of the adiabatic potential energy, E_- , has minima along $\langle 100 \rangle$ directions with

$$E_- = E_{\langle 100 \rangle} = \frac{1}{2\sqrt{3}} (\sqrt{7}C_4 - \sqrt{5}|D_4|) \quad (41)$$

if $C_4 < (1/\sqrt{35})|D_4|$. $\langle 110 \rangle$ minima occur for

$$\frac{1}{\sqrt{35}} |D_4| < C_4 < \frac{5}{\sqrt{35}} |D_4|,$$

with

$$E_- = E_{\langle 110 \rangle} = -\frac{1}{8\sqrt{3}} (\sqrt{7}C_4 + 3\sqrt{5}|D_4|). \quad (42)$$

Thus the region of the (C_4, D_4) plane in which $\langle 110 \rangle$ absolute minima occur is much smaller for Δ states than it is for Π states, although the parameter D_4 is different in the two cases [see Eq. (16)]. If $C_4 > (5/\sqrt{35})|D_4|$, the orientation of the molecular axis corresponding to absolute minima is tilted away from $\langle 111 \rangle$ towards $\langle 110 \rangle$ in a $\{1\bar{1}0\}$ plane. The minima of E_- are given by

$$E_- = E_{\langle lln \rangle_+} = -\frac{\sqrt{7}}{3\sqrt{3}}C_4 - \frac{2\sqrt{5}}{3\sqrt{3}} \frac{D_4^2}{\sqrt{35}C_4 - |D_4|}. \quad (43)$$

The corresponding orientations are $\langle lln \rangle_+$ with

$$l^2 = \frac{1}{3} \left[1 + 2 \frac{|D_4|}{\sqrt{35}C_4 - |D_4|} \right], \quad (44a)$$

and

$$n^2 = \frac{1}{3} \left[1 - 4 \frac{|D_4|}{\sqrt{35}C_4 - |D_4|} \right]. \quad (44b)$$

As for a Π state, for $D_4=0$ and $C_4 > 0$, the orientation of the molecule is along $\langle 111 \rangle$ directions. For $|D_4| > 0$, the minima tilt away from $\langle 111 \rangle$ with an angle increasing with $|D_4|$ until they reach $\langle 110 \rangle$ for $|D_4| = (\sqrt{35}/5)C_4$. This behavior is quite similar to that of a Π -state molecule in the sense that the coupling of the electronic orbital state to the hindered rotation of the molecule (rotronic coupling) lifts the orbital degeneracy.

2. $\Lambda=3$: Φ state

For $\Lambda \geq 2$, since all $Z_{l,2\Lambda}$ are equal to 0 for $2\Lambda > l$, off-diagonal matrix elements of fourth order are all equal to 0, and the lowest-order terms within the square root of Eq. (17) correspond to $l=6$. Therefore, Φ states will behave essentially in the same manner as the nondegenerate Σ states (see Sec. III A). Although terms with

$$E_{\pm}(\theta_0, \varphi_0) = C_3 V_{30} + C_4 V_{40} \pm \{ D_3^2 [(V_{3,2\Lambda}^c)^2 + (V_{3,2\Lambda}^s)^2] + 2D_3 D_4 [V_{3,2\Lambda}^c V_{4,2\Lambda}^c + V_{3,2\Lambda}^s V_{4,2\Lambda}^s] + D_4^2 [(V_{4,2\Lambda}^c)^2 + (V_{4,2\Lambda}^s)^2] \}^{1/2}. \quad (46)$$

