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Vibronic Model for the Relaxed Excited State of the *F* Center. I. General Solution

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An exact solution is given, using methods familiar from the theory of the dynamic Jahn-Teller effect of orbitally degenerate states, for the vibronic problem posed by a model for the excited state of the *F* center suggested by recent experiments on Stark effects in *F*-band luminescence of alkali halides. In this model, nondegenerate 2*s* and 2*p* electronic states interact in cubic symmetry via a triply degenerate odd-parity (Γ_4^-) vibrational mode. From the exact wave functions for the resulting vibronic levels of the coupled electron-lattice system, expressions are derived for the following quantities: radiative lifetimes of the various levels; change in radiative lifetime of the vibronic ground state in an electric field, when this level is a nondegenerate *s*-like state; polarization induced in luminescence from the *s*-like ground state by electric fields, magnetic fields, and applied stress; change in the *g* factor of the ground state because of the vibronic mixing; and reduction factors for the splitting of degenerate levels by applied magnetic fields and stress. These results take a particularly simple form when the coupling to the Γ_4^- modes is strong. From a comparison of these theoretical results with the experimental data for the alkali halides, it is concluded that, contrary to earlier interpretations, the experimental situation cannot be in or close to the strong-coupling regime. An estimate of this coupling strength to the Γ_4^- modes from a moment analysis of the vibrational broadening of the *F* band in absorption and of stress-induced linear dichroism indicates that this coupling is probably weak for KCl, and that the Jahn-Teller coupling of 2*p* states to the Γ_3^+ and/or Γ_5^+ modes is stronger. This estimate is supported by an analysis of the form of the stable distorted configurations given by the adiabatic energy surfaces of the static problem, when simultaneous coupling to all three types of modes Γ_3^+, Γ_4^-, and Γ_5^+ is considered. An interpretation of the experimental data on the basis of this analysis indicates that for KCl the 2*s* state must be below 2*p* by about 0.1 eV in the cubic configuration corresponding to the relaxed position of the symmetric Γ_1^+ mode. Also discussed is the relationship of the exact solution of the vibronic problem to an approximate treatment given by Bogan: The adiabatic states introduced by Bogan can be identified with different groups of the exact vibronic states in the strong-coupling limit, but the approximate treatment is shown to have given rise to misleading interpretations of some of the experimental results.

I. INTRODUCTION

The results of a number of recent experiments on luminescence in the *F* band of various alkali halides, particularly Stark-effect studies by Bogan and Fitchen,[1] Kühnert,[2] and Stiles, Fontana, and Fitchen,[3] have been interpreted as showing that a 2*s*-like level lies below the 2*p* level in the relaxed excited state of the *F* center. Whereas the earlier prevailing view[4] had been that absorption and luminescence in the *F* band involved only the 2*p* excited states, recent theoretical studies have indeed shown that the 2*s* electronic state may lie very close in energy to the 2*p* states and may be the lower state in the relaxed configuration.[5,6] These states should be coupled by odd-parity vibrational modes, and the resulting vibronic levels of the coupled electron-lattice system will then be mixtures of the 2*s* and 2*p* electronic states. This mixing has been thought to be strong,[1,3] and it plays a crucial role in determining properties of the *F* center such as the radiative lifetime of the excited state and the polarization of the luminescence induced by an electric field, magnetic field, or applied stress. However, no satisfactory theoretical treatment of this dynamic mixing of the 2*s* and 2*p* electronic states has been given, and interpretation of the experiments has therefore been possible only on the basis of a semiclassical approximate theory developed by Bogan.[1,7] The limitations on Bogan's treatment have not been known, however, particularly as they concern its applicability in the regime of fairly strong electron-lattice coupling, in which the experimental situation has been interpreted to lie.

The purpose of the present paper is to give an exact solution of the vibronic problem posed by a model for the excited state of the *F* center which incorporates the principal features indicated by the recent work, namely, nondegenerate 2*s* and 2*p* electronic states interacting in cubic symmetry via a triply degenerate odd-parity (Γ_4^-) vibrational mode.[8] Using the wave functions for the resulting vibronic states of the coupled electron-lattice system, we then derive results for various quantities that have been measured in the recent experiments, including the radiative lifetime of the various vibronic levels, the change in radiative lifetime of the vibronic ground state in an electric field, and the polarization induced in the luminescence from the ground state by electric fields, magnetic fields, and applied stress. Our solution of this problem is valid over the entire range of coupling strength, and it is found in fact to assume a particularly simple form in the strong-coupling regime.

On the basis of this analysis of the vibronic model, we then discuss the interpretation of the experimental data for F centers in alkali halides. We are there able to show that these data are inconsistent with the assumption that the experimental situation is in or very close to the strong-coupling regime for the Γ_4^- vibrational modes, contrary to the earlier interpretation of these data. Indeed, we conclude from this study that those alkali halides for which data are available are probably in the weak-coupling regime. Rather than apply the full formal theory to the weak-coupling case, for which it is unnecessarily cumbersome, we have investigated this limit in the following paper[9] using simple perturbation theory, and we consider there a quantitative interpretation of the available data on this basis.

The method we have used in solving this vibronic problem is very similar to that used in treating the dynamic Jahn-Teller effect of orbitally degenerate states, and especially to the work of Moffitt and Thorson[10] and Longuet-Higgens, Opik, Pryce, and Sack[11] on the orbital doublet state. The present problem would not in a strict sense be said to involve a Jahn-Teller effect, since the coupling due to the vibrational modes here is between *nondegenerate* electronic states and the Jahn-Teller theorem[12] is therefore not applicable. (Such a system is often described as exhibiting a "pseudo-Jahn-Teller effect.") Nevertheless, the physics of the two situations is essentially the same, as Opik and Pryce[13] have noted previously, and accumulated experience[14, 15] with the Jahn-Teller problem provides a valuable guide to the usefulness of the present model for the excited state of the F center, while also indicating the method of solution. Indeed, with sufficiently strong coupling to the odd-parity vibrational mode, the cubic configuration in the present case is unstable with respect to asymmetric distortions, as we show in Sec. III A, in a manner reminiscent of a Jahn-Teller instability. Moreover, if the $2s$ and $2p$ states were accidentally degenerate, this instability would involve a linear splitting of the electronic degeneracy exactly as in the Jahn-Teller effect.

One difficulty with the model used in this paper is that it does not include the true Jahn-Teller coupling of the p states to the even-parity Γ_3^+ and Γ_5^+ modes, although this coupling in the excited state of the F center may in fact be even stronger than the coupling to the odd modes. Including the even-mode coupling makes the dynamic problem too complicated for an exact solution to be possible. Nevertheless, we have been able to solve the corresponding static problem when all three types of modes are included, and we have determined the form of the stable distorted configuration for the various ranges of relative coupling strengths. These results enable us to determine the range in which the dynamic solution of the simpler model is relevant, and moreover they enable us to draw qualitative conclusions about the way this dynamic solution would be modified if the even-mode coupling were included.

We also discuss at the end of the paper the relationship between our exact solution of the vibronic model and the approximate treatment given by Bogan.[1, 7] The states introduced by Bogan can be identified with the various groups of the exact vibronic states, but the approximate treatment is shown to have given rise to misleading interpretations of some of the experimental results. In particular, previous determinations[3] of Bogan's mixing coefficient α, which is supposed to give the amount of electronic p state mixed into the s-like vibronic ground state, have greatly overestimated the size of this parameter.

II. VIBRONIC MODEL

We consider nondegenerate s (Γ_1^+) and p (Γ_4^-) electronic states[16] interacting in cubic symmetry (point group O_h) via a triply degenerate Γ_4^- vibrational mode Q_x, Q_y, Q_z. In the configuration of cubic symmetry ($Q_x = Q_y = Q_z = 0$) the electronic singlet state, which we denote by $|2s\rangle$, is taken to have an energy E_{sp} relative to the triplet state $|p_x\rangle$, $|p_y\rangle$, $|p_z\rangle$. The purely electronic part of the model Hamiltonian is therefore taken to be

$$\mathcal{H}_e = \tfrac{1}{2} E_{sp} \rho_0 , \tag{2.1}$$

where ρ_0 denotes the electronic operator given by

$$\rho_0 = + |2s\rangle\langle 2s| - |p_x\rangle\langle p_x| - |p_y\rangle\langle p_y| - |p_z\rangle\langle p_z| . \tag{2.2}$$

The vibrational part of the Hamiltonian is taken to be that appropriate to a three-dimensional simple harmonic oscillator,

$$\mathcal{H}_L = (2\mu)^{-1}[P_x^2 + P_y^2 + P_z^2 + (\mu\omega)^2(Q_x^2 + Q_y^2 + Q_z^2)] , \tag{2.3}$$

where ω is the angular frequency of the mode, μ its effective mass, and P_i the momentum conjugate to Q_i. Finally, the coupling of the electronic states that is linear in the distortions Q_x, Q_y, Q_z is given by

$$\mathcal{H}_{eL} = G(Q_x\rho_x + Q_y\rho_y + Q_z\rho_z) , \tag{2.4}$$

where G is a coupling coefficient and

$$\rho_i = |p_i\rangle\langle 2s| + |2s\rangle\langle p_i| . \tag{2.5}$$

The full Hamiltonian $\mathcal{H}$ of our vibronic model is then given by

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_L + \mathcal{H}_{eL} . \tag{2.6}$$

III. SOLUTION IN GENERAL CASE

A. Static Problem: Adiabatic Energy Surfaces and Configurations of Minimum Energy

As in the study of the static Jahn-Teller effect,[13] it is useful in the present case to analyze the static problem defined by the Hamiltonian (2.6) when the vibrational kinetic-energy terms $(2\mu)^{-1}P_i^2$ in $\mathcal{H}_L$ are omitted. The linear combinations of the electronic states that diagonalize the Hamiltonian for any choice of Q_x, Q_y, Q_z are then easily obtained. We find that two states are linear combinations of s and p and have energies

$$E = \tfrac{1}{2}\mu\omega^2 r^2 \pm \tfrac{1}{2}(E_{sp}^2 + 4G^2r^2)^{1/2} , \tag{3.1a}$$

where $r = (Q_x^2 + Q_y^2 + Q_z^2)^{1/2}$, while two involve the p states alone and correspond to the double root of the secular equation

$$E = \tfrac{1}{2}\mu\omega^2 r^2 - \tfrac{1}{2}E_{sp} . \tag{3.1b}$$

These energy surfaces have spherical symmetry in Q space and are plotted for representative cases in Fig. 1. The configuration of minimum energy is obtained by finding the stationary points of the lower root in Eq. (3.1a). The minimum occurs at $r = r_0$ given by

$$r_0^2 = (G/\mu\omega^2)^2 - (E_{sp}/2G)^2 \tag{3.2}$$

provided the coupling is sufficiently strong so that

$$E_G > \tfrac{1}{4}\left|E_{sp}\right| , \tag{3.3}$$

where we have defined

$$E_G = G^2/2\mu\omega^2 . \tag{3.4}$$

The energy at the minimum is

$$E = -E_G[1 + (E_{sp}/4E_G)^2] . \tag{3.5}$$

The energy E_G thus provides a measure of the strength of the electron-lattice coupling to the Γ_4^- modes, and for strong coupling $(E_G \gg \tfrac{1}{4}|E_{sp}|)$ it gives the approximate depth of the well in Figs. 1(a) and 1(b) and therefore is the analog of the stabilization energy E_{JT} in the Jahn-Teller problem.[13,14] On the other hand, when the coupling is weak so that the condition (3.3) is not satisfied, the minimum occurs at $r = 0$ and is given by $E = -\tfrac{1}{2}|E_{sp}|$, the energy of the lower of the s and p states. No well develops in this case, therefore, and the cubic configuration remains stable [Figs. 1(c) and 1(d)].

The more general static problem of s and p states, including linear Jahn-Teller coupling of the p states to Γ_3^+ and Γ_5^+ modes, has been considered by Opik and Pryce.[13] As they have shown, one can prove in the general case that the stationary points have cubic, tetragonal, trigonal, or rhombic symmetry. By carrying out the somewhat tedious algebra of the method used by Opik and Pryce, we have been able to show that the configurations of minimum energy are those given in Table I for the various regions defined by the relative strengths of the coupling with the different modes. In particular, the rhombic stationary points are never minima. There are two types of minima having tetragonal or trigonal symmetry. In one of these the electronic state in the minimum configuration is pure p; we have $Q_x = Q_y = Q_z = 0$; and the minimum results from the Jahn-Teller coupling of the p states to the Γ_3^+ or Γ_5^+ modes alone and does not involve the s state in any way. In the other type of minimum (which we call the s-p mixed type in Table I), the electronic state is a mixture of s and p, and there is a nonzero distortion *both* in the space of the Γ_4^- Q's and in that of the Q's of *either* Γ_3^+ *or* Γ_5^+. In this latter case, energetically equivalent minima occur at points related by inversion symmetry in Γ_4^- Q space, and the number of minima is therefore twice

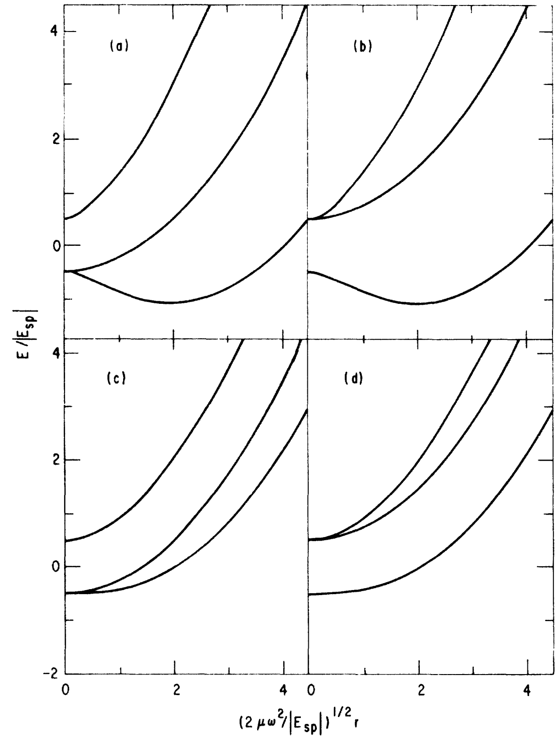

FIG. 1. Adiabatic energy surfaces for electronic s and p states interacting in cubic symmetry via a triply degenerate Γ_4^- vibrational mode. The energy surfaces have spherical symmetry in Q space. Plotted for representative cases is the ratio of the energy E to the magnitude of the energy difference E_{sp} of the s and p states in the cubic configuration $(Q=0)$, as a function of $(2\mu\omega^2/|E_{sp}|)^{1/2}r$, where r is the radial coordinate in Q space, $r = (Q_x^2 + Q_y^2 + Q_z^2)^{1/2}$[see Eqs. (3.1a) and (3.1b) of text]. The coupling energy is denoted by E_G [Eq. (3.4)]. (a) $E_{sp} > 0$, $E_G/|E_{sp}| = 1$; (b) $E_{sp} < 0$, $E_G/|E_{sp}| = 1$; (c) $E_{sp} > 0$, $E_G/|E_{sp}| = 0.2$; (d) $E_{sp} < 0$, $E_G/|E_{sp}| = 0.2$.

