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Absorption-line-shape model for F-center – CN^--molecule defect pairs in CsCl

J. West and K. T. Tsen
Department of Physics, Arizona State University, Tempe, Arizona 85287

S. H. Lin*
Department of Chemistry, Arizona State University, Tempe, Arizona 85287

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A systematic study of the temperature-dependent absorption spectra of F_H (CN^-) defect pairs in a CsCl host crystal is presented. At the lowest temperatures, two distinct absorption peaks are observed. As the temperature is increased, the separation of the peaks decreases, the relative oscillator strengths change, and the peaks broaden. These experimental results are explained by a simple model which considers that the nearly degenerate $2s$ and $2p_z$ electronic states of the F center are strongly mixed by the intrinsic and displacement dipole moments of the CN^- molecule. From this study, one obtains important parameters such as coupling constants, effective phonon mode frequencies participating in the absorption process, and a parameter describing the degree of $2s$-$2p_z$ mixing, which are crucial for testing the physical models proposed for the electronic to vibrational energy-transfer process in this defect system.

I. INTRODUCTION

F centers (an electron bound to an anion vacancy) are the simplest electronic defects with O_h symmetry in ionic crystals. They are easily moved "building blocks," allowing for the construction of other point defects from various combinations, i.e., F aggregate centers,[1,2] F centers with atomic defects as partners (F_A centers),[3–5] and F centers with molecular defects as partners (F_H centers). Recently, it has been demonstrated[6–9] that under visible laser excitation $F_H(CN^-)$ and $F_H(OH^-)$ defect pairs exhibit electronic to vibrational (e-v) energy transfer from the excited F electron into the localized vibrational modes of the companion molecule when it is located at the $\langle 100 \rangle$ nearest-neighbor position. The $F_H(CN^-)$ defect pair has potential application as an infrared laser source,[6] utilizing transitions of the vibrational levels of the CN^- molecule. In previous emission and Raman scattering studies of the e-v energy transfer process, it has been shown that the relative amounts of energy transferred into specific vibrational levels of the CN^- molecule are found[10–15] to depend strongly on both temperature and incident laser wavelength. Halama and coworkers[13–15] were able to interpret their quasi-steady-state Raman data on $F_H(OH^-)$ defect pairs in KCl and $F_H(CN^-)$ defect pairs in CsCl in terms of dipole-dipole and super molecule models, respectively. The results of their analysis were not conclusive, however, due to the large number of fitting parameters involved in each of the models. We note that all of the parameters determining the relative e-v energy-transfer rates for the dipole-dipole model, and all but one or two parameters, depending on incident laser wavelength, for the super molecule model are explicitly involved in, and can be determined from, the analysis of the absorption spectra.[13–16] The purpose of this study is to measure the temperature dependence of the absorption spectra of $F_H(CN^-)$ defect pairs in CsCl and to independently determine, with a simple model, the parameters mentioned above. In particular, we determine the values of the following physical quantities: the coupling constants and effective phonon mode frequencies describing the electron-phonon interactions, and the peak position of each absorption band as a function of temperature. The ratio of the measured strength of the absorption bands suggests that there is a strong mixing of one of the excited p-like states with an excited s-like state, and we also obtain a parameter directly measuring the degree of this mixing.

We note that previous explanations concerning the absorption process of these F_H defects by Gash[17,18] are not satisfactory due to the omission of the excited s-like electronic state in the calculations.[19,20] Also, the nature of those calculations precludes the determination of any temperature dependence of the locations of the absorption peaks, any details concerning their shapes, or comparisons of their relative absorption magnitudes, all of which are essential to fully test the models for the e-v energy transfer process.

The analysis presented in this paper is very general in nature, and includes the effects of the major perturbations introduced by the CN^- molecule. The influence of phonon and spin-orbit interactions are also included. In our model calculations, the electronic wave functions of the excited states of the F center are assumed to be of $2p$ and $2s$ character, and the ground state is $1s$ in character. It is also assumed that the CN^- molecule and its dipole moments lie along the $\langle 100 \rangle$ axis, and that the position of the center of mass of the CN^- molecule along this axis may be a function of temperature. The paper is organized in the following way: The experimental method and results are presented in Sec. II. The theoretical model for interpreting the experimental results is presented in Sec. III. The experimental analysis and discussion are presented in Sec. IV, and a brief conclusion is given in Sec. V.

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II. EXPERIMENTAL METHOD AND RESULTS

All of the data presented here were obtained from the same sample and taken on a Varian Cary 5 (UV-Vis-NIR) spectrometer. The sample of CsCl, with approximate dimensions of $3\times5\times1$ mm^3, was grown by the Bridgeman technique in the Utah Crystal Growth Laboratory and additively colored with about 2×10^{16} cm^{-3} F centers and contained 7×10^{-4} mole ratios of CN$^-$. The sample was polished with a water-ethanol mixture before each experiment to provide clean faces and then attached to a copper sample holder with conducting vacuum grease, which also provided thermal contact for the sample. Copper conducting paste was used as thermal contact between the sample holder and the cold finger of a closed-cycle helium refrigerator with quartz optical windows (Air Products model No. DE202 head and 1R04WSL compressor). The refrigerator is capable of providing temperatures ranging from 15 to 300 K when used with a temperature controller (Scientific Instruments Inc., Model No. 5500-5).