The new invariant terms for Σ and Π states are

$$V_{30}(\theta_0, \varphi_0) = \sqrt{15}f_3, \quad (47)$$

$$(V_{32}^c)^2 + (V_{32}^s)^2 = 1 - 4f_4 + 9f_6, \quad (48)$$

and

$$V_{32}^c V_{42}^c + V_{32}^s V_{42}^s = 2\sqrt{35}f_3(1 - 3f_4), \quad (49)$$

where [see Eqs. (18) and (19)]

$$f_3 = lmn. \quad (50)$$

For Π states, the adiabatic potential energy (up to fourth order) is therefore given by

$$E_{\pm} = \sqrt{15}C_3 f_3 + \frac{\sqrt{7}}{2\sqrt{3}} C_4 (1 - 5f_4) \pm \{ D_3^2 (1 - 4f_4 + 9f_6) + 4\sqrt{35}D_3 D_4 f_3 (1 - 3f_4) + \frac{35}{3} D_4^2 (f_4^2 - 3f_6) \}^{1/2}. \quad (51)$$

For Σ states, the adiabatic potential energy is obtained

higher values of l will still lift the degeneracy, this perturbation will be small.

IV. MOLECULAR IMPURITIES AT TETRAHEDRAL SITES

The expression for the crystal field used so far [Eqs. (3)–(6)] is valid for both O and O_h point-group symmetries, provided that only terms up to eighth order are included. For example, a ninth-order term for O symmetry is not present for O_h . This term would contribute to the adiabatic potential energy in the case of heteronuclear diatomic molecules but not for homonuclear ones. Since the term is ninth order, its contribution would be very small.

In tetrahedral symmetry, however, there exists a third- (and a seventh-) order term in the crystal field for both T and T_d point-group symmetries, an additional sixth-order term for T and T_h , as well as different higher-order terms. Thus for homonuclear diatomic molecules, the adiabatic potential energy is the same for O , O_h , and T_d symmetries since the odd-order terms do not contribute. However, for heteronuclear diatomic molecules, all five symmetries are different.

The theory developed in Sec. II applies to heteronuclear diatomic molecules at sites of T and T_d symmetries if the third-order term is taken into account in the crystal-field potential [see Eqs. (3)–(6)]. This term is⁴⁰

$$V_3(\theta, \varphi) = Z_{32}^s(\theta, \varphi) \quad (45)$$

and can be rotated to the coordinate system fixed in the molecule using Eq. (7). The sums in Eqs. (12)–(14) will now include the additional term $l=3$. If we consider only terms up to $l=4$, the equivalent of Eq. (17) for heteronuclear diatomic molecules in T or T_d symmetries is

from Eq. (51) by setting $D_3=D_4=0$. The possible minima are then along $\langle 100 \rangle$ directions if $C_4 < 0$ and $|C_3| > (\sqrt{35}/2\sqrt{3})|C_4|$, and along $\langle 111 \rangle$ directions in all other cases.

For Π states, if only the lowest-order ($l=3$) terms are included, the minima are along $\langle 111 \rangle$ directions if $D_3=0$ (and $C_3 \neq 0$). As $|D_3|$ increases, the minimum-energy orientations tilt towards $\langle 100 \rangle$ in a $\{110\}$ plane. For $|D_3| = (\sqrt{15}/4)|C_3|$, the orientation is $\langle 100 \rangle$ and remains $\langle 100 \rangle$ for larger values of $|D_3|$.

V. DISCUSSION AND CONCLUSION

There is a large amount of experimental data on diatomic molecular negative ions of the chalcogenides (O_2^- , S_2^- , etc.) as impurities in the alkali halides. It is particularly striking that, in their ground electronic state, these $^2\Pi_g$ impurities are always oriented along $\langle 110 \rangle$ axes, whereas comparably abundant data on diatomic impurity

ions in a Σ ground state (OH^- , CN^- , etc.) show that $\langle 110 \rangle$ orientations are uncommon. In this paper it has been shown that a coupling of the doubly degenerate orbital to the hindered rotation in the crystal field, which must occur, explains the observed $\langle 110 \rangle$ orientations of the Π -state ions, and other observed properties as well. Furthermore, the explanation only requires the lowest-order term in the potential ($l=4$)—the term expected to be the largest—without assuming specific values of higher-order terms, as is needed to explain $\langle 110 \rangle$ orientations of Σ -state ions.