TABLE I. Configuration of minimum energy for simultaneous coupling of nondegenerate s and p electronic states to modes of symmetry Γ_3^+, Γ_5^+, and Γ_4^-. The range of the coupling energies E_G (Γ_4^-), $(E_{JT})_E$ (Γ_3^+), and $(E_{JT})_T$ (Γ_5^+), over which the indicated configuration is the minimum, is given below.[a] Also given are the minimum energy,[b] the number of energetically equivalent minima, and the irreducible representations of O_h spanned by the distorted states.

		$(E_{JT})_E > (E_{JT})_T$	
Configuration:	Cubic s state, $r=0$	Tetragonal Jahn-Teller type	Tetragonal s-p mixed type
$E_{sp} < 0 \begin{cases} (E_{JT})_E < \lvert E_{sp} \rvert \\ \end{cases}$	$E_G < \frac{1}{4} \lvert E_{sp} \rvert$		$E_G > \frac{1}{4} \lvert E_{sp} \rvert$
$(E_{JT})_E > \lvert E_{sp} \rvert$		$E_G < \frac{1}{2}(E_{JT})_E - \frac{1}{4} \lvert E_{sp} \rvert$	$E_G > \frac{1}{2}(E_{JT})_E - \frac{1}{4} \lvert E_{sp} \rvert$
$E_{sp} > 0$		$E_G < \frac{1}{2}(E_{JT})_E + \frac{1}{4}E_{sp}$	$E_G > \frac{1}{2}(E_{JT})_E + \frac{1}{4}E_{sp}$
Energy[b]	$E = E_{sp}$	$E = -(E_{JT})_E$	$E = -\left(\frac{(4E_G - E_{sp})^2 + 4(E_{JT})_E E_{sp}}{4[4E_G - (E_{JT})_E]}\right)$
No. of equivalent minima	1	3	6
Irreducible reps. spanned (O_h)	Γ_1^+	Γ_4^-	$\Gamma_1^+ + \Gamma_3^+ + \Gamma_4^-$
		$(E_{JT})_T > (E_{JT})_E$	
Configuration:	Cubic s state, $r=0$	Trigonal Jahn-Teller type	Trigonal s-p mixed type
$E_{sp} < 0 \begin{cases} (E_{JT})_T < \lvert E_{sp} \rvert \\ \end{cases}$	$E_G < \frac{1}{4} \lvert E_{sp} \rvert$		$E_G > \frac{1}{4} \lvert E_{sp} \rvert$
$(E_{JT})_T > \lvert E_{sp} \rvert$		$E_G < \frac{1}{2}(E_{JT})_T - \frac{1}{4} \lvert E_{sp} \rvert$	$E_G > \frac{1}{2}(E_{JT})_T - \frac{1}{4} \lvert E_{sp} \rvert$
$E_{sp} > 0$		$E_G < \frac{1}{2}(E_{JT})_T + \frac{1}{4}E_{sp}$	$E_G > \frac{1}{2}(E_{JT})_T + \frac{1}{4}E_{sp}$
Energy[b]	$E = E_{sp}$	$E = -(E_{JT})_T$	$E = -\left(\frac{(4E_G - E_{sp})^2 + 4(E_{JT})_T E_{sp}}{4[4E_G - (E_{JT})_T]}\right)$
No. of equivalent minima	1	4	8
Irreducible reps. spanned (O_h)	Γ_1^+	$\Gamma_2^- + \Gamma_4^-$	$\Gamma_1^+ + \Gamma_2^- + \Gamma_4^- + \Gamma_5^+$

[a] E_{sp} is the energy of the s electronic state relative to that of the p state in the cubic configuration. The coupling energy E_G for Γ_4^- modes is defined in Eq. (3.4) of the text. The Jahn-Teller energies $(E_{JT})_E$ and $(E_{JT})_T$ for the Γ_3^+ and Γ_5^+ modes, respectively, are defined by Eq. (3.6) of the text.

[b] In this table the energy of the minimum is given relative to the zero of energy taken to coincide with the energy of the electronic p state in the cubic configuration.

that found for the case of pure Jahn-Teller coupling alone. In summarizing these results in Table I we use the Jahn-Teller energies $(E_{JT})_E$ and $(E_{JT})_T$ for the coupling of the p states to the Γ_3^+ and Γ_5^+ modes, respectively. These are related to the coupling coefficients, effective masses, and frequencies of the modes as follows:

$$(E_{JT})_E = V_E^2/2\mu_E\omega_E^2, \quad (E_{JT})_T = 2V_T^2/3\mu_T\omega_T^2. \tag{3.6}$$

where our notation is the same as that used in earlier papers on Jahn-Teller effects in an orbital triplet state.[17]

Including the Jahn-Teller coupling to the Γ_3^+ and Γ_5^+ modes has the important effect of destroying the spherical symmetry found in Eq. (3.1) and Fig. 1 for Γ_4^--mode coupling alone [except in the exceptional case in which $(E_{JT})_E = (E_{JT})_T$]. Because this symmetry provides the key to the ensuing solution of the dynamic problem, we have not been able to include coupling to the Γ_3^+ and Γ_5^+ modes in our treatment of this problem.

B. Dynamic Problem: Solving for Vibronic Eigenstates

The spherical symmetry of the static problem for Γ_4^- coupling only, as found in Eq. (3.1) and Fig. 1, results from the invariance of the model Hamiltonian (2.6) under a continuous group of simultaneous rotations of the electronic and vibrational coordinates. We shall exploit this symmetry in a manner similar to that used previously by Moffitt and Thorson[10] and Longuet-Higgins *et al.*[11] in treating the dynamic Jahn-Teller effect of an orbital doublet state. We introduce a vibrational angular-momentum operator $\vec{L}$ with components L_x, L_y, L_z given by

$$L_z = \hbar^{-1}(Q_x P_y - Q_y P_x), \tag{3.7}$$

etc., and we take as a complete set of functions of the angular coordinates θ, φ in Q space ($Q_z = r\cos\theta$, $Q_x = r\sin\theta\cos\varphi$, $Q_y = r\sin\theta\sin\varphi$) the spherical harmonics $Y_{L,m}(\theta, \varphi)$ (defined with the phase relationship of Condon and Shortley[18]) for which we have

$$L_z Y_{L,m}(\theta, \varphi) = m Y_{L,m}(\theta, \varphi), \tag{3.8a}$$

$$(L_x \pm i L_y) Y_{L,m}(\theta, \varphi) = +[L \mp m)(L \pm m + 1)]^{1/2} Y_{L,m\pm1}(\theta, \varphi). \tag{3.8b}$$

We also introduce the electronic orbital angular-momentum operator $\vec{l}$ with components represented within the electronic basis $|2s\rangle$, $|p_x\rangle$, $|p_y\rangle$, $|p_z\rangle$ by

$$l_z = -i|p_x\rangle\langle p_y| + i|p_y\rangle\langle p_x|, \tag{3.9}$$

etc. The state $|2s\rangle$ is thus an eigenstate of $\vec{l}^{\,2}$ with $l = 0$, while the p states may be combined with the conventional choice of phases to give eigenstates $|l, l_z'\rangle$ of $\vec{l}^{\,2}$ and l_z,

$$|1, 0\rangle = |p_z\rangle, \quad |1, \pm 1\rangle = \mp(2)^{-1/2}(|p_x\rangle \pm i|p_y\rangle). \tag{3.10}$$

Both $\vec{L}$ and $\vec{l}$ commute with $\mathcal{H}_e$ and $\mathcal{H}_L$, the electronic and vibrational terms in the Hamiltonian, but neither commutes with the coupling term $\mathcal{H}_{eL}$. However, the total angular-momentum operator

$$\vec{J} = \vec{L} + \vec{l} \tag{3.11}$$

does commute with $\mathcal{H}_{eL}$ and thus with the full Hamiltonian $\mathcal{H}$ in Eq. (2.6). Vibronic eigenstates of $\mathcal{H}$ may therefore be classified by the eigenvalues of $\vec{J}^{\,2} = J(J+1)$ $(J = 0, 1, 2, \ldots)$ and $J_z = M$. In addition, if we introduce the inversion operator I in Q space, where

$$I Y_{L,m}(\theta, \varphi) = (-1)^L Y_{L,m}(\theta, \varphi), \tag{3.12}$$

we find that

$$\Lambda = I\rho_0 \tag{3.13}$$

also commutes with $\mathcal{H}$ and with $\vec{J}$, where ρ_0 is defined in Eq. (2.2) and represents the electronic inversion operator. We can therefore also classify an eigenstate of $\mathcal{H}$ by the eigenvalue $\Lambda' = \pm 1$, which we call the parity of the state. Since only states with the same eigenvalues J, J_z, and Λ' can be mixed by $\mathcal{H}$, we see that we have obtained in this way a means of separating the vibronic wave functions for the dynamic problem into nonmixing sets.

Eigenfunctions of $\vec{J}^{\,2}$ and J_z formed from the s electronic state are given simply by

$$|J, M; L, s\rangle = Y_{L,m}(\theta, \varphi)|2s\rangle, \tag{3.14}$$

where $J = L$, $M = m$, and the function has the parity $(-1)^L$. The corresponding eigenfunctions $|J, M; L, p\rangle$ formed from the p states may be obtained as linear combinations of the products of $Y_{L,m}(\theta, \varphi)$ with the electronic states (3.10), from a table of Wigner coefficients given by Condon and Shortley.[19] For these states, using a given L, we have $J = L-1$, L, $L+1$ (except for $L = 0$, for which $J = 1$ only), and $\Lambda' = (-1)^{L+1}$. It follows that any eigenfunction of $\mathcal{H}$ which belongs to J, $J_z = M$ and has $\Lambda' = (-1)^J$ can be expressed in the general form (which we call type I)

$$\Psi_{\mathrm{I}}(J, M, \Lambda') = f_1(J, r)\,|J, M; J, s\rangle + f_2(J, r)\,|J, M; J-1, p\rangle$$
$$+ f_3(J, r)\,|J, M; J+1, p\rangle, \tag{3.15}$$

where the $f_i(J, r)$ are functions of the radii coordinate r. (For $J = 0$ the term in f_2 is absent.) Eigenfunctions also belonging to J, $J_z = M$ but having $\Lambda' = (-1)^{J+1}$, on the other hand, take the form (type II)

$$\Psi_{\mathrm{II}}(J, M, \Lambda') = f_4(J, r)\,|J, M; J, p\rangle. \tag{3.16}$$

All eigenfunctions of the model Hamiltonian (2.6) belong to one or the other of these two types of vibronic state.

