

## Solution of a Vibronic Model for the Relaxed Excited State of the $F$ Center

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An exact solution is given for the vibronic problem posed by nondegenerate  $s$  and  $p$  electronic states interacting in cubic symmetry via a triply degenerate  $T_{1u}$  vibrational mode. In the strong-coupling limit the vibronic ground state is found to be  $s$ -like, irrespective of the order of the  $s$  and  $p$  electronic states in the unrelaxed configuration. Applications to the interpretation of Stark effects and other experiments on  $F$  centers in alkali halides are discussed.

The possibility that a  $2s$ -like level lies below the  $2p$  level in the relaxed excited state of the  $F$  center in alkali halides was first suggested by the discovery by Swank and Brown<sup>1</sup> that  $F$ -center radiative lifetimes are  $\approx 10^{-6}$  sec instead of  $\approx 10^{-8}$  sec as expected. That this is indeed the correct level ordering has now been shown for KCl and several other alkali halides by recent experiments on Stark effects in  $F$ -center luminescence by Bogan and Fitchen,<sup>2</sup> Stiles, Fontana, and Fitchen,<sup>3</sup> and Kühnert.<sup>4</sup> This finding contrasts with the earlier prevailing view<sup>5</sup> that absorption and luminescence in the  $F$  band involved only the  $2p$  excited states. It contrasts also with the experimental results for KCl by Chiarotti *et al.*,<sup>6</sup> which has theoretical support<sup>7,8</sup> for other alkali halides as well, that  $2s$  lies above  $2p$  in the unrelaxed configuration corresponding to  $F$ -band absorption. Interpretation of these and related experiments has, however, been handicapped by the lack of a suitable vibronic model describing the electron-lattice coupling and in particular the resulting dynamic mixing of the  $2s$  and  $2p$  electronic states. The purpose of this Letter is to outline an exact solution of the vibronic problem posed by "Bogan's model,"<sup>2,3</sup> namely, that of nondegenerate  $2s$  and  $2p$  electronic states interacting in cubic symmetry via a triply degenerate  $T_{1u}$  vibrational mode, and to indicate some of its implications. This solution follows very closely that given a decade ago by Moffitt and Thorson<sup>9</sup> and by Longuet-Higgins *et al.*<sup>10</sup> for the dynamic Jahn-Teller effect of an orbital doublet  $E$  state coupled to an  $E$  mode.

The Hamiltonian we consider is

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_L + \mathcal{H}_{eL}, \quad (1)$$

where  $\mathcal{H}_L$  describes the elastic and kinetic energy of the vibrational modes  $Q_x, Q_y, Q_z$ :

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

with  $\omega$  the angular frequency of the mode and  $\mu$  its effective mass, while  $P_i$  is the momentum conjugate to  $Q_i$ . The electronic singlet state  $|s\rangle$  is taken to have an energy  $E_{sp}$  relative to the triplet state  $|p_x\rangle, |p_y\rangle, |p_z\rangle$  in the configuration of cubic symmetry ( $Q_x = Q_y = Q_z = 0$ ), so that

$$\mathcal{H}_e = \frac{1}{2} E_{sp} \rho_0. \quad (3)$$

Here  $\rho_0$  denotes an electronic operator given by

$$\rho_0 = + |s\rangle\langle s| - |p_x\rangle\langle p_x| - |p_y\rangle\langle p_y| - |p_z\rangle\langle p_z|. \quad (4)$$

The splittings and mixing of the electronic states by the distortions  $Q_x, Q_y, Q_z$  are then given by

$$\mathcal{H}_{eL} = V(Q_x \rho_x + Q_y \rho_y + Q_z \rho_z), \quad (5)$$

where

$$\rho_i = |p_i\rangle\langle s| + |s\rangle\langle p_i|. \quad (6)$$

We introduce a vibrational angular momentum operator  $\vec{L}$ , with components  $L_x, L_y, L_z$  given by

$$L_z = \hbar^{-1} (Q_x P_y - Q_y P_x), \quad (7)$$

etc., and the electronic orbital-angular-momentum operator  $\vec{I}$ , the components of which may be represented within the space of the states  $|s\rangle, |p_x\rangle, |p_y\rangle, |p_z\rangle$  by

$$I_z = -i |p_x\rangle\langle p_y| + i |p_y\rangle\langle p_x|, \quad (8)$$

etc. It may be shown easily that the components of the total-angular-momentum operator

$$\vec{J} = \vec{L} + \vec{I} \quad (9)$$

commute with the full Hamiltonian (1), so that the vibronic eigenstates of Eq. (1) may be classified by the eigenvalues of  $\vec{J}^2 = J(J+1)$  ( $J=0, 1, 2, \dots$ ) and  $J_z = M$ . In addition, we find that the operator

$$\Lambda = I \rho_0 \quad (10)$$

commutes with the Hamiltonian (1) and with  $\vec{J}$ , where  $I$  is the inversion operator in  $Q$  space, and  $\rho_0$  is defined in Eq. (4) and represents the elec-

tronic inversion operator. We can therefore also classify each eigenstate of Eq. (1) by the eigenvalues  $\Lambda' = \pm 1$ , which we shall term the parity of the state.