Degenerate electronic orbitals are usually coupled to the crystal via the vibrations of the ions, leading to the well-known *vibrational-electronic*, or vibronic, Jahn-Teller coupling. Such a coupling is also undoubtedly significant in the case of diatomic molecular impurities having an orbitally degenerate ground state. In this work, vibrations are not accounted for; only the hindered rotation of the molecule has been included. The results obtained are a manifestation of the Jahn-Teller effect in which the degenerate orbital is coupled to rotational (instead of vibrational) degrees of freedom, leading to a *rotational-electronic*, or rotronic, coupling. In this case, one cannot make the small-amplitude approximation used for the vibronic coupling. The analogous simplification for rotronic coupling is accomplished by arguing that the rapidly varying terms in the potential can be ignored, i.e., we kept only the lowest-order terms in the spherical harmonics.

For octahedral sites, one finds that all of the observed properties can be understood in terms of the simplest possible expression for the potential, involving only the lowest-order (fourth-order) terms. The $\langle 110 \rangle$ equilibrium orientations always result if the rotronic coupling is comparable to or larger than the coupling to the axially symmetric charge distribution of the molecule. Because of the lower symmetry of this orientation, the degeneracy is lifted. A splitting of the ${}^2\Pi_g$ ground state (as well as of the ${}^2\Pi_u$ excited state) has indeed been measured in some systems [$\text{RbI}:\text{S}_2^-$ (Ref. 21) and $\text{KI}:\text{S}_2^-$ (Ref. 38)]. The amplitude of this splitting, which is about 0.06 eV, provides an order of magnitude for the rotronic Jahn-Teller energy.

Because of the lifting of the degeneracy, the π orbital must be oriented along a specific direction. Our theory predicts that the only possible orientations of the π_g orbital are along a $\langle 110 \rangle$ or $\langle 111 \rangle$ direction perpendicular to the molecular axis, depending on the sign of the coupling constant to the Π state (D_4). Experimentally, $\langle 110 \rangle$ orientations^{17–20} of the π_g wave function occur as frequently as $\langle 100 \rangle$ orientations.^{17–20,24,25,38} Furthermore, in agreement with experimental observations, the theory predicts that 90° reorientation dominates 60° reorientation for a significant range of parameters.

Although in their ${}^2\Pi_g$ ground state all Π -state diatomic molecular impurities in the alkali halides have $\langle 110 \rangle$ equilibrium orientation,^{15–27} some are reported to have $\langle 111 \rangle$ (Ref. 29) or $\langle 100 \rangle$ (Ref. 30) orientations in their ${}^2\Pi_u$ excited state, most being oriented along $\langle 110 \rangle$.^{29–31} This can be understood if we assume that the rotronic coupling is somewhat weaker in the excited state. The theory then predicts that actual minima do not occur for exactly $\langle 111 \rangle$ but rather for $\langle lln \rangle$ orientations. If the tilt

angle is small, the difference would be difficult to detect experimentally. In the case of $\langle 100 \rangle$ orientations, the rotronic Jahn-Teller coupling does not lift the degeneracy. Therefore, in real systems, a vibronic coupling will occur and render the tetragonal symmetry unstable, lowering the symmetry and lifting the degeneracy. This problem is currently under study.

Another prediction which as yet has not been experimentally substantiated is that $\langle 111 \rangle$ orientations of the molecular axis are unstable: a molecule having $\langle 111 \rangle$ equilibrium orientation without rotronic coupling to the Π state will be tilted away from the $\langle 111 \rangle$ towards the $\langle 110 \rangle$ directions as the coupling increases, thereby lifting the degeneracy. The limit of this tilting is the $\langle 110 \rangle$ orientation.