Two experiments were performed. In the first, the sample was heated to ~250 °C and quenched in the dark to room temperature to dissociate F aggregate centers. The sample was then transferred in the dark to the refrigerator and cooled to 20 K. After allowing 30 min for the sample temperature to equilibrate, spectra were taken at temperatures of 20, 40, 60, 80, 100, and 130 K. The spectra associated with this experiment will be referred to as the "quenched" spectra. For the second experiment, the sample was quenched according to the previous procedure, but exposed to a 10-mW He-Ne laser for 30 min when the sample temperature was at ~170 K causing the formation of the F_H(CN$^-$) aggregates.[19] The He-Ne laser beam was defocused so that the entire face of the sample was exposed and uniformly aggregated. The sample was then cooled directly to a temperature of 20 K, and data taken as described for the previous case. This set of spectra will be referred to as the "aggregated" spectra.

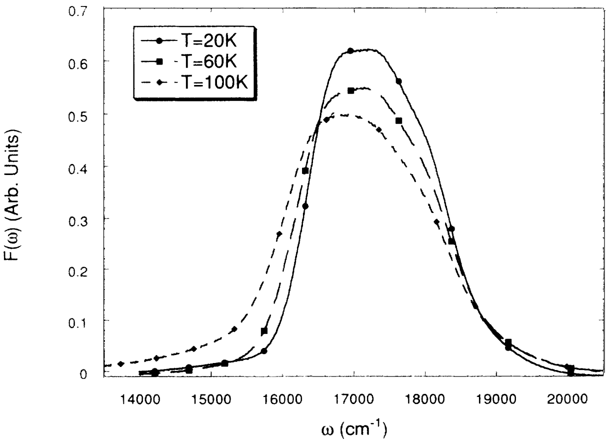

FIG. 1. The absorption-band-shape functions of F-center defects in CsCl before aggregation to the CN$^-$ molecular ions at $T=20$, 60, and 100 K. The bands are consistent with those produced from pure F centers in CsCl.

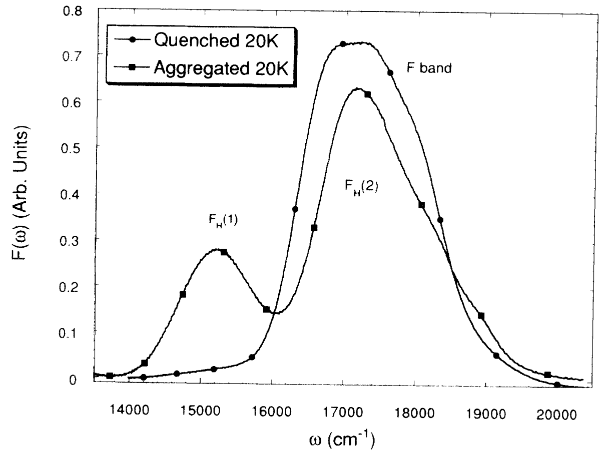

FIG. 2. A comparison of the absorption-band-shape function at $T=20$ K of the F-center defects before aggregation (solid dots) and after aggregation to the CN$^-$ molecular ions forming the F_H(CN$^-$) defect pair (solid squares).

In Fig. 1, the absorption spectra for the quenched experiment are presented for temperatures of 20, 60, and 100 K. These spectra are consistent with those obtained from CsCl samples containing *only* F-center defects. It is noticed that each spectrum is not a single absorption band, but rather a combination of three distinct bands.[20–22] This structure has been satisfactorily explained by the splitting of the $2p$ electronic states of the F center by Jahn-Teller and spin-orbit effects.[23–25] As the temperature increases, the widths of the absorption bands increase due to electron-phonon coupling, while the positions of the bands shift to lower energies due to lattice expansion and distortion between phonon mode frequencies in the different electronic states.[16]

Figure 2 shows the absorption spectra at a temperature of 20 K for the quenched and aggregated experiments, respectively. It illustrates the dramatic effects of the CN$^-$

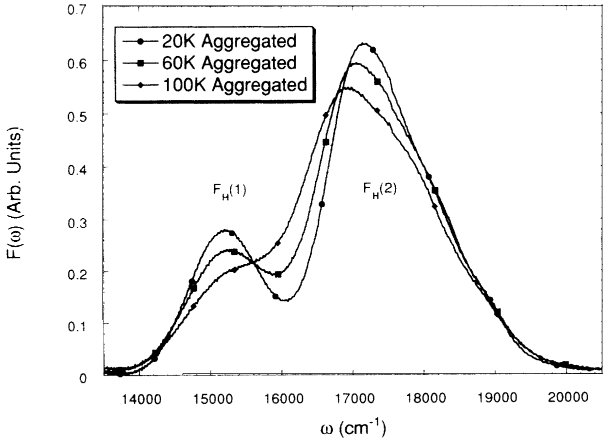

FIG. 3. The absorption band-shape functions of F_H(CN$^-$) in CsCl. The temperatures are the same as in Fig. 1. At the higher temperatures, the separation of the $F_H(1)$ and the $F_H(2)$ bands decreases, the relative areas change, and both bands broaden.