It is straightforward to show that the only nonzero matrix elements of $\mathcal{H}_{eL}$, as given by Eq. (2.4), among the "angular" functions $|J, M; L, p\rangle$ and $|J, M; J, s\rangle$ are given by

$$\langle J, M; J+1, p\,|\mathcal{H}_{eL}|\,J, M; J, s\rangle = -Gr[(J+1)/(2J+1)]^{1/2}, \tag{3.17}$$

$$\langle J, M; J-1, p\,|\mathcal{H}_{eL}|\,J, M; J, s\rangle = +Gr[J/(2J+1)]^{1/2}.$$

(The matrix elements imply integration over the electronic coordinates as well as over the angular coordinates θ and φ in Q space.) Introducing the Schrödinger representation for $\mathcal{H}_L$ in Eq. (2.3),

$$\mathcal{H}_L = \mathcal{D}_r + (\hbar^2/2\mu r^2)\vec{L}^2 + \tfrac{1}{2}\mu\omega^2 r^2, \tag{3.18}$$

where

$$\mathcal{D}_r = -\frac{\hbar^2}{2\mu} r^{-2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right), \tag{3.19}$$

we now substitute the type-I wave function (3.15) into Schrödinger's equation for the Hamiltonian (2.6). The angular functions may be eliminated by using their orthonormality, together with Eqs. (3.17) and (3.18), and we get the following three coupled differential equations for the radial functions $f_i(J, r)$ $(i = 1, 2, 3)$ and the vibronic energy eigenvalue E:

$$\left(\mathcal{D}_r + \frac{\hbar^2}{2\mu r^2} J(J+1) + \tfrac{1}{2}\mu\omega^2 r^2 + \tfrac{1}{2}E_{sp} - E\right) f_1(J, r)$$
$$+ Gr\left(\frac{J}{2J+1}\right)^{1/2} f_2(J, r) - Gr\left(\frac{J+1}{2J+1}\right)^{1/2} f_3(J, r) = 0, \tag{3.20a}$$

$$\left(\mathcal{D}_r + \frac{\hbar^2}{2\mu r^2} J(J-1) + \tfrac{1}{2}\mu\omega^2 r^2 - \tfrac{1}{2}E_{sp} - E\right) f_2(J, r)$$
$$+ Gr\left(\frac{J}{2J+1}\right)^{1/2} f_1(J, r) = 0, \tag{3.20b}$$

$$\left(\mathcal{D}_r + \frac{\hbar^2}{2\mu r^2}(J+1)(J+2) + \tfrac{1}{2}\mu\omega^2 r^2 - \tfrac{1}{2}E_{sp} - E\right) f_3(J, r)$$

$$-Gr\left(\frac{J+1}{2J+1}\right)^{1/2} f_1(J,\ r)=0\ . \qquad (3.20\text{c})$$

A similar substitution of the type-II functions into Schrödinger's equation yields simply

$$[\mathfrak{D}_r+(\hbar^2/2\mu r^2)J(J+1)+\tfrac{1}{2}\mu\omega^2r^2-\tfrac{1}{2}E_{sp}-E]f_4(J,r)=0, \qquad (3.21)$$

which is identical with the radial equation for a three-dimensional simple harmonic oscillator. A type-II vibronic state has the opposite parity from that of a type-I state belonging to the same J; it is made up entirely from the p electronic states, and it is completely independent of $\mathcal{H}_{eL}$. Energies of the type-II states therefore coincide with those of the vibrational levels of the p electronic state in the complete absence of s-p vibrational coupling. (There are, it must be noted, no type-II states having $J=0$.)

It is useful for our subsequent work to express the vibronic states in the form

$$\Psi=\Phi_s|2s\rangle+\Phi_x|p_x\rangle+\Phi_y|p_y\rangle+\Phi_z|p_z\rangle, \qquad (3.22)$$

where the Φ's are the appropriate complex functions of $\vec{Q}$ normalized so that

$$\int(|\Phi_s|^2+|\Phi_x|^2+|\Phi_y|^2+|\Phi_z|^2)\,d\vec{Q}=1\ . \qquad (3.23)$$

For the type-I states, $\Psi_{\text{I}}(J,\ M,\ \Lambda')$ in Eq. (3.15), we find from Eqs. (3.10), (3.14), and the expressions for $|J,\ M;\ L,\ p\rangle$ obtained from tables of Wigner coefficients[19] that we have the following expressions for the Φ's:

$$\Phi_{\text{I}s}(J,\ M,\ \Lambda')=f_1(J,\ r)\,Y_{J,M}(\theta,\ \varphi), \qquad (3.24\text{a})$$

$$\Phi_{\text{I}z}(J,\ M,\ \Lambda')=\left(\frac{(J-M)(J+M)}{J(2J-1)}\right)^{1/2} f_2(J,r)Y_{J-1,M}(\theta,\varphi)$$

$$-\left(\frac{(J-M+1)(J+M+1)}{(J+1)(2J+3)}\right)^{1/2}$$

$$\times f_3(J,\ r)\,Y_{J+1,M}(\theta,\ \varphi), \qquad (3.24\text{b})$$

$$\Phi_{\text{I}x}(J,\ M,\ \Lambda')\pm i\Phi_{\text{I}y}(J,\ M,\ \Lambda')$$
$$=\pm\left(\frac{(J\mp M-1)(J\mp M)}{J(2J-1)}\right)^{1/2} f_2(J,\ r)Y_{J-1,M\pm1}(\theta,\ \varphi)$$
$$\pm\left(\frac{(J\pm M+1)(J\pm M+2)}{(J+1)(2J+3)}\right)^{1/2} f_3(J,\ r)\,Y_{J+1,M\pm1}(\theta,\ \varphi)\ . \qquad (3.24\text{c})$$

For the type-II states $\Psi_{\text{II}}(J,\ M,\ \Lambda')$ in Eq. (3.16), we have

$$\Phi_{\text{II}s}(J,\ M,\ \Lambda')=0, \qquad (3.25\text{a})$$

$$\Phi_{\text{II}z}(J,M,\ \Lambda')=M[J(J+1)]^{-1/2}f_4(J,\ r)Y_{J,M}(\theta,\ \varphi)\ , \qquad (3.25\text{b})$$

$$\Phi_{\text{II}x}(J,\ M,\ \Lambda')\pm i\Phi_{\text{II}y}(J,\ M,\ \Lambda')=\left(\frac{(J\mp M)(J\pm M+1)}{J(J+1)}\right)^{1/2}$$
$$\times f_4(J,\ r)\,Y_{J,M\pm1}(\theta,\ \varphi)\ . \qquad (3.25\text{c})$$

We will consider in Sec. V various properties of the two types of states $\Psi_{\text{I}}(J,\ M,\ \Lambda')$ and $\Psi_{\text{II}}(J,M,\Lambda')$ that may be related to the general form of their wave functions. We proceed now to seek solutions of Eq. (3.20) for the type-I states in the limit of strong coupling.

IV. STRONG-COUPLING LIMIT

The terms that couple the three differential equations (3.20) for the radial functions $f_i(J,\ r)$ of the type-I vibronic eigenstates result from $\mathcal{H}_{eL}$ and may be represented by a symmetric matrix,

$$U=\begin{pmatrix} 0 & +Gr[J/(2J+1)]^{1/2} & -Gr[(J+1)/(2J+1)]^{1/2} \\ +Gr[J/(2J+1)]^{1/2} & 0 & 0 \\ -Gr[(J+1)/(2J+1)]^{1/2} & 0 & 0 \end{pmatrix}. \qquad (4.1)$$

They are large when the coupling is strong, and in this case it is appropriate to introduce an orthogonal transformation of the f_i that brings U to diagonal form. This transformation is given by

$$F_1=2^{-1/2}f_1-\left(\frac{J}{2(2J+1)}\right)^{1/2} f_2+\left(\frac{J+1}{2(2J+1)}\right)^{1/2} f_3,$$

$$F_2=2^{-1/2}f_1+\left(\frac{J}{2(2J+1)}\right)^{1/2} f_2-\left(\frac{J+1}{2(2J+1)}\right)^{1/2} f_3, \qquad (4.2)$$

$$F_3=\left(\frac{J+1}{2J+1}\right)^{1/2} f_2+\left(\frac{J}{2J+1}\right)^{1/2} f_3,$$

for which we have

$$UF_1=-GrF_1,\quad UF_2=+GrF_2,\quad UF_3=0\ . \qquad (4.3)$$

From the definitions (4.2) and Eq. (3.20), we find the coupled differential equations satisfied by the F_i to be

$$[\mathfrak{D}_r+(\hbar^2/2\mu r^2)(J^2+J+1)+\tfrac{1}{2}\mu\omega^2r^2-Gr-E]F_1$$
$$+[\tfrac{1}{2}E_{sp}-(\hbar^2/2\mu r^2)]F_2+(\hbar^2/2\mu r^2)$$
$$\times[2J(J+1)]^{1/2}F_3=0, \qquad (4.4\text{a})$$

$$[\mathfrak{D}_r+(\hbar^2/2\mu r^2)(J^2+J+1)+\tfrac{1}{2}\mu\omega^2r^2+Gr-E]F_2$$
$$+[\tfrac{1}{2}E_{sp}-(\hbar^2/2\mu r^2)]F_1-(\hbar^2/2\mu r^2)$$

$$\times[2J(J+1)]^{1/2}F_3=0\ , \qquad (4.4b)$$

$$[\mathfrak{D}_r+(\hbar^2/2\mu r^2)J(J+1)+\tfrac{1}{2}\mu\omega^2r^2-\tfrac{1}{2}E_{sp}-E]F_3$$
$$+(\hbar^2/2\mu r^2)[2J(J+1)]^{1/2}(F_1-F_2)=0\ . \qquad (4.4c)$$

With the radial differential equations thus transformed, we see from Eqs. (4.3) and (4.4) that the coupling $\mathcal{H}_{eL}$ introduces a term $-Gr$ in the effective potential energy for F_1, a term $+Gr$ for F_2, and no term in G at all for F_3. If we have $G>0$ (for $G<0$ the roles of F_1 and F_2 are interchanged), the effective potential energy

$$V_{\text{eff}}(F_1)=\tfrac{1}{2}\mu\omega^2r^2-Gr \qquad (4.5)$$

for F_1 therefore has a minimum at $r=G/\mu\omega^2$, where $V_{\text{eff}}=-G^2/2\mu\omega^2$. The depth of the potential well given by Eq. (4.5) is therefore equal to E_G as given by Eq. (3.4), and we recognize the resemblance of $V_{\text{eff}}(F_1)$ to the lowest adiabatic energy surface in Fig. 1(a) [except, of course, near $r=0$, where the effect of a nonzero value for E_{sp} is omitted from Eq. (4.5)]. Similarly the effective potential energies for F_2 (with $G>0$) and F_3 resemble the highest and middle surfaces in Fig. 1(a), respectively.

When the coupling is sufficiently strong, there will be low-energy solutions of Eq. (4.4) having wave functions localized near the potential minimum. For $r\sim G/\mu\omega^2$, the difference between the potential energies for F_1, F_2, and F_3 is $Gr\sim 2E_G$, while the terms in Eq. (4.4) that couple the different equations are proportional to E_{sp} and $(\hbar^2/2\mu r^2)\sim\hbar\omega(\hbar\omega/4E_G)$. Accordingly, if we have $E_G\gg|E_{sp}|$ and $E_G\gg\hbar\omega$, it will be a good approximation to drop these coupling terms and to seek the low-energy vibronic states by solving the remaining simple radial differential equation (4.4a) for F_1. The term $(\hbar^2/2\mu r^2)(J^2+J+1)$ is approximately constant in the vicinity of the minimum, however, so that the relative energy of the low-energy states is given by

$$E_{\text{I}}(J)=J(J+1)\,\hbar\omega(\hbar\omega/4E_G)\ . \qquad (4.6)$$

In the strong-coupling limit, therefore, the lowest type-I vibronic state is a nondegenerate s-like state ($J=0$, $\Lambda'=+1$), while the first excited state is a p-like triplet ($J=1$, $\Lambda'=-1$), the separation of these levels being given by

$$E_{\text{I}}(1)-E_{\text{I}}(0)=\tfrac{1}{2}\hbar\omega(\hbar\omega/E_G)\ . \qquad (4.7)$$

Since these levels lie lower than the lowest type-II state [a state with $J=1$, $\Lambda'=+1$, and $E=(-\tfrac{1}{2}E_{sp}+\tfrac{5}{2}\hbar\omega)$ as obtained from Eq. (3.21)] by an energy of approximately E_G, the type-I s-like level is the vibronic ground state of the system and the p-like level the first excited state. The order of these levels in strong coupling is therefore independent of the sign of E_{sp}, that is, of the order of the s and p electronic states in the cubic configuration.

Since, under our assumption that $E_G\gg\hbar\omega$, the energy differences of at least the lowest few type-I states (s, p, d, f, ... -like, with $J=0, 1, 2, 3, \ldots$) as given by Eq. (4.6) are $\ll\hbar\omega$, the radial function F_1 obtained by solving Eq. (4.4a) will be approximately the same for these different levels. Since for these states $F_2\sim F_3\sim 0$, we find on inverting Eq. (4.2) that the vibronic wave function for these states is given by Eq. (3.15), with

$$f_1(J,r)=+(2)^{-1/2}F_1\,,$$
$$f_2(J,r)=-[J/2(2J+1)]^{1/2}F_1\,, \qquad (4.8)$$
$$f_3(J,r)=+[(J+1)/2(2J+1)]^{1/2}F_1\,.$$

Normalization of the wave function requires in this case that

$$\int_0^\infty r^2F_1^2\,dr=1\ . \qquad (4.9)$$

V. PROPERTIES OF VIBRONIC STATES

A. Radiative Lifetime

We will now consider the properties of the vibronic eigenstates of the dynamic problem, and we will show how these are related to the properties of the s and p electronic states. We first obtain the lifetime of vibronic states, such as those given by Eqs. (3.15) and (3.16), for radiative decay to a simple nondegenerate s-like electronic ground state, which we denote by $|1s\rangle$. We take the matrix elements of the electric-dipole-moment operator $\vec{D}$ between $|1s\rangle$ and the electronic p states to be given by

$$D=\langle 1s|D_\eta|\rho_\eta\rangle\,, \qquad (5.1)$$

where $\eta=x$, y, or z. As in the work of Henry, Schnatterly, and Slichter,[20] we assume that the vibronic states $\Psi_n(1s)$ associated with $|1s\rangle$ have the simple-product form

$$\Psi_n(1s)=\Phi_n(Q)\,|\,1s\,\rangle \qquad (5.2)$$

and that the associated vibrational functions $\Phi_n(Q)$ form a complete set in the space of the vibrational modes:

$$\sum_n\ \Phi_n^*(Q)\Phi_n(Q')=\delta(Q-Q')\ . \qquad (5.3)$$

The rate of spontaneous emission of light of energy E and polarization η, resulting from a transition from a vibronic level with wave function Ψ_b and energy E_b to the electronic ground state $|1s\rangle$, is given[4] by

$$i_\eta(b,E)=C\sum_n|\langle\Psi_b|D_\eta|\Psi_n(1s)\rangle|^2\delta(E_b-E_n-E)\,, \qquad (5.4)$$

where

$$C=(4nE^3/3\hbar^4c^3)(\mathcal{E}_{\text{eff}}/\mathcal{E}_0)^2\,, \qquad (5.5)$$

n being the refractive index of the medium, c the speed of light in vacuum, and $\mathcal{E}_{\text{eff}}/\mathcal{E}_0$ the local-field correction. In most of this work we will ignore the variation of C over the energy range of the states $\Psi_n(1s)$ to which the transitions occur, on the assumption that the width of the emisson band is small compared with its mean energy. Integrating Eq. (5.4) over E, we then have for $I_\eta(b)$, the total probability per unit time of the emission of a photon of polarization η,

$$I_\eta(b) = C \sum_n |\langle \Psi_b | D_\eta | \Psi_\eta(1s)\rangle|^2 . \tag{5.6}$$