When applied to a Δ state at sites of octahedral symmetry, the theory predicts very similar results: $\langle 111 \rangle$ orientations are unstable and the molecular axis is tilted towards $\langle 110 \rangle$. However, $\langle 110 \rangle$ equilibrium orientations occur for a significantly smaller range of parameters for Δ states than for Π states. Furthermore, the degeneracy is lifted for all stable orientations of the molecular axis.

At sites of tetrahedral symmetry, the overall picture remains the same for homonuclear diatomic molecules since the lowest-order terms are identical to those in octahedral symmetry. However, for heteronuclear diatomic molecular impurities at sites of T and T_d point-group symmetry, there exists a third-order term ($l=3$ in spherical harmonics) which renders $\langle 111 \rangle$ orientations unstable against a tipping towards $\langle 100 \rangle$ in a $\{110\}$ plane.

Furthermore, one should point out that this theory not only changes the interpretation of experiments on isolated impurity ions, but also changes the understanding of their cooperative behavior. In particular, there exists a considerable interest in alkali superoxides and much is known about these crystals. The alkali superoxides are roughly crystals having the NaCl structure, which is usually distorted, with O_2^- ions replacing the halogen ions. They have several structural phases which depend, in part, upon the orientation of the O_2^- ions. It is generally recognized that the Jahn-Teller effect plays a role in determining the structure.⁴² However, it now seems that prior studies of this problem have been incomplete. For example, Halverson⁴³ argues that a Renner effect will cause a tilting of the O_2^- molecule from a tetragonal orientation. Within our theory, no behavior quite like the Renner effect can occur, and the closest we come to a phenomenon such as Halverson suggests is the ultimate instability of the $\langle 100 \rangle$ orientations, when the rotronic coupling is sufficiently large to yield $\langle 110 \rangle$ orientations.

Finally, we remark that in the high-temperature phases of the superoxides, the O_2^- ions are approximately along the $\langle 111 \rangle$ axes but disordered and undergoing a hindered rotation.⁴⁴ This appears reasonable in view of the instability of the $\langle 111 \rangle$ directions for isolated ions. Hindered rotation about the $\langle 111 \rangle$ direction should occur as suggested by Fig. 3.

In summary, the rotronic Jahn-Teller effect explains in a straightforward manner much of what has been observed for Π -state molecular impurities in the alkali halides, and must be included when describing the Jahn-

Teller effect for molecular impurities having a degenerate orbital state and undergoing hindered rotation.

ACKNOWLEDGMENTS

One of the authors (T.L.E.) thanks Werner Känzig, the Eidgenössische Technische Hochschule in Zürich, and the Swiss National Science Foundation for their hospitality during the early phase of his work on this problem. The remainder of the work was supported by the Robert A. Welch Foundation under Grant No. C-850.

APPENDIX: ROTATION MATRICES AND AXIAL HARMONICS

Let (x, y, z) be the axes for a coordinate system fixed in the crystal (the cubic axes of the crystal) and used to describe the crystal-field potential [Eq. (6)]. The coordinate system fixed in the molecular impurity (x', y', z') , has the z' axis lying along the molecular axis. The polar and azimuthal angles in this coordinate system are θ', φ' . The rotation between the two coordinates systems is described by three Euler angles $\theta_0, \varphi_0, \psi_0$, which are usually defined in the following manner.

(1) Rotation about z by φ_0 :

$$(x, y, z) \rightarrow (x_1, y_1, z_1 = z) .$$

(2) Rotation about y_1 by θ_0 :

$$(x_1, y_1, z_1) \rightarrow (x_2, y_2 = y_1, z_2) .$$

(3) Rotation about z_2 by ψ_0 :

$$(x_2, y_2, z_2) \rightarrow (x', y', z' = z_2) .$$

Now, z' lies along the molecular axis, and (θ_0, φ_0) are the polar and azimuthal angles of z' with respect to the lattice. Since the molecule is symmetric with respect to ψ_0 , we can set ψ_0 equal to 0. The standard expressions for writing spherical harmonics in rotated coordinate systems use the rotation matrices $D_{mk}^{(l)}$:⁴⁵