We can form eigenfunctions of  $\vec{J}^2$  and  $J_z$  as linear combinations of products of the electronic functions with spherical harmonics  $Y_{Lm}(\vec{Q})$  in  $Q$  space, using tables of Wigner coefficients.<sup>11</sup> Using  $Y_{Lm}(\vec{Q})$  for a given  $L$ , we obtain from  $|s\rangle$  the eigenfunctions

$$|J, M; L, s\rangle = Y_{Lm}(\vec{Q})|s\rangle \quad (11)$$

with  $J=L$ ,  $M=m$ , which have the parity  $\Lambda' = (-1)^L$ . From the  $p$  states we obtain eigenfunctions  $|J, M; L, p\rangle$  with  $J=L-1, L, L+1$  (except for  $L=0$ , for which  $J=1$  only), for which  $\Lambda' = (-1)^{L+1}$ . We can accordingly express an eigenfunction of the Hamiltonian (1) which belongs to  $J, J_z=M$  and has  $\Lambda' = (-1)^J$  in the general form (which we call type I)

$$\begin{aligned} \Psi_I(J, M, \Lambda') = & f_1(J, r)|J, M; J, s\rangle \\ & + f_2(J, r)|J, M; J-1, p\rangle \\ & + f_3(J, r)|J, M; J+1, p\rangle, \end{aligned} \quad (12)$$

where the  $f_i(J, r)$  are functions of the radial coordinate  $r = (Q_x^2 + Q_y^2 + Q_z^2)^{1/2}$ . (For  $J=0$  the term in  $f_2$  is absent.) An eigenfunction of (1) also belonging to  $J, J_z=M$  but having  $\Lambda' = (-1)^{J+1}$  has the simpler general form (type II)

$$\Psi_{II}(J, M, \Lambda') = f_4(J, r)|J, M; J, p\rangle. \quad (13)$$

Substituting the type-I function (12) in the Schrödinger equation for the Hamiltonian (1), we can show easily that  $f_i(J, r)$  ( $i=1, 2, 3$ ) must satisfy three coupled radial differential equations, in which the off-diagonal terms result from the interaction  $\mathcal{H}_{eL}$  in Eq. (5). In contrast, the simple differential equation similarly obtained for  $f_4(J, r)$  in the type-II function (13) turns out to be independent of  $\mathcal{H}_{eL}$  and is therefore the same as that for the radial function of the unperturbed three-dimensional simple harmonic oscillator corresponding to  $\mathcal{H}_L$  is Eq. (2).

In the strong-coupling limit of  $\mathcal{H}_{eL}$ , when the stabilization energy  $E_S = V^2/2\mu\omega^2$  (the analog of the Jahn-Teller energy<sup>9,10</sup>) is large with respect to both  $\hbar\omega$  and  $E_{sp}$ , it may be shown that the lowest type-I levels have wave functions localized radially near  $r_0 = |V|/\mu\omega^2$  and relative energies

$$E(J) = J(J+1)\hbar^2/2\mu r_0^2. \quad (14)$$

In this limit, the vibronic ground state is thus an  $s$ -like level ( $J=0, \Lambda' = +1$ ), and the first excited

state a  $p$ -like level ( $J=1, \Lambda' = -1$ ) with an excitation energy

$$\Delta E_{10} = \frac{1}{2}\hbar\omega(\hbar\omega/E_S), \quad (15)$$

irrespective of the order of the  $s$  and  $p$  electronic levels in the cubic configuration.

The radiative lifetime  $\tau_r(J)$  of a type-I vibronic level is easily shown to be inversely proportional to the fraction of electronic  $p$  state which its wave function (12) contains [i.e., to  $\int r^2(f_2^2 + f_3^2) dr$ ]. In the strong-coupling limit,  $\tau_r(J)$  is found to be independent of  $J$  for the low-energy levels, and it is given approximately by twice the radiative lifetime  $\tau_r(p)$  of the electronic  $p$  state in the cubic configuration. The strong-coupling limit thus corresponds to equal mixing of the  $s$  and  $p$  electronic states, as one expects.