Using the general form (3.22) for Ψ_b, we then obtain from Eqs. (5.1), (5.2), and the completeness relation (5.3), the result

$$I_\eta(b) = CD^2 \int |\Phi_\eta(b)|^2 d\vec{Q} . \tag{5.7}$$

The reciprocal of the radiative lifetime $\tau_r(b)$ of the state Ψ_b is obtained by summing $I_\eta(b)$ over all polarizations η,

$$\tau_r^{-1}(b) = CD^2 \int [|\Phi_x(b)|^2 + |\Phi_y(b)|^2 + |\Phi_z(b)|^2] d\vec{Q} \tag{5.8a}$$

$$= CD^2 [1 - \int |\Phi_s(b)|^2 d\vec{Q}] , \tag{5.8b}$$

where in obtaining the latter form we have used the normalization from Eq. (3.23). It follows that any state for which $\Phi_s(b) = 0$ has a radiative lifetime equal to what we would obtain for the electronic p states in the absence of electron-lattice coupling, namely,

$$\tau_r(p) = (CD^2)^{-1} . \tag{5.9}$$

We therefore obtain a radiative lifetime given by $\tau_r(p)$ for all the type-II vibronic states given by Eq. (3.16), which are made up from the p electronic states alone. For the type-I states, on the other hand, we have from Eqs. (3.15) and (5.8) the general result

$$\tau_r^{-1}(J) = \tau_r^{-1}(p) \int_0^\infty r^2 [f_2^2(J, r) + f_3^2(J, r)] dr . \tag{5.10}$$

In the case of strong coupling this reduces simply to

$$\tau_r^{-1}(J) = \tfrac{1}{2} \tau_r^{-1}(p) \tag{5.11}$$

for the low-energy states for which the f_i are given by Eq. (4.8), where we have also used Eq. (4.9). With strong coupling, therefore, the radiative lifetime $\tau_r(J)$ of the low-energy vibronic states is the same for the different states and equals $2\tau_r(p)$. This factor 2, of course, results from the fact that in strong coupling these low-energy type-I states are equal mixtures of the s and p electronic states, as is seen from Eqs. (4.8) and (4.9).

B. Stark Effects in Emission

If a uniform electric field F is applied to the crystal along the z direction, the perturbation[21] of the defect is given by

$$\mathcal{H}_F = -D_z F_e , \tag{5.12}$$

where F_e is the local effective field. We will now consider the effect of such a field on the vibronic states, their radiative lifetime, and the polarization of their luminescence.

The components of the electric-dipole-moment operator $\vec{D}$ transform like x, y, z, so that the perturbation $\mathcal{H}_F$ can have nonzero matrix elements only between vibronic states of opposite parity Λ' for which the difference in J is 0 or ±1. Since we have taken the field in the z direction, we have the additional selection rule $\Delta M = 0$. We take the matrix elements of $\vec{D}$ between $|2s\rangle$ and the electronic p states to be given by

$$d = \langle 2s | D_\eta | p_\eta \rangle . \tag{5.13}$$

It is then straightforward to show from Eq. (3.15) and the definition of the angular functions that the only nonzero matrix elements of $\mathcal{H}_F$ between different type-I states are given by

$$\langle \Psi_{\mathrm{I}}(J, M, \Lambda') | \mathcal{H}_F | \Psi_{\mathrm{I}}(J+1, M, -\Lambda') \rangle = d'_J(M) F_e$$

$$= dF_e \left(\frac{(J+1)^2 - M^2}{J+1} \right)^{1/2} \int_0^\infty r^2 dr [(2J+1)^{-1/2} f_1(J,r)$$

$$\times f_2(J+1, r) - (2J+3)^{-1/2} f_3(J, r) f_1(J+1, r)] . \tag{5.14}$$

There are, of course, no nonzero matrix elements of $\mathcal{H}_F$ among type-I states having the same value of J, because they all have the same parity $\Lambda' = (-1)^J$. However, between type-I and type-II states of the same J we have nonzero matrix elements given by

$$\langle \Psi_{\mathrm{I}}(J, M, \Lambda') | \mathcal{H}_F | \Psi_{\mathrm{II}}(J, M, -\Lambda') \rangle = dF_e M [J(J+1)]^{-1/2}$$

$$\times \int_0^\infty r^2 f_1(J, r) f_4(J, r) dr . \tag{5.15}$$

We now consider the effect of the electric field in perturbing a nondegenerate type-I vibronic level with $J = 0$. Such an s-like level is the vibronic ground state of the $2s$-p manifold over a rather wide range of circumstances,[22] including the strong-coupling limit as we have seen in Sec. IV, and we are then particularly interested in the effect of various perturbations on this state because it determines the polarization of the luminescence and the radiative lifetime of 0 °K. We can write the perturbed state $\Psi_{\mathrm{I}}^F(0, 0, +1)$ to second order in F_e as

$$\Psi_{\mathrm{I}}^F(0, 0, +1) = (1 + aF_e^2) \Psi_{\mathrm{I}}^0(0, 0, +1) + bF_e \Psi_{\mathrm{I}}(1, 0, -1)$$

$$+ cF_e^2 \Psi_{\mathrm{I}}(2, 0, +1) + eF_e^2 \Psi'_{\mathrm{I}}(0, 0, +1) . \tag{5.16}$$

There is no coupling via $\mathcal{H}_F$ to the type-II states in this case, since $M = 0$ in Eq. (5.15). The functions $\Psi_{\mathrm{I}}(1, 0, -1)$, $\Psi_{\mathrm{I}}(2, 0, +1)$, and $\Psi'_{\mathrm{I}}(0, 0, +1)$ in Eq. (5.16) in the general case will be linear combinations of the eigenstates of the unperturbed dynamic problem, since there are nonzero matrix elements as in Eq. (5.14) to many of the eigenstates of higher energy. The term $eF_e^2\Psi_{\mathrm{I}}'(0,\,0,\,+1)$ represents the second-order contribution of $J=0$ states different from the unperturbed state $\Psi_{\mathrm{I}}^0(0,\,0,\,+1)$. However, the predominant perturbation of the ground state will often be due to the states with $J=1,\,2$ that lie closest in energy, since the energy difference appearing in the denominator of the perturbation coefficients a, b, and c in Eq. (5.16) is smallest for these states. As we will show later, in the strong-coupling limit it is for many purposes only these nearest states that are important, and we will limit our analysis here to this simple case. The generalization necessary when coupling is to more than one state or when coupling to other $J=0$ states must be included can be made in a straightforward way.

We therefore take the perturbation in Eq. (5.16) to involve only the state of lowest energy from each of the sets of p- and d-like type-I eigenstates with $J=1$ and 2. The coefficients a, b, and c in Eq. (5.16) are then given in terms of the reduced dipole matrix elements defined in Eq. (5.14) by

$$a=-\tfrac{1}{2}b^2\,,$$

$$b=-\frac{d_0'(0)}{E_{\mathrm{I}}(1)-E_{\mathrm{I}}(0)}, \qquad (5.17)$$

$$c=+\frac{d_0'(0)\,d_1'(0)}{[E_{\mathrm{I}}(1)-E_{\mathrm{I}}(0)][E_{\mathrm{I}}(2)-E_{\mathrm{I}}(0)]}\,,$$

and the second-order shift in the energy of the $J=0$ ground state is

$$\Delta E(0)=-\frac{[d_0'(0)]^2F_e^2}{E_{\mathrm{I}}(1)-E_{\mathrm{I}}(0)}\,. \qquad (5.18)$$

The change in the radiative lifetime of this level to order F_e^2 may be obtained easily from Eq. (5.8b) if we use Eqs. (5.16) and (3.24a) to obtain the coefficient of $|2s\rangle$ in the perturbed wave function. (For simplicity, we ignore any perturbation of the electronic ground state $|1s\rangle$ caused by the applied field, on the assumption that the dominant effects are due to the mixing of the states $|2s\rangle$ and $|2p\rangle$, which are assumed to be close together in energy compared to the separation of the states $|1s\rangle$ and $|2p\rangle$.) Because of the orthogonality of the spherical harmonics $Y_{0,0}$ and $Y_{2,0}$ under integration over $\vec{\mathrm{Q}}$, we see that the term in $\Psi_{\mathrm{I}}(2,\,0,\,+1)$ in Eq. (5.16) does not contribute to the lifetime to order F_e^2, and we have

$$\tau_r^{-1}(0^F)=\tau_r^{-1}(0)-CD^2F_e^2\Big[2a\int|\Phi_s(0)|^2\,d\vec{\mathrm{Q}}$$
$$+b^2\int|\Phi_s(1)|^2\,d\vec{\mathrm{Q}}\,\Big]. \qquad (5.19)$$

Using Eqs. (5.8b) and (5.17), we therefore have

$$\Delta[\tau_r^{-1}(0)]=F_e^2\left(\frac{d_0'(0)}{E_{\mathrm{I}}(1)-E_{\mathrm{I}}(0)}\right)^2[\tau_r^{-1}(1)-\tau_r^{-1}(0)]\,. \qquad (5.20)$$

The change in radiative lifetime of the ground state[23] is therefore proportional to the difference in lifetime between the s-like ground state and the p-like state that is mixed with it by the field.

A more complicated result than that for the radiative lifetime is obtained for the linear polarization $P(0)$ induced by the field in the luminescence from the $J=0$ ground state. To calculate this induced polarization, we must use Eq. (5.7) and the expressions given for $\Phi_{\mathrm{I}\eta}(J,\,M,\,\Lambda')$ ($\eta=x,\,y,\,z$) in Eq. (3.24). Defining the polarization P in the usual way,

$$P=\frac{I_\parallel-I_\perp}{I_\parallel+I_\perp}\,, \qquad (5.21)$$

where in the present situation we have $I_\parallel=I_z$, $I_\perp=I_x=I_y$, we obtain to order F_e^2

$$P(0)=\tfrac{3}{2}F_e^2\Big[\int_0^\infty r^2f_3^2(0,\,r)\,dr\Big]^{-1}$$
$$\times\int_0^\infty r^2\{b^2[f_2^2(1,\,r)+(10)^{-1}f_3^2(1,\,r)]$$
$$-(2)^{1/2}cf_3(0,\,r)f_2(2,\,r)\}\,dr\,. \qquad (5.22)$$

In the general case, the expression for $P(0)$ in Eq. (5.22) depends on the wave functions in a complicated way and shows no simple relationship to the change in radiative lifetime, Eq. (5.20). In the strong-coupling limit we may simplify Eq. (5.22), however, using Eqs. (4.8) and (4.9), to obtain

$$P(0)=\tfrac{3}{5}F_e^2(b^2+c\sqrt{5})\,. \qquad (5.23)$$

In this limit, we have from Eq. (5.14),

$$d_0'(0)=-(3)^{-1/2}d,\quad d_1'(0)=-2(15)^{-1/2}d, \qquad (5.24)$$

so that we obtain from Eq. (5.17),

$$P(0)=\tfrac{1}{3}d^2F_e^2[E_{\mathrm{I}}(1)-E_{\mathrm{I}}(0)]^{-2}, \qquad (5.25)$$

where we have used the relationship $[E_{\mathrm{I}}(2)-E_{\mathrm{I}}(0)]=3[E_{\mathrm{I}}(1)-E_{\mathrm{I}}(0)]$ from Eq. (4.6). The change in the radiative lifetime is zero in the strong-coupling limit, aside from the change resulting from the shift in the emission band,[23] the expression in Eq. (5.20) vanishing because $\tau_r(J)$ was shown in Eq. (5.11) to be independent of J in this limit. This result is also evident from Eq. (5.19), because, as we have seen, in the strong-coupling limit the low-energy states are equal mixtures of the s and p electronic states, so that $\int|\Phi_s(J)|^2\,d\vec{\mathrm{Q}}=\frac{1}{2}$. The radiative lifetime is therefore independent of how these states are mixed and is given by $2\tau_r(p)$. The conclusion that the field-induced change in the radiative lifetime is zero in the strong-coupling limit remains valid even when coupling to states of higher energy, such as those associated with the middle and upper energy surfaces in Fig. 1 which were ignored in deriving Eq. (5.20), is included.

Bogan and Fitchen[1] observed a shift proportional to F^2 in the average energy of the luminescence. This is not, however, equal to the level shift $\Delta E(0)$

given by Eq. (5.18), because the intensity distribution of the emission over the vibrational levels of the $|1s\rangle$ state is, in general, changed by mixing the excited states into the $J=0$ ground state. We have not succeeded in obtaining a simple general formula analogous to Eq. (5.20) or (5.22) either for this average energy shift or for the field-induced broadening of the emission band.