$$Y_{lm}(\theta, \varphi) = \sum_{k=-l}^l D_{mk}^{(l)}(\theta_0, \varphi_0, \psi_0) Y_{lk}(\theta', \varphi') , \quad (\text{A1})$$

where

$$D_{mk}^{(l)}(\theta_0, \varphi_0, \psi_0) = e^{ik\psi_0} e^{im\varphi_0} d_{mk}^{(l)}(\theta_0) , \quad (\text{A2})$$

and

$$d_{mk}^{(l)}(\theta_0) = \sum_t (-1)^{t+m-k} \frac{[(l+k)!(l-k)!(l+m)!(l-m)]^{1/2}}{(l-m-t)!(l+k-t)!t!(t+m-k)!} [\cos(\frac{1}{2}\theta_0)]^{2l-(2t+m-k)} [\sin(\frac{1}{2}\theta_0)]^{2t+m-k} . \quad (\text{A3})$$

The sum runs over all possible values of t , i.e., from $(k-m)$ (or 0) up to $(l-m)$ if $k > 0$, and from $(l+k)$ up to $(l-m)$ if $k < 0$. The relations between axial harmonics in both coordinate systems follow from the definitions given in Eqs. (1) and (A1):

$$Z_{l0}(\theta, \varphi) = D_{00}^{(l)}(\theta_0) Z_{l0}(\theta') + \frac{1}{\sqrt{2}} \sum_{k=1}^l D_{0k}^{c(l)}(\theta_0) Z_{lk}^c(\theta', \varphi') , \quad (\text{A4a})$$

$$\begin{aligned} Z_{lm}^c(\theta, \varphi) &= \sqrt{2} D_{m0}^{(l)}(\theta_0) \cos(m\varphi_0) Z_{l0}(\theta') \\ &+ \sum_{k=1}^l [D_{mk}^c(\theta_0) \cos(m\varphi_0) Z_{lk}^c(\theta', \varphi') \\ &- D_{mk}^s(\theta_0) \sin(m\varphi_0) Z_{lk}^s(\theta', \varphi')] , \end{aligned} \quad (\text{A4B})$$

and

$$\begin{aligned} Z_{lm}^s(\theta, \varphi) &= \sqrt{2} D_{m0}^{(l)}(\theta_0) \sin(m\varphi_0) Z_{l0}(\theta') \\ &+ \sum_{k=1}^l [D_{mk}^c(\theta_0) \sin(m\varphi_0) Z_{lk}^c(\theta', \varphi') \\ &+ D_{mk}^s(\theta_0) \cos(m\varphi_0) Z_{lk}^s(\theta', \varphi')] , \end{aligned} \quad (\text{A4c})$$

where

$$\begin{aligned} D_{m0}^{(l)}(\theta_0) &= (-1)^m d_{m0}^{(l)}(\theta_0) , \\ D_{mk}^c(\theta_0) &= (-1)^m [(-1)^k d_{mk}^{(l)}(\theta_0) + d_{m,-k}^{(l)}(\theta_0)] , \\ D_{mk}^s(\theta_0) &= (-1)^m [(-1)^k d_{mk}^{(l)}(\theta_0) - d_{m,-k}^{(l)}(\theta_0)] . \end{aligned} \quad (\text{A5})$$

Thus it is possible to write all terms of the crystal field in the coordinate system which is convenient for calculating matrix elements.

We are now interested in all matrix elements of the type

$$\langle \psi_{\Lambda}^i(r, \theta', \varphi') | r^l Z_{lm}^j(\theta', \varphi') | \psi_{\Lambda}^k(r, \theta', \varphi') \rangle ,$$

where the ψ_{Λ}^i are wave functions for the doubly degenerate orbital states. The indices i, j, k stand for c, s .