If the  $s$ -like ( $J=0$ ) vibronic level is lowest, the change in the low-temperature radiative lifetime of the system due to an applied electric field  $F$  results primarily from the admixture of the near- $p$ -like level ( $J=1$ ) into this lowest level. The resulting change in the lifetime is given by

$$\Delta[\tau_r^{-1}(0)] = [p'F/\Delta E_{10}]^2[\tau_r^{-1}(1) - \tau_r^{-1}(0)], \quad (16)$$

where  $p'$  is the electric-dipole matrix element between these two levels. The corresponding induced linear polarization  $P$  of the luminescence depends in addition on the second-order admixture of the  $d$ -like level ( $J=2$ ) and does not appear in general to be related simply to the change in lifetime as given by Eq. (16). This result contrasts with Bogan's semiclassical treatment,<sup>2</sup> on the basis of which it was concluded that the ratio of  $P$  to the lifetime change gave a simple way to determine the mixing coefficient  $\alpha$ . [The quantity  $\alpha^2/(1+\alpha^2)$  in Bogan's treatment is the equivalent in the present analysis to  $\int r^2 f_3^2 dr$  for the  $s$ -like ground state.]

Comparing our conclusions with the experimental results, one sees that an attractive feature of this vibronic model that was not anticipated on the basis of Bogan's treatment is that it *predicts* that, even though the  $s$  electronic level is above the  $p$  level in the cubic configuration corresponding to  $F$ -band absorption, with sufficiently strong coupling the vibronic ground state is  $s$ -like, as found experimentally. However, if this were the true cause of the  $s$ - $p$  level crossing in the relaxed state, we would expect from Eq. (15) to find that the excitation energy of the  $p$ -like level would be substantially less than typical phonon energies (since  $E_S \gg \hbar\omega$  for strong coupling), whereas experimental values<sup>3</sup> for  $\Delta E_{10}$  (0.18 eV for KCl,

and 0.017 eV for KF and NaF), determined from the temperature dependence of the radiative lifetime, are not this small. Moreover, if we were in the strong-coupling limit the radiative lifetime of the lowest levels would be independent of  $J$ , as noted, so that the Stark effect in the lifetime would vanish according to Eq. (16). This of course is not the case experimentally, and the lifetime of the  $s$ -like level is estimated<sup>3</sup> to be about 3 times that of the  $p$ -like level. It thus appears that we cannot be in the strong-coupling limit, and that it is unlikely that the  $s$ - $p$  crossing is caused by the vibronic coupling to the  $T_{1u}$  modes. This crossing is probably due to the change in the electronic parameters resulting from the large symmetric mode ( $A_{1g}$ ) relaxation, as indicated by the calculations of Fowler, Calabrese, and Smith<sup>7</sup> and Wood and Opik.<sup>8</sup>

A quantitative comparison of the predictions of the vibronic model with the many relevant experimental data is not possible until numerical solutions of the equations have been obtained for the intermediate coupling regime, and until estimates can be made of the effects of the additional (and probably stronger) coupling to the  $E_g$  and  $T_{2g}$  modes. Nevertheless, aside from providing a solution to the problem posed by Bogan's work,<sup>2</sup> the vibronic model has additional features that fit qualitatively the experimental facts:

(1) Applied stress mixes the  $d$ -like excited state ( $J=2, \Lambda'=+1$ ) into the  $s$ -like vibronic ground state, the coupling arising from the strain-induced splitting of the  $p$  electronic states. Such mixing leads to stress-induced polarization of luminescence as observed by Hetrick and Compton,<sup>12</sup> which is independent of temperature at low temperature.

(2) Because the lowest  $s$ - and  $p$ -like levels have opposite parity  $\Lambda'$ , they *cannot* be coupled by an applied magnetic field or by spin-orbit interaction. These perturbations couple the  $s$ -like ground state only with type-II excited states with  $J=1, \Lambda'=+1$ , which have excitation energies relative to the ground state on the order of  $E_s$

or, if  $E_{sp}$  is negative, ( $E_s - E_{sp}$ ). The excited levels mixed into the ground state by magnetic or spin perturbations are therefore entirely different from those admixed by electric field or applied stress and may lie much higher in energy. This result is consistent with the very small, temperature-independent magnetic circular polarization of  $F$ -center luminescence observed in KF below 4.2°K by Fontana and Fitchen<sup>13</sup> and Fontana.<sup>14</sup>

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