In concluding this discussion of the Stark effects, we want to show that for strong coupling it is the lowest p- and d-like levels with $J=1$ and 2 that are mainly responsible for perturbing the s-like ground state. For all three of these levels the radial functions $f_i(J, r)$ are given to a good approximation in Eq. (4.8) in terms of the same function F_1, the lowest-energy solution of Eq. (4.4a) (for which $F_2 \sim F_3 \sim 0$). There are, of course, higher-energy solutions $F_1^{(n)}$ of Eq. (4.4a), and the resulting sequence of levels for a given J has an energy separation $\sim \hbar\omega$, but to a good approximation these are orthogonal to F_1: $\int r^2 F_1 F_1^{(n)}\, dr \sim 0$. We see therefore from Eqs. (4.8) and (5.14) that states formed with these higher-energy radial functions $F_1^{(n)}$ will have negligibly small matrix elements of $\mathcal{H}_F$ with the low-energy states formed from F_1. On the other hand, there are nonzero matrix elements of $\mathcal{H}_F$ to states associated with the middle energy surface in Fig. 1 and formed from F_3 (for which $F_1 \sim F_2 \sim 0$). For such states, however, the perturbation-energy denominator in Eq. (5.17) is $\sim 2E_G$. Since $E_G \gg \hbar\omega$ for strong coupling, the effect of such states on the ground state is thus negligible compared to that of the low-energy states whose separations are given by Eq. (4.6). The latter are therefore the only ones that contribute significantly in perturbing the ground state in the strong-coupling limit.

C. Reduction Factors for Vibronic States

The $(2J+1)$-fold degeneracy of one of the vibronic levels is lifted by a perturbation that lifts the threefold degeneracy of the electronic p states $|p_x\rangle$, $|p_y\rangle$, and $|p_z\rangle$ in the cubic configuration. We may relate the matrix elements of such a perturbation within a given level to the electronic interaction by introducing "reduction factors" analogous to those which have proved useful in the theory of the dynamic Jahn-Teller effect.[14] The form which this interaction takes within a level is of course determined by symmetry, but the size of the matrix elements and thus the magnitude of the initial linear splitting of the level are proportional to the appropriate reduction factor, which itself depends only on the strength of the electron-lattice coupling $\mathcal{H}_{eL}$.

A perturbation that splits a p (Γ_4^-) state in first order must belong to one of the irreducible representations Γ_3^+, Γ_4^+, or Γ_5^+ or O_h. Representative electronic operators of these three types may be defined in terms of the components l_x, l_y, and l_z of the orbital angular momentum given by Eq. (3.9), which themselves belong to Γ_4^+. For Γ_3^+ we may use $l_z^2 - \frac{1}{2}(l_x^2 + l_y^2)$ and $(3/4)^{1/2}(l_x^2 - l_y^2)$, and for Γ_5^+, $(3/4)^{1/2} \times (l_x l_y + l_y l_x)$, $(3/4)^{1/2}(l_y l_z + l_z l_y)$, and $(3/4)^{1/2}(l_z l_x + l_x l_z)$. However, taking account of the full rotational symmetry of our vibronic model in the combined space of electronic and vibrational coordinates, we recognize that these last five electronic operators transform in the same way as a set of functions belonging to $J=2$ with parity $\Lambda' = +1$. The reduction factors for Γ_3^+ and Γ_5^+ operators in any given level are therefore the same in our model, instead of being independent parameters as they would be if the model had only cubic (O_h) symmetry. We recognize also that l_x, l_y, and l_z transform as $J=1$, $\Lambda' = +1$.

To obtain reduction factors for these two sets of operators in a given level, we need evaluate only one nonzero matrix element for one operator from each set. We will do this only for the type-I states of Eq. (3.15), for which we obtain

$$\begin{aligned} &\langle \Psi_{\rm I}(J, M, \Lambda') | l_z | \Psi_{\rm I}(J, M, \Lambda') \rangle = M J^{-1} K_J(T_1), \\ &\langle \Psi_{\rm I}(J, M, \Lambda') | l_z^2 - \tfrac{1}{2}(l_x^2 + l_y^2) | \Psi_{\rm I}(J, M, \Lambda') \rangle \\ &\qquad = -(2J^2)^{-1}[J(J+1) - 3M^2] K_J(E), \end{aligned} \tag{5.26}$$

with the reduction factors $K_J(T_1)$ for Γ_4^+ operators and $K_J(E)$ for Γ_3^+ and Γ_5^+ operators given by

$$\begin{aligned} K_J(T_1) &= \int_0^\infty r^2 [f_2^2(J, r) - J(J+1)^{-1} f_3^2(J, r)]\, dr, \\ K_J(E) &= \int_0^\infty r^2 [J(2J-1)^{-1} f_2^2(J, r) \\ &\qquad + J^2(J+1)^{-1}(2J+3)^{-1} f_3^2(J, r)]\, dr . \end{aligned} \tag{5.27}$$

$K_J(T_1)$ is the appropriate reduction factor for perturbations such as a magnetic field or spin-orbit interaction, while $K_J(E)$ is appropriate for splittings due to applied stress. For strong coupling and states given by Eq. (4.8), we find the limiting values

$$K_J(T_1) = 0, \quad K_J(E) = J^2(2J-1)^{-1}(2J+3)^{-1}. \tag{5.28}$$

In the strong-coupling limit the magnetic splitting of the low-energy states is therefore completely quenched, as we expect from the similar result for a dynamic Jahn-Teller effect (these results pertain to the Zeeman effect due to the orbital magnetic moment but not, of course, to that due to spin). The effect of applied stress is not entirely quenched, however; we have in particular for a p-like level $(J=1)$ the limiting value $K_1(E) = \frac{1}{5}$, so that the strain splitting of this level is reduced by 80% compared to the splitting of the electronic p states.

D. Magnetic Polarization of Emission

A magnetic field H applied in the z direction gives rise to the orbital Zeeman interaction

$$\mathcal{H}_H^{\mathrm{orb}} = g_L \mu_B H l_z , \tag{5.29}$$

where $\mu_B = e\hbar/2mc$ is the Bohr magneton and g_L is the orbital g factor of the electronic p states. We omit electron spin for the time being and consider the effect of $\mathcal{H}_H^{\mathrm{orb}}$ in inducing circular polarization in the luminescence from the vibronic ground state, which we again take to be an s-like state (type I) with $J=0$, $\Lambda' = +1$.

The matrix elements of the components of $\vec{1}$ must obey the selection rules $\Delta J = 0$ or 1 and cannot connect two states with $J=0$, since $\vec{1}$ transforms as $J=1$. Moreover, since $\vec{1}$ commutes with ρ_0 and therefore with Λ, it can only couple states of the same parity Λ'. It follows that $\mathcal{H}_H^{\mathrm{orb}}$ in Eq. (5.29) cannot couple an s-like (type-I) state ($J=0$, $\Lambda' = +1$) to any other type-I state, since the only such states that would satisfy the selection rule $\Delta J = 1$ are the p-like states, which have $\Lambda' = -1$. As a consequence, the only vibronic states having nonzero matrix elements of $\mathcal{H}_H^{\mathrm{orb}}$ with an s-like state are type-II states (3.16) with $J=1$. The states that are mixed into the vibronic ground state by a magnetic field are therefore altogether distinct from those which are admixed by an electric field. We have for these matrix elements,

$$\langle \Psi_{\mathrm{II}}(1,\ 0,\ +1) | \mathcal{H}_H^{\mathrm{orb}} | \Psi_{\mathrm{I}}(0,\ 0,\ +1) \rangle = -(2/3)^{1/2} g_L \mu_B H \int_0^\infty r^2 f_3(0,\ r) f_4(1,\ r)\, dr . \tag{5.30}$$

The perturbed ground state is then to first order in H,

$$\Psi_{\mathrm{I}}^H(0,\ 0,\ +1) = \Psi_{\mathrm{I}}(0,\ 0,\ +1) + g_L \mu_B H \sum_n t_n \Psi_{\mathrm{II}}^{(n)}(1,\ 0,\ +1), \tag{5.31}$$

where the summation is over the various type-II states with $J=1$, $M=0$, and we have

$$t_n = +(2/3)^{1/2} [E_{\mathrm{II}}^{(n)}(1) - E_{\mathrm{I}}(0)]^{-1} \times \int_0^\infty r^2 f_3(0,\ r) f_4^{(n)}(1,\ r)\, dr . \tag{5.32}$$

Using Eq. (5.7) with $\Phi_\pm = (2)^{-1/2}(\Phi_x \mp i\Phi_y)$ to obtain the emission probabilities $I_+(0)$ and $I_-(0)$ for light with left- and right-handed circular polarization, respectively, along the magnetic field, we obtain from Eqs. (3.24c) and (3.25c)

$$I_\pm(0) = \tfrac{1}{2} C D^2 \int_0^\infty r^2 \Big(\mp (2/3)^{1/2} f_3(0,\ r) + g_L \mu_B H \sum_n t_n f_4^{(n)}(1,\ r) \Big)^2 dr \tag{5.33}$$

and

$$I_+(0) - I_-(0) = -(4/3) C D^2 g_L \mu_B H \times \sum_n \left[\int_0^\infty r^2 f_3(0,\ r) f_4^{(n)}(1,\ r)\, dr \right]^2 \times [E_{\mathrm{II}}^{(n)}(1) - E_{\mathrm{I}}(0)]^{-1} . \tag{5.34}$$

We can simplify this result if we can replace $[E_{\mathrm{II}}^{(n)}(1) - E_{\mathrm{I}}(0)]$ by $[\bar{E}_{\mathrm{II}} - E_{\mathrm{I}}(0)]$, which represents the average energy difference between the ground state and the type-II states with which it interacts significantly, and which for strong coupling is approximately equal to $2E_G$. The functions $f_4^{(n)}(1,\ r)$ form a complete set of radial functions satisfying

$$\sum_n \int_0^\infty r'^2 g(r') f_4^{(n)}(J,\ r) f_4^{(n)}(J,\ r')\, dr' = g(r) \tag{5.35}$$

for an arbitrary $g(r)$, so that we have for Eq. (5.34),

$$I_+(0) - I_-(0) = -(4/3) C D^2 g_L \mu_B H [\bar{E}_{\mathrm{II}} - E_{\mathrm{I}}(0)]^{-1} \times \int_0^\infty r^2 f_3^2(0,\ r)\, dr = -(4/3) g_L \mu_B H \tau_r^{-1}(0) [\bar{E}_{\mathrm{II}} - E_{\mathrm{I}}(0)]^{-1}, \tag{5.36}$$

where we have used Eqs. (5.9) and (5.10). We may express this result finally in the form

$$\Delta_d(0) \equiv \frac{I_+(0) - I_-(0)}{I_+(0) + I_-(0)} = -\frac{2 g_L \mu_B H}{\bar{E}_{\mathrm{II}} - E_{\mathrm{I}}(0)} . \tag{5.37}$$

The negative sign of $\Delta_d(0)$ thus favors emission of light right circularly polarized when the propagation vector is in the direction of the magnetic field.

When we take into account the electron spin, we must include the spin-orbit interaction

$$\mathcal{H}_{so} = \lambda \vec{1} \cdot \vec{S}, \tag{5.38}$$

which also mixes the ground state only with the type-II excited states. Introducing the spin states $|+\tfrac{1}{2}\rangle$ and $|-\tfrac{1}{2}\rangle$ quantized with respect to the z direction, we have for the perturbed ground state

$$\Psi_{\mathrm{I}}'(0,\ 0,\ +1;\ \pm\tfrac{1}{2}) = \Psi_{\mathrm{I}}(0,\ 0,\ +1) |\pm\tfrac{1}{2}\rangle \mp (2)^{-1/2} \lambda \sum_n t_n \Psi_{\mathrm{II}}^{(n)}(1,\ \pm 1,\ +1) |\mp\tfrac{1}{2}\rangle \pm \frac{1}{2} \lambda \sum_n t_n \Psi_{\mathrm{II}}^{(n)}(1,\ 0,\ +1) |\pm\tfrac{1}{2}\rangle, \tag{5.39}$$

where t_n was given in Eq. (5.32). The second term on the right-hand side of Eq. (5.39) leads to a small probability that the spin will flip in the optical transition to the electronic ground state $|1s\rangle$, while the third term induces circular polarization in the luminescence by interfering with the matrix elements from the first term. The calculation of this polarization resulting from a net spin polarization $\langle S_z \rangle$ proceeds exactly as in the derivation of Eq. (5.37). Combining this result with that of Eq. (5.37) under the same simplifications assumed in the earlier derivation, we obtain for the total circular polarization $\Delta(0)$ of the emission from the vibronic ground state

$$\Delta(0) \equiv \frac{I_+(0) - I_-(0)}{I_+(0) + I_-(0)} = -\frac{2(g_L \mu_B H + \lambda \langle S_z \rangle)}{\bar{E}_{\mathrm{II}} - E_{\mathrm{I}}(0)} . \tag{5.40}$$

We have defined $\langle S_z \rangle = \tfrac{1}{2}(p_+ - p_-)$, where p_+ and p_- denote, respectively, the probabilities that the spin has values $S_z = +\frac{1}{2}$ and $-\frac{1}{2}$ in the vibronic ground state of the excited electronic state, and we have $(p_+ + p_-) = 1$.

E. *g* Factor of Relaxed Excited State

We can now easily calculate the change δg in the g factor of the s-like vibronic ground state, which results from the vibronic mixing of the s and p electronic states. Using the wave function as given by Eq. (5.39), which is correct to first order in the spin-orbit interaction, we evaluate the diagonal matrix elements of $\mathcal{H}_H^{\text{orb}}$ as given by Eq. (5.29) and define δg by the relation

$$\pm\tfrac{1}{2}\delta g \mu_B H = \langle \Psi_{\text{I}}'(0,\ 0,\ +1;\ \pm\tfrac{1}{2}) | \mathcal{H}_H^{\text{orb}} | \Psi_{\text{I}}'(0,\ 0,\ +1;\ \pm\tfrac{1}{2}) \rangle\,. \tag{5.41}$$

From Eqs. (5.30), (5.32), and (5.39), we obtain

$$\delta g = -(4/3)\lambda g_L \sum_n [E_{\text{II}}^{(n)}(1) - E_{\text{I}}(0)]^{-1} \times \left[\int_0^\infty r^2 f_3(0,\ r) f_4^{(n)}(1,\ r)\, dr\right]^2. \tag{5.42}$$

Replacing $[E_{\text{II}}^{(n)}(1) - E_{\text{I}}(0)]$ by the average energy difference $[\overline{E}_{\text{II}} - E_{\text{I}}(0)]$ as done previously, and using the completeness relation Eq. (5.35), we obtain the general result

$$\delta g = -\frac{4}{3}\, \frac{\lambda g_L}{\overline{E}_{\text{II}} - E_{\text{I}}(0)}\, \frac{\tau_r(p)}{\tau_r(0)}\,, \tag{5.43}$$

where we have also made use of Eq. (5.10). Since the spin-orbit parameter λ is presumably negative, as has been found to be so in the unrelaxed configuration for all of the alkali halides for which it has been measured, we see from Eq. (5.43) that this vibronic contribution to the g shift in the relaxed excited state should be positive.