In the present problem, the wave functions are characterized by a dependence on φ' as $\cos(\Lambda\varphi')$ for ψ_{Λ}^c and $\sin(\Lambda\varphi')$ for ψ_{Λ}^s , and the quantum number Λ is equal to 1 (for a Π state), 2 (for a Δ state), 3 (for a Φ state), etc. Since Z_{lm}^c and Z_{lm}^s are proportional to $\cos(m\varphi')$ and $\sin(m\varphi')$, respectively, the only nonzero matrix elements will be those with $m=0$ or $m=2\Lambda$. This selection rule restricts all sums in Eqs. (A4) to the term $k=2\Lambda$. It is now possible to write explicitly all terms of the expansion for the crystal-field potential [Eqs. (3)–(5)] in the rotated coordinate system. For $l=4, 6$, and 8 we have

$$\begin{aligned}
V_l(\theta, \varphi) &= V_{l0}(\theta_0, \varphi_0) Z_{l0}(\theta', \varphi') \\
&+ V_{l,2\Lambda}^c(\theta_0, \varphi_0) Z_{l,2\Lambda}^c(\theta', \varphi') \\
&+ V_{l,2\Lambda}^s(\theta_0, \varphi_0) Z_{l,2\Lambda}^s(\theta', \varphi'), \quad (\text{A6})
\end{aligned}$$

where

$$\begin{aligned}
V_{40} &= \frac{1}{2\sqrt{3}} [\sqrt{7}D_{00}^{(4)}(\theta_0) + \sqrt{10}D_{40}^{(4)}(\theta_0)\cos(4\varphi_0)], \\
V_{4,2\Lambda}^c &= \frac{1}{2\sqrt{6}} [\sqrt{7}D_{0,2\Lambda}^{c(4)}(\theta_0) + \sqrt{10}D_{4,2\Lambda}^{c(4)}(\theta_0)\cos(4\varphi_0)], \\
V_{4,2\Lambda}^s &= -\frac{\sqrt{5}}{2\sqrt{3}} D_{4,2\Lambda}^{s(4)}(\theta_0)\sin(4\varphi_0), \quad (\text{A7}) \\
V_{60} &= \frac{1}{2\sqrt{2}} [D_{00}^{(6)}(\theta_0) - \sqrt{14}D_{40}^{(6)}(\theta_0)\cos(4\varphi_0)], \\
V_{6,2\Lambda}^c &= \frac{1}{4} [D_{0,2\Lambda}^{c(6)}(\theta_0) - \sqrt{14}D_{4,2\Lambda}^{c(6)}(\theta_0)\cos(4\varphi_0)], \\
V_{6,2\Lambda}^s &= \frac{\sqrt{7}}{2\sqrt{2}} D_{4,2\Lambda}^{s(6)}(\theta_0)\sin(4\varphi_0), \quad (\text{A8})
\end{aligned}$$

and

$$\begin{aligned}
V_{80} &= \frac{1}{8\sqrt{3}} [3\sqrt{11}D_{00}^{(8)}(\theta_0) + 2\sqrt{14}D_{40}^{(8)}(\theta_0)\cos(4\varphi_0) \\
&+ \sqrt{130}D_{80}^{(8)}(\theta_0)\cos(8\varphi_0)], \\
V_{8,2\Lambda}^c &= \frac{1}{8\sqrt{6}} [3\sqrt{11}D_{0,2\Lambda}^{c(8)}(\theta_0) + 2\sqrt{14}D_{4,2\Lambda}^{c(8)}(\theta_0)\cos(4\varphi_0) \\
&+ \sqrt{130}D_{8,2\Lambda}^{c(8)}(\theta_0)\cos(8\varphi_0)], \\
V_{8,2\Lambda}^s &= -\frac{1}{8\sqrt{6}} [2\sqrt{7}D_{4,2\Lambda}^{s(8)}(\theta_0)\sin(4\varphi_0) \\
&+ \sqrt{65}D_{8,2\Lambda}^{s(8)}(\theta_0)\sin(8\varphi_0)]. \quad (\text{A9})
\end{aligned}$$

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