F. Stress-Induced Polarization of Emission

The linear polarization of the emission that results when stress is applied to the crystal may be derived in a manner similar to that used in Sec. V B to obtain the electric-field-induced polarization, but the calculation is simpler because the stress-induced polarization is a first-order effect. For simplicity, we shall consider only the case of uniaxial stress applied in the [001] or [111] direction, and we consider as before only the polarization of the emission from an s-like ground state.

The coupling of the electronic p states to a uniform strain introduced in the crystal by an applied stress may be expressed in a standard form[14, 17] for an orbital triplet state in cubic symmetry as

$$\mathcal{H}_S = V_2(e_\theta \mathcal{E}_\theta + e_\epsilon \mathcal{E}_\epsilon) + V_3(e_{yz}\mathcal{T}_\xi + e_{zx}\mathcal{T}_\eta + e_{xy}\mathcal{T}_\zeta), \tag{5.44}$$

where we define the electronic operators as $\mathcal{E}_\theta = l_z^2 - \frac{1}{2}(l_x^2 + l_y^2)$, $\mathcal{E}_\epsilon = (\frac{1}{2}\sqrt{3})(l_x^2 - l_y^2)$, $\mathcal{T}_\xi = l_y l_z + l_z l_y$, $\mathcal{T}_\eta = l_z l_x + l_x l_z$, $\mathcal{T}_\zeta = l_x l_y + l_y l_x$. V_2 and V_3 are appropriate strain strain coupling coefficients, e_{ij} is a component of the strain tensor

$$e_{ij} = e_{ji} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)\,, \tag{5.45}$$

and we define

$$\begin{aligned} e_\theta &= e_{zz} - \tfrac{1}{2}(e_{xx} + e_{yy})\,, \\ e_\epsilon &= (\tfrac{1}{2}\sqrt{3})(e_{xx} - e_{yy})\,. \end{aligned} \tag{5.46}$$

From the transformation properties of the electronic operators in Eq. (5.44), noted already in Sec. V C, we see that their matrix elements with respect to the vibronic states must obey the selection rules $\Delta J \leq 2$, $\Delta\Lambda' = 0$. In particular, the only states admixed in first order with an s-like (type-I) state are the d-like type-I states with $J = 2$, $\Lambda' = +1$. Assuming uniaxial stress along [001] so that the only nonzero component of the strain is e_θ, we obtain then for the perturbed ground-state wave function

$$\Psi_{\text{I}}^S(0,\ 0,\ +1) = \Psi_{\text{I}}(0,\ 0,\ +1) + s\Psi_{\text{I}}(2,\ 0,\ +1), \tag{5.47}$$

where

$$s = -(2)^{-1/2} V_2 e_\theta [E_{\text{I}}(2) - E_{\text{I}}(0)]^{-1} \times \int_0^\infty r^2 f_3(0,\ r) f_2(2,\ r)\, dr\,. \tag{5.48}$$

As discussed in Sec. V B, we limit our treatment to the case in which only the perturbation from the nearest level with $J = 2$ is important. The probabilities $I_z(0)$ and $I_x(0)$ for emission with polarization parallel and perpendicular the stress, respectively, are then obtained from Eq. (5.7) with Φ_z and Φ_x given by Eqs. (5.47), (3.22), and (3.24). Defining the polarization P as in Eq. (5.21), we obtain finally the result

$$P(0) = \tfrac{3}{2} V_2 e_\theta [E_{\text{I}}(2) - E_{\text{I}}(0)]^{-1} \times \left[\int_0^\infty r^2 f_3(0,\ r) f_2(2,\ r)\, dr\right]^2. \tag{5.49}$$

In the strong-coupling limit this is found from Eqs. (4.8) and (4.9) to be given by

$$P(0) = (3/20) V_2 e_\theta [E_{\text{I}}(2) - E_{\text{I}}(0)]^{-1}\,. \tag{5.50}$$

For a uniaxial stress along [111] we have $e_\theta = e_\epsilon = 0$ and $e_{xy} = e_{yz} = e_{zx} = \frac{1}{2} e_T$. A similar analysis then leads to results for the polarization identical to Eqs. (5.49) and (5.50) if $V_2 e_\theta$ is replaced by $V_3 e_T$ in these expressions.

VI. COMPARISON WITH EXPERIMENT

A number of different experiments have now been carried out which yield information concerning the nature of the relaxed excited state of the F center; we will consider in this section principally the measurements of the radiative lifetime and its temperature dependence,[3, 24] the change in the radiative lifetime in an applied electric field,[3] and the polarization induced in the luminescence by electric fields,[1,2] magnetic fields,[25,26] and applied stresses.[27] The fact that the radiative lifetime in KCl, KBr, KI, and NaCl was found by Swank and Brown[24] to be from 10 to 100 times longer than one expects from the oscillator strength in absorption can be explained, as Fowler[28] has shown, if the $2p$ electronic state in the relaxed configuration is very much more diffuse spatially than in the unrelaxed configuration. Alternatively, Swank and Brown suggested that the longer lifetime might result because the lowest level of the excited state in the relaxed configuration is a state of even parity, such as the $2s$ state, so that luminescence requires the simultaneous emission of a phonon. The latter model, with a nondegenerate state lowest, is favored by the evidence that this lowest state is not split by stress or by an electric or magnetic field. Such evidence is provided, in the data of Hetrick and Compton,[27] for KCl, NaCl, RbCl, and NaF with an applied stress, in that of Bogan and Fitchen[1] for KCl, KF, RbCl, and NaF with an electric field, and in that of Fontana and Fitchen[25,26] for KF and KCl with a magnetic field, by the absence of any temperature-dependent component varying as T^{-1}, which should result from such a splitting, in the polarization of the luminescence occurring at low temperature in the presence of the external perturbation. A nondegenerate ground state is also consistent with the observation[29,30] of a simple isotropic electron-spin resonance in the relaxed excited state. The suggestion that this lowest state is an s-like level of even parity is supported by the fact, shown by Stiles *et al.*[3] for KCl, NaF, and KF, that its radiative lifetime *decreases* in an electric field, presumably because the field mixes this state with an excited odd-parity p-like state having a shorter lifetime. This model, which is the basis of the interpretation given by Bogan and Fitchen[1] and by Stiles *et al.*[3] for the Stark effects in the luminescence, does not of course preclude the possibility that the $2p$ electronic state is spatially diffuse, as in Fowler's calculations,[28] even though it is not the lowest level in the relaxed configuration. Indeed, the recent detailed calculations of Wood and Opik,[6] which place the $2s$ state below $2p$ in the relaxed configuration for KCl, KBr, KI, and NaCl, give strong support to the hypothesis that the $2p$ state expands substantially as a result of the symmetric lattice relaxation associated with the large Stokes shift.[31]

The temperature dependence of the radiative lifetime[3] and of the electric-field-induced polarization of the luminescence[1] enables us to determine the energy separation δE between the lowest level of the excited electronic state in the relaxed configuration and the nearest excited level. To correct for the effect of the temperature-dependent shift of the F band on the radiative lifetime τ_r through the factor E^3 in Eq. (5.5), we define a quantity[3]

$$M^2 = (\tau_r \langle E^3 \rangle)^{-1} . \tag{6.1}$$

The temperature dependence of M^2 below ~100 °K was then found by Stiles *et al.*[3] to be described quite well for KCl, KF, and NaF by the expression

$$\frac{M^2(T)}{M^2(0)} = \frac{1 + 3R e^{-\delta E/kT}}{1 + 3\, e^{-\delta E/kT}} . \tag{6.2}$$

This expression is appropriate if the lowest level is s-like and the excited state a p-like triplet, and R is then the ratio of the lifetimes of these levels,

$$R = \tau_r(0)/\tau_r(1) . \tag{6.3}$$

The excitation energy δE was found to be 18 meV for KCl and 17 meV for KF and NaF, the corresponding values for R being 2.75, 2.75, and 5.6, respectively. Similar values for δE (18, 16, 12, and 15.5 meV for KCl, KF, NaF, and RbCl, respectively) were obtained by Bogan and Fitchen[1] from a similar analysis of the temperature dependence of the electric-field-induced polarization of the luminescence. A similar but somewhat smaller value for δE in KCl, 14.2 meV, has also been obtained by Ruedin[30] from the temperature dependence of the spin-lattice relaxation time (Orbach process) in the relaxed excited state. For KF, however, Ruedin's value $\delta E = 7.1$ meV is less than half that obtained from the Stark-effect studies. Ruedin has also obtained in this way values for δE for a number of crystals for which the Stark-effect data are not available: NaCl, 9.4 meV; KBr, 9.4 meV; KI, 6.5 meV; RbBr, 7 meV; RbI, 7.2 meV.

To test if our vibronic model with strong electron-lattice coupling for the Γ_4^- vibrational modes might be appropriate for an interpretation of these data, we can compare these values for δE with the separation of the lowest vibronic levels predicted by Eq. (4.7). Since we must have $E_G \gg \hbar\omega$ if this model with strong coupling is appropriate, it follows from Eq. (4.7) that δE should be very much smaller than one-half the energy of the effective vibrational mode which best represents the coupling of the F center with the Γ_4^- modes of its environment. This is, however, clearly not the case. In KI and KBr, an optically active Γ_4^- mode of the F center has been identified[32] at 10.2 and 12.3 meV, lying within the gap between the acoustic- and optical-phonon branches of the perfect crystal. In KCl there is no such gap, but the highest phonon energy of the crystal (the LO mode at $\vec{q} = 0$, with $\hbar\omega_{\mathrm{LO}} = 26.8$ meV), as determined by neutron diffraction,[33] is less than twice the experimental value for δE. Indeed, this value for δE is very close to the energy[33] of the TO mode (at $\vec{q} = 0$) $\hbar\omega_{\mathrm{TO}} = 18.5$ meV. Similarly, for RbCl[34] we have $\hbar\omega_{\mathrm{TO}} = 15.4$ meV, $\hbar\omega_{\mathrm{LO}} = 21.4$ meV; for RbBr[35] $\hbar\omega_{\mathrm{TO}} = 11.2$ meV, $\hbar\omega_{\mathrm{LO}} = 16.1$ meV; and for RbI[35]

$\hbar\omega_{TO} = 9.7$ meV, $\hbar\omega_{LO} = 13.4$ meV. For KF, NaF, and NaCl, δE is somewhat smaller relative to these phonon energies ($\hbar\omega_{TO} = 23.4$ meV, $\hbar\omega_{LO} = 40.2$ meV for KF[35]; $\hbar\omega_{TO} = 31.0$ meV, $\hbar\omega_{LO} = 52.5$ meV for NaF[36]; $\hbar\omega_{TO} = 21.4$ meV, $\hbar\omega_{LO} = 32.7$ meV for NaCl[37]), but not enough so to possibly be consistent with Eq. (4.7) if we have $E_G \gg \hbar\omega$. We conclude from this comparison that the strong-coupling model is not consistent with the experimental values for δE.

We have also seen that the strong-coupling model predicts that the radiative lifetimes are the same for the different low-energy levels and are equal to $2\tau_r(p)$ according to Eq. (5.11). The fairly large values for the lifetime ratio R obtained from the data are therefore also inconsistent with the strong-coupling model, In addition, we have seen that the electric-field-induced change in the radiative lifetime of the lowest level should approach zero in the strong-coupling limit, since the s and p electronic states are then already fully mixed by the vibronic coupling, and we would expect from Eqs. (5.20) and (5.25) that $\Delta M^2(0)/M^2(0)$ [obtained[23] from $\Delta\tau_r(0)/\tau_r(0)$ using Eq. (6.1)] would then be much smaller than the induced polarization $P(0)$. In fact these quantities are found to have values that differ by less than a factor of 2.[1,3] We conclude from these various data that the experimental situation cannot be in or very near the strong-coupling limit, and that an interpretation of these results must be sought instead in the regime of weak or intermediate coupling strength. This conclusion contrasts with previous interpretations[1-3] of the Stark-effect measurements, which concluded that the $2s$ and $2p$ electronic states were strongly mixed by the coupling with the Γ_4^- vibrational modes.

If the coupling is at least moderately strong, an estimate for the coupling energy E_G can be obtained from the diamagnetic part of the magnetic circular polarization of the luminescence, as given by Eq. (5.37), since in this case the energy denominator in this equation is approximately equal to $2E_G$ and we have

$$\Delta_d(0) = -g_L\mu_B H/E_G\,. \qquad (6.4a)$$

Fontana and Fitchen[25] obtained the value $\Delta_d(0)/H = -(6\pm1)\times10^{-8}$ for KF (H in gauss), and Fontana[26] found $\Delta_d(0)/H = -(9\pm1)\times10^{-8}$ for KCl. The orbital g factor as obtained for the unrelaxed configuration from a moment analysis of the magnetic circular dichroism of the F-band absorption is $g_L = 0.95 \pm 0.1$ for KCl[38] and $g_L \sim 1$ for KF.[39] Using this value of g_L to approximate that for the relaxed configuration, we obtain from Eq. (6.4a) the estimates 0.095 and 0.06 eV, respectively, for E_G in KF and KCl. These values, if correct, would be indicative of a coupling of intermediate strength, since they are several times larger than the energies of optical-mode phonons in these crystals.

Alternatively, if the coupling is weak and if we have $E_{sp} < 0$, so that the $2s$ electronic state is below $2p$ in the cubic configuration, the energy denominator in Eq. (5.37) is approximately $|E_{sp}|$ and we have

$$\Delta_d(0) = -2g_L\mu_B H/|E_{sp}|\,. \qquad (6.4b)$$

This interpretation of the data then leads to estimates for $|E_{sp}|$ of 0.19 and 0.12 eV, respectively, for KF and KCl.

We may seek an independent estimate for E_G from a moment analysis of the vibrational broadening of the F band in absorption and of the stress-induced linear dichroism. (It must be noted, however, that such an analysis of the absorption data gives the coupling strengths for the various modes appropriate to the unrelaxed configuration, and these may be changed significantly in the relaxed configuration because of the large relaxation of the totally symmetric mode.) Henry and co-workers[20,40] have shown that, if in the excited state of the F center one considers only the $2p$ electronic states and their linear coupling to the Γ_1^+, Γ_3^+, and Γ_5^+ vibrational modes, the second moment of the F band in absorption is the sum of four separate terms resulting from the spin-orbit splitting and these three types of modes:

$$\langle E^2\rangle = \langle E^2\rangle_{so} + \langle E^2\rangle_1 + \langle E^3\rangle_3 + \langle E^2\rangle_5\,. \qquad (6.5)$$

If we approximate the broadening due to each type of mode as resulting from a single mode of a suitably averaged frequency, the vibrational components take the form

$$\begin{aligned} \langle E^2\rangle_1 &= (\hbar\omega_1)\,E_A \coth(\hbar\omega_1/2kT)\,, \\ \langle E^2\rangle_3 &= (\hbar\omega_3)(E_{JT})_E \coth(\hbar\omega_3/2kT)\,, \qquad (6.6) \\ \langle E^2\rangle_5 &= \tfrac{3}{2}\,(\hbar\omega_5)(E_{JT})_T \coth(\hbar\omega_5/2kT)\,, \end{aligned}$$

where $(E_{JT})_E$ and $(E_{JT})_T$ are the Jahn-Teller energies for the $2p$ state as defined in Eq. (3.6), and E_A is the corresponding stabilization energy associated with the Γ_1^+ totally symmetric mode. The spin-orbit component $\langle E^2\rangle_{so}$ can be determined from magneto-optic experiments, while the three vibrational components in Eq. (6.6) can be determined separately from the second moment, Eq. (6.5), and the first and third moments of the stress-induced linear dichroism for stress applied along $\langle 100\rangle$ and $\langle 110\rangle$.[20,40] Such measurements have been made for F centers by Schnatterly[41] and Hetrick,[42] and the latter has determined the separate average frequencies ω_1, ω_3, and ω_5 for KCl from the temperature dependence of the separate vibrational components of Eq. (6.6).

This analysis has been generalized by Loader[43] to take into account the proximity of the $2s$ electronic state and to include its coupling with the $2p$ state via the Γ_4^- vibrational modes. Provided the second-moment calculation includes the intensity transferred to the $1s \to 2s$ transition by this coupling, Loader showed that Eq. (6.5) is replaced by

$$\langle E^2\rangle = \langle E^2\rangle_{so} + \langle E^2\rangle_1 + \langle E^2\rangle_3 + \langle E^2\rangle_5 + \langle E^2\rangle_4 \,, \tag{6.7}$$

where the additional term is given simply by

$$\langle E^2\rangle_4 = (\hbar\omega_4)\, E_G \coth(\hbar\omega_4/2kT), \tag{6.8}$$

ω_4 being the effective frequency of the Γ_4^- mode and E_G the energy defined in Eq. (3.4). The other terms in Eq. (6.7) have precisely the same significance as in Eq. (6.6) and depend only on the coupling of the $2p$ state to the Γ_1^+, Γ_3^+, and Γ_5^+ modes. The second moment, Eq. (6.7), is entirely independent of the coupling of the $2s$ state to the Γ_1^+ mode. Loader further showed that the stress experiments in this situation determine not $\langle E^2\rangle_1$, $\langle E^2\rangle_3$, and $\langle E^2\rangle_5$, but rather the linear combinations $\langle E^2\rangle_1 - \frac{1}{9}\langle E^2\rangle_4$, $\langle E^2\rangle_3 + \frac{2}{3}\langle E^2\rangle_4$, and $\langle E^2\rangle_5 + \frac{4}{9}\langle E^2\rangle_4$. From Hetrick's data[42] for 7 °K, we accordingly obtain for KCl the values

$$\begin{aligned}(\hbar\omega_1)E_A - \tfrac{1}{9}(\hbar\omega_4)E_G &= (2.5 \pm 0.2)\times 10^{-3}\ \mathrm{eV}^2\,,\\ (\hbar\omega_3)(E_{\mathrm{JT}})_E + \tfrac{2}{3}(\hbar\omega_4)E_G &= (0.61 \pm 0.08)\times 10^{-3}\ \mathrm{eV}^2\,,\\ \tfrac{3}{2}(\hbar\omega_5)(E_{\mathrm{JT}})_T + \tfrac{4}{9}(\hbar\omega_4)E_G &= (1.2 \pm 0.1)\times 10^{-3}\ \mathrm{eV}^2\,.\end{aligned} \tag{6.9}$$

The averaged phonon energies which Hetrick obtained for these three components of $\langle E^2\rangle$ (and which for Loader's model therefore represent not $\hbar\omega_1$, $\hbar\omega_3$, and $\hbar\omega_5$ but rather the appropriate average of these energies with $\hbar\omega_4$) were 15, 9, and 13 meV, respectively.

An upper bound for E_G for KCl may now be obtained from the second equation in Eq. (6.9), if we neglect $(E_{\mathrm{JT}})_E$. We take as an estimate for $\hbar\omega_4$ the experimental separation $\delta E = 18$ meV obtained for the lowest levels, since according to our analysis of the vibronic model this separation should be less than the phonon energy. Our result is then $E_G \le 0.05$ eV. This and the first of Eqs. (6.9) leads to a value for E_A of 0.17 eV, while from the third of these equations we obtain the bounds $0.04 \le (E_{\mathrm{JT}})_T \le 0.06$ eV.[44] There is, however, no evident reason why $(E_{\mathrm{JT}})_E$ should be small compared with $(E_{\mathrm{JT}})_T$, and indeed we obtain as an upper bound for $(E_{\mathrm{JT}})_E$ from Eq. (6.9) (by neglecting E_G and taking $\hbar\omega_3 = 9$ meV) the result $(E_{\mathrm{JT}})_E \le 0.07$ eV. It seems likely, therefore, that the actual value of E_G in KCl (for the unrelaxed configuration) is significantly less than the upper bound and probably no more than 0.01 or 0.02 eV. This estimate constitutes, in our view, rather strong evidence that the coupling to the Γ_4^- modes is actually quite weak, at least for KCl, and that the interpretation given by Eq. (6.4b) is therefore the better one for the magnetic circular polarization data.

Further support for this view may be obtained by considering Table I, where we listed our conclusions from Sec. III A concerning the configuration of minimum energy for the $2s$ and $2p$ states when simultaneous vibronic coupling with the Γ_3^+, Γ_4^-, and Γ_5^+ modes is considered. From our estimates above for $(E_{\mathrm{JT}})_T$ and $(E_{\mathrm{JT}})_E$ from the absorption data, we see that the larger of these is at least some four times larger than the corresponding value of $\hbar\omega$. This represents a fairly strong Jahn-Teller coupling, and there should be a corresponding strong quenching[14] of matrix elements of electronic interactions between vibronic states associated with different equivalent minima on the electronic energy surfaces. In particular, the tunneling splitting between vibronic states belonging to different irreducible representations of the cubic group and made up from the states of minimum energy in these distorted configurations should be substantially less than the corresponding phonon energies $\hbar\omega$. Looking at the last line in Table I, we see that these low-energy vibronic states over most of the range of coupling energies comprise either a triply degenerate (p-like) Γ_4^- level or else several tunneling levels belonging to different Γ_i. Experimentally, however, we have seen that the evidence is that the ground state is an s-like singlet with the lowest excited state some 17–18 meV higher in KCl, a separation at least comparable with representative phonon energies. The only entry in Table I that is consistent with this situation is the one in which the $2s$ state is below $2p$ ($E_{sp} < 0$) and the minimum is in the cubic configuration. For this to be the case, we require from Table I that the following three conditions be satisfied: $(E_{\mathrm{JT}})_E < |E_{sp}|$, $(E_{\mathrm{JT}})_T < |E_{sp}|$, and $E_G < \frac{1}{4}|E_{sp}|$. Returning to our earlier estimate of $(E_{\mathrm{JT}})_T$ from the absorption data, we see that these conditions then require $|E_{sp}| \gtrsim 0.06$ eV in agreement with the value $|E_{sp}| = 0.12$ eV we obtained for KCl from Eq. (6.4b). The condition on E_G in the relaxed configuration is then $E_G < 0.03$ eV, in agreement with our earlier estimate.

These arguments seem to be quite persuasive for KCl, and presumably also for the other alkali halides which show similar behavior but for which the data are less complete, that the coupling with the Γ_4^- modes is actually fairly weak ($E_G \lesssim \hbar\omega_4$) and that the Jahn-Teller coupling of the $2p$ states to the Γ_3^+ and/or Γ_5^+ modes is probably stronger. The $2s$ state must then be below the $2p$ state by 0.1 to 0.2 eV in the cubic configuration corresponding to the relaxed position of the symmetric Γ_1^+ mode. This conclusion is consistent with our earlier conclusion that the data on F-center emission do not agree with the predictions of the vibronic model with strong coupling to the Γ_4^- modes. We consider an interpretation of these data on the basis of an analysis of the opposite limit, that of weak coupling, in the following paper.[9]

VII. DISCUSSION

We have given an exact solution for the vibronic model posed by the Stark effect studies of Bogan and Fitchen and Stiles, *et al.*, and it is of interest now to compare this solution with the semiclassical approximate theory developed by Bogan.[1,7] Bogan assumed that in the cubic configuration the $2s$ electronic state is slightly lower in energy than the $2p$ state, and that these states are mixed by a fluctuating electric field due to longitudinal-optical phonons. Taking the instantaneous orientation of this field to be given by a unit vector $\hat{a}(t)$ having components (a_1, a_2, a_3) with respect to the cubic axes, Bogan assumed that the mixing of the electronic states could be treated as adiabatic. The lowest state then has the instantaneous form

$$|2s'\rangle = (1+\alpha^2)^{-1/2}(|2s\rangle + \alpha\,|p\rangle), \qquad (7.1)$$

where $|p\rangle$ denotes the linear combination

$$|p\rangle = a_1|2p_x\rangle + a_2|2p_y\rangle + a_3|2p_z\rangle, \qquad (7.2)$$

and α is a parameter giving the extent of the mixing. The $2p$ states are split by this interaction, the state

$$|2p_1'\rangle = (1+\alpha^2)^{-1/2}(|p\rangle - \alpha\,|2s\rangle) \qquad (7.3)$$

being displaced to higher energy, while the two orthogonal states

$$\begin{aligned} |2p_2'\rangle &= b_1|2p_x\rangle + b_2|2p_y\rangle + b_3|2p_z\rangle, \\ |2p_3'\rangle &= c_1|2p_x\rangle + c_2|2p_y\rangle + c_3|2p_z\rangle, \end{aligned} \qquad (7.4)$$

remain unaffected. Here (b_1, b_2, b_3) and (c_1, c_2, c_3) denote the components of two mutually perpendicular unit vectors $\hat{b}$ and $\hat{c}$ that are also perpendicular to $\hat{a}$. The radiative lifetime $\tau_r(0)$ of the ground state is accordingly given in terms of the lifetime $\tau_r(p)$ of the unperturbed $2p$ states [Eq. (5.9)] and a time-averaged value of the square of the mixing coefficient α by

$$\tau_r^{-1}(0) = [\alpha^2/(1+\alpha^2)]\,\tau_r^{-1}(p). \qquad (7.5)$$

In the presence of an externally applied electric field, Bogan noted that a further mixing of $|2s'\rangle$ and $|2p_1'\rangle$ occurs, and he obtained a relation between the linear polarization $P(0)$ thereby induced in the luminescence from the ground state and the field-induced change in the radiative lifetime,

$$P(0) = -\tfrac{3}{2}(1+\alpha^2)\,\tau_r^{-1}(0)\,\Delta\tau_r(0). \qquad (7.6)$$

This relation has been used by Stiles *et al.*[3] to obtain a value for α^2 from the experimental data.

From experience with the dynamic Jahn-Teller effect,[14] one expects that the adiabatic or Born-Oppenheimer approximation to the vibronic states should be valid in the strong-coupling limit, and we therefore expect the closest correspondence between Bogan's theory and the exact solution to occur in this limit. We first define (a_1, a_2, a_3) corresponding to a point in Q space by

$$Q_x = -a_1 r, \quad Q_y = -a_2 r, \quad Q_z = -a_3 r, \qquad (7.7)$$

so that $\mathcal{H}_{eL}$ in Eq. (2.4) may be written as

$$\mathcal{H}_{eL} = -Gr(a_1\rho_x + a_2\rho_y + a_3\rho_z). \qquad (7.8)$$

It may then be shown by straightforward algebra that any type-I vibronic state given by Eq. (3.15), for which the radial functions f_1, f_2, and f_3 are given for strong coupling in terms of F_1 alone by Eq. (4.8), may be expressed in the form

$$\Psi_{\mathrm{I}}(J, M, \Lambda') = Y_{J,M}(\theta, \varphi)F_1(r)\psi_-, \qquad (7.9\text{a})$$

where

$$\psi_- = (2)^{-1/2}(|2s\rangle + a_1|p_x\rangle + a_2|p_y\rangle + a_3|p_z\rangle) \qquad (7.10\text{a})$$

is the electronic eigenfunction associated with the lowest-energy surface in Fig. 1 and Eq. (3.1a) (for $G>0$, $E_G \gg |E_{sp}|$) at the point in Q space given by Eq. (7.7). We see that Eq. (7.9a) has the form of a simple Born-Oppenheimer product of a vibrational function $Y_{J,M}(\theta, \varphi)F_1(r)$ with an electronic function ψ_- which is identical with Bogan's state $|2s'\rangle$ in the case of complete mixing, $\alpha = 1$. Similarly, type-I wave functions associated with the highest-energy surface in Fig. 1 and Eq. (3.1a), for which f_1, f_2, and f_3 are given in strong coupling from Eq. (4.2) in terms of F_2 alone ($G>0$), may be shown to have the form

$$\Psi_{\mathrm{I}}(J, M, \Lambda') = Y_{J,M}(\theta, \varphi)F_2(r)\psi_+, \qquad (7.9\text{b})$$

$$\psi_+ = (2)^{-1/2}(|2s\rangle - a_1|p_x\rangle - a_2|p_y\rangle - a_3|p_z\rangle), \qquad (7.10\text{b})$$

where ψ_+ is identical with Bogan's $|2p_1'\rangle$ for $\alpha = 1$. Finally, type-I functions given for strong coupling in terms of F_3 alone and associated with the middle surface in Fig. 1 and Eq. (3.1b) may be expressed as linear combinations of products of vibrational functions with Bogan's states $|2p_2'\rangle$ and $|2p_3'\rangle$ in Eq. (7.4). The same is true of any type-II function given by Eq. (3.16). Bogan's states are therefore identified in the strong-coupling limit ($\alpha = 1$) with the adiabatic electronic states associated with the three energy surfaces in Fig. 1. This result may be seen directly from Eqs. (7.4) and (7.10), using $\mathcal{H}_{eL}$ in the form given in Eq. (7.8), since we have

$$\mathcal{H}_{eL}\psi_\pm = \pm Gr\psi_\pm, \quad \mathcal{H}_{eL}|2p_2'\rangle = \mathcal{H}_{eL}|2p_3'\rangle = 0, \qquad (7.11)$$

where we have used the relations $(\hat{a}\cdot\hat{b}) = (\hat{a}\cdot\hat{c}) = 0$.

Away from the strong-coupling limit, we have seen from the exact solution that states of type I, in general, involve all three radial functions F_1, F_2, and F_3, which satisfy the coupled differential equations (4.4). The terms in these equations that couple F_1 with F_2 involve the electronic cubic-field splitting E_{sp} as well as the dynamical term $(\hbar^2/2\mu r^2)$ resulting from the centrifugal force. However, only the latter couples F_1 and F_2 to F_3. If, therefore, E_G is large compared with $\hbar\omega$ but not perhaps with respect to E_{sp}, it will be a good approximation for states depending primarily on F_1 or F_2 to omit F_3, and such a state may then be expressed in the form

$$\begin{aligned}\Psi_{\mathrm{I}}(J, M, \Lambda') &= Y_{J,M}(\theta, \varphi)[F_1(r)\psi_- + F_2(r)\psi_+] \\ &= Y_{J,M}(\theta, \varphi)\, 2^{-1/2}\{[F_1(r)+F_2(r)]|2s\rangle \\ &\quad + [F_1(r)-F_2(r)]\,|p\rangle\}. \qquad (7.12)\end{aligned}$$

Comparing this with Eq. (7.1), we see that the ratio $[F_1(r)-F_2(r)]/[F_1(r)+F_2(r)]$ plays the role of Bogan's mixing coefficient α when the mixing is not complete. The expression (7.12) is *exact* for an s-like state $(J=0)$ since we have then from Eq. (4.2) that F_3 is identically zero (since $f_2=0$ for $J=0$). We may pursue this analogy further by using Eq. (5.8) to evaluate the radiative lifetime of the state (7.12); using the normalization $\int(F_1^2+F_2^2)r^2\,dr = 1$ and comparing our result with Eq. (7.5), we obtain the correspondence to Bogan's averaged value of α^2 for the state $|2s'\rangle$,

$$\alpha^2/(1+\alpha^2) \sim \tfrac{1}{2} - \int_0^\infty r^2 F_1(r)\, F_2(r)\, dr \qquad (7.13)$$

in terms of F_1 and F_2 appropriate to the vibronic ground state.

On the other hand, when E_G is not large compared to $\hbar\omega$, we know from the dynamic Jahn-Teller effect that we may not neglect the dynamical mixing between the adiabatic states associated with the different energy surfaces in Fig. 1. This mixing is due to the vibrational kinetic-energy term in the Hamiltonian, and it occurs because the adiabatic electronic states, which diagonalize the static Hamiltonian [as in Sec. III A and Eq. (7.11)], are functions of $\vec{Q}$. This dynamical mixing is evident in the terms in $(\hbar^2/2\mu r^2)$ which couple F_1 with F_2 (that is, ψ_- with ψ_+) in the differential Eqs. (4.4), and also in the similar terms which couple F_1 and F_2 with F_3 (for $J\neq 0$) (that is, ψ_- and ψ_+ with $|2p_2'\rangle$ and $|2p_3'\rangle$). In the general case we must expect to retain all of these terms in calculating the wave functions, and we may not expect the vibronic states to be given correctly as simple Born-Oppenheimer products of vibrational functions with the adiabatic electronic states given by the static Hamiltonian. With weak or intermediate coupling, therefore, we may not expect that Bogan's adiabatic states will provide an accurate basis for a simplified treatment of the vibronic system.

There are, of course, an infinite number of energy levels of our vibronic problem, and indeed an infinite number for any set of eigenvalues (J, M, Λ'). With strong coupling, that group of low-energy type-I vibronic states accurately represented by Eq. (7.9a) should clearly be identified with Bogan's state $|2s'\rangle$, while the high-energy type-I states given by Eq. (7.9b) should be identified with his $|2p_1'\rangle$. The type-II states and those type-I states given in terms of F_3, both of which according to Eqs. (3.21) and (4.4c) satisfy the same radial equation and therefore have the same energy spectrum when the coupling to F_1 and F_2 can be neglected, should be identified with $|2p_2'\rangle$ and $|2p_3'\rangle$. There is, therefore, no one-to-one correspondence to be expected between Bogan's adiabatic states and the exact energy levels of the vibronic system. There is, however, a definite correspondence in the strong-coupling regime between Bogan's states and groups of the vibronic states.

Bogan and Fitchen[1] and Stiles *et al.*[3] identified the activation energy δE, which appeared in the temperature dependence (6.2) of the radiative lifetime and that of the electric-field-induced polarization, with the time average of the energy difference between the state $|2s'\rangle$ and the states $|2p_1'\rangle$, $|2p_2'\rangle$, and $|2p_3'\rangle$, which were treated for this purpose as being approximately degenerate. It is clear from our discussion that this identification is wrong and that δE should be identified with the excitation energy of the excited vibronic state nearest to the vibronic ground state. In the strong-coupling regime both of these states would be of the form of Eq. (7.9a) in the group identified with Bogan's state $|2s'\rangle$, the ground state being the lowest s-like level with $J=0$ and the excited state the lowest p-like level with $J=1$ and an excitation energy given by Eq. (4.7). As we have already remarked in Sec. VI, Eq. (4.7) does not fit the experimental F-center data, and we concluded there that the system cannot really be in the strong-coupling limit. We will discuss the significance of δE in the weak-coupling limit in the following paper.[9]

Equation (7.6), used by Stiles *et al.*[3] to determine α from the data, is not generally valid, although we will see in the following paper[9] that it does turn out to be correct (for $\alpha^2 \sim 0$) in the weak-coupling limit. For strong coupling, as we have seen in Sec. V B, $\Delta\tau_r(0)/\tau_r(0)$ approaches zero because the s and p electronic states are fully mixed by the vibronic coupling. $P(0)$, on the other hand, approaches a large value given by Eq. (5.25), which reflects the fact that the effect of an electric field in polarizing the low-energy group of vibronic states associated with $|2s'\rangle$ is not quenched by the electron-phonon coupling. Equation (7.6) therefore may not be used to estimate α, and the values thus obtained by Stiles *et al.* ($\alpha^2 \sim 0.5$ for KCl and KF), which suggested a fairly strong coupling, appear from our estimates of the coupling strength in Sec. VI to be considerably too large.

In their interpretation of the magnetic circular polarization of the luminescence in terms of Bogan's theory, Fontana and Fitchen[25] assumed the energy of the p states mixed into the ground state by the field to be given by δE as obtained from the temperature dependence of the lifetime. They accordingly obtained a value for the orbital g factor of the electronic $2p$ states which was anomalously small, 0.04 for KF and 0.06 for KCl compared with values ~1 measured in absorption. We have seen however in Sec. V D that it is only the type-II states with $J=1$ which are admixed by a magnetic field with the s-like ground state in first-order perturbation theory, and these states are in general much higher in energy than the first excited type-I state, which is responsible for the temperature dependence of the lifetime. We have indicated in Sec. VI [Eqs. (6.4a) and (6.4b)] how the circular-polarization data should be correctly interpreted in the limiting cases of strong and weak coupling, and we will consider this question further for the weak-coupling case in the following paper.[9]

We have observed that a weakness of the treatment we have given of the dynamic problem, at least for application to realistic situations, is that is does not include the true Jahn-Teller coupling of the electronic p states to the even-parity Γ_3^+ and Γ_5^+ modes. We were able, however, to solve exactly the corresponding static problem when coupling to all the modes, Γ_3^+, Γ_5^+, and Γ_4^-, was considered (Sec. III A), and the nature of the stable configuration for the various ranges of coupling energies was given in Table I. We want now to indicate qualitatively how including the coupling to Γ_3^+ and Γ_5^+ modes should affect the vibronic states, particularly those of low energy. From Table I we see that, if the Γ_4^- coupling, as indicated by E_G, is sufficiently weak, and if either the Jahn-Teller coupling to Γ_3^+ or Γ_5^+ modes is sufficiently strong or if p lies below s in the cubic configuration, the stable distorted configurations are determined entirely by the Jahn-Teller coupling and there is no mixing of the s and p electronic states in these configurations. Clearly our treatment of the dynamic problem would be inappropriate in this regime, and one would do better to analyze this case as one involving a dynamic Jahn-Teller effect in the p states. The weak coupling to the s state via the Γ_4^- modes could then be treated by perturbation theory, using as unperturbed states the vibronic states of the Jahn-Teller system. On the other hand, if E_G is sufficiently large so that the stable configurations are of the tetragonal or trigonal s-p mixed type in Table I, such a treatment will not suffice. However, we may then obtain from the last line in Table I the symmetry type of the low-energy tunneling states that are formed from the lowest energy vibrational state in each distorted configuration. For the tetragonal type of distortion these span $\Gamma_1^+ + \Gamma_3^+ + \Gamma_4^-$, so that these states have the same symmetry as the low-energy s-like ($J=0$; Γ_1^+) and p-like ($J=1$; Γ_4^-) states of our vibronic model with only Γ_4^- coupling, together with the Γ_3^+ states from the d-like states ($J=2$; Γ_3^+, Γ_5^+). We recognize therefore that as the coupling to the Γ_3^+ modes is increased, the d-like vibronic states of our model are split into their Γ_3^+ and Γ_5^+ components, and the Γ_1^+, Γ_4^-, and Γ_3^+ states of lowest energy tend to bunch together. A similar bunching also occurs for groups of higher levels, and reduction factors for the various states are changed to reflect the increased quenching of off-diagonal matrix elements of operators coupling the electronic states appropriate to the different distorted configurations. Alternatively, if the distortion is of the trigonal s-p mixed type, the tunneling states span $\Gamma_1^+ + \Gamma_2^- + \Gamma_4^- + \Gamma_5^+$ are drawn from the vibronic levels with $J=0$, 1, 2, and 3 of our model. Qualitatively, at least, it is therefore possible to see how to modify the predictions of our simplified model if the true Jahn-Teller coupling is important. Again, we will consider these modifications to the theory in more detail for the weak-coupling case, in the following paper.[9]

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[22] An examination of the coupled differential equations (4.4) suggests that the $J = 0$ state is lowest not only in the strong-coupling limit ($E_G \gg |E_{sp}|$, $E_G \gg \hbar\omega$) but more generally if $E_G \gtrsim |E_{sp}|$ (we assume $|E_{sp}| > \hbar\omega$). If $E_{sp} < 0$, an s-like state lies lowest in the weak-coupling range ($E_G \ll |E_{sp}|$) as well, so that in this case the ground state is probably $J = 0$ for all coupling strengths. When $E_{sp} > 0$, however, a p-like level ($J = 1$) is lowest for weak coupling.

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[44] Adding these values for E_A and the Jahn-Teller energy [the larger of $(E_{JT})_T$ and $(E_{JT})_E$], we obtain a value < 0.24 eV for the energy of the $2p$ state in its relaxed configuration relative to its value in the unrelaxed configuration. This is less than half the value required to account for the large Stokes shift between the absorption and emission peaks in KCl. The reason for this discrepancy is uncertain. In Wood and Opik's theoretical calculations (Ref. 6), on the other hand, a much larger value $\backsim 0.6$ eV was found for E_A, which thus fits the observed Stokes shift much better than the value inferred from the experimental moments.