aggregation on the absorption spectra, creating a large splitting of the $F_H(1)$ and $F_H(2)$ bands. The absorption spectra obtained at temperatures of 20, 60, and 100 K for the aggregated system are shown in Fig. 3. The low-temperature spectrum ($T=20$ K) is similar to that which has been observed in other investigations.[6,8] It is noticed that the magnitude of the splitting between the $F_H(1)$ and $F_H(2)$ bands decreases as the temperature increases (they do not just broaden into each other). In addition, the ratio of the areas $F_H(2){:}F_H(1)$ is found to be temperature dependent, with the ratio of oscillator strengths being approximately 4:1 at $T=20$ K and 5:1 at $T=130$ K. These ratios suggest a strong mixing of the $2s$ and $2p_z$ electronic states in this defect system.

III. THEORETICAL INTERPRETATION

Despite their simple appearance, $F_H(\mathrm{CN}^-)$ defect pairs in CsCl are not amiable to *ab initio* calculations. The primary difficulty is the diffuse nature of the *F*-center wave functions, which implies that interactions of the *F* electron with the ions in the host crystal must be considered to be long ranged.[26] Additional difficulties arise from the Cs^+ cations of the host crystal, which (1) are large, and therefore requires the inclusion of the *d*-level states in the calculations,[27] (2) have a large polarizability,[17,28] and (3) may be involved in relatively large lattice relaxations. In addition, the "mixed" nature of the $F_H(\mathrm{CN}^-)$ system, containing an *F*-center defect, a covalent molecular ion, and an ionic host environment, makes the application of a single method (density functional[29] or tight binding,[30] for example) difficult. These difficulties do not, however, preclude a simple theoretical treatment of the system.

The $2s$ electronic state of the *F* electron is not included in the calculations of the absorption properties of *F*-center defects in various host crystals by many other authors, due to the usual dipole selection rules.[31–36] Excluding the $2s$ state in the theoretical calculations is not valid in the case of strong mixing of the $2p$ and $2s$ states, such as in $F_H(\mathrm{CN}^-)$ defect pairs, or when Stark effects[37,38] or strong vibronic couplings are involved.[27,39] The fact that the ratio of the areas of the $F_H(2)$ and $F_H(1)$ absorption bands is significantly different from 2:1 suggests that there is a significant mixing of the $2s$ and $2p_z$ states by the presence of the CN^- molecule. We notice that the symmetry of the $F_H(\mathrm{CN}^-)$ defect is the same as that in Stark effect experiments when the external field is along the $\langle 100\rangle$ direction. In our simple theoretical model, we will treat the mixing of the $2s$ and $2p_z$ states in the $F_H(\mathrm{CN}^-)$ defect system in a manner similar to that used by Bogan and Fitchen[37] in their analysis of Stark effect experiments of pure *F*-center defects. It is expected that the mixing of the $2s$ state with the $2p_z$ state would be much stronger than that of the $1s$ state, since the energy of the $2s$ state is much closer to that of the $2p$ states.[26,40,41] Preliminary calculations, using the wave functions of Sivasankar, Sankar, and Whippey[34] indicate that the amount of $1s$ character mixed into the $2p_z$ state would be less than 1%. The mixing of the $1s$ electronic state with the other basis states will therefore be ignored in our calculations.

A. Interactions

We assume a simple one-electron model with the excited electronic states of the unperturbed *F* center represented by diffuse hydrogenlike states of $2p$-like ($|x\rangle, |y\rangle, |z\rangle$), and $2s$-like ($|2s\rangle$) wave functions, similar to those used by Bogan and Fitchen. As shown in Fig. 4, we assume that the center of mass of the CN^- molecule always lies on the positive *z* axis.[8] As a result, the symmetry of the $F_H(\mathrm{CN}^-)$ defect system is reduced from O_h to C_{4v}. In addition, the position of the center of mass of the CN^- molecule may also depend on temperature. If the center of mass of the CN^- molecule is not located at the Cl^- anion site (see Fig. 4), a displacement dipole perturbation, in addition to the intrinsic dipole perturbation, will be present.[18] For the C_{4v} symmetry, it can be determined[42] by group theoretical considerations that phonon modes of A_1, A_2, B_1, B_2, and E symmetry may couple to the electronic states. This electron-phonon coupling produces a broadening of the absorption bands, as well as possible mixing of the electronic states via Jahn-Teller effects.[23–25] The spin-orbit coupling in *F* centers, and the similar $F_H(\mathrm{OH}^-)$ defect pair, has been measured, and found to be significant,[19,23,43] and is therefore included in our analysis.

The system Hamiltonian is taken to be $H=H_0+H'$, where H_0 is the Hamiltonian of the *F*-center system, including the effect of host crystal reconfiguration and changes in ionic polarizabilities due to the replacement of the Cl^- anion by the *F*-center electron. H' represents the direct interactions of the CN^- dipole moments with the *F* electron, as well as indirect interactions through induced changes in the host crystal environment, such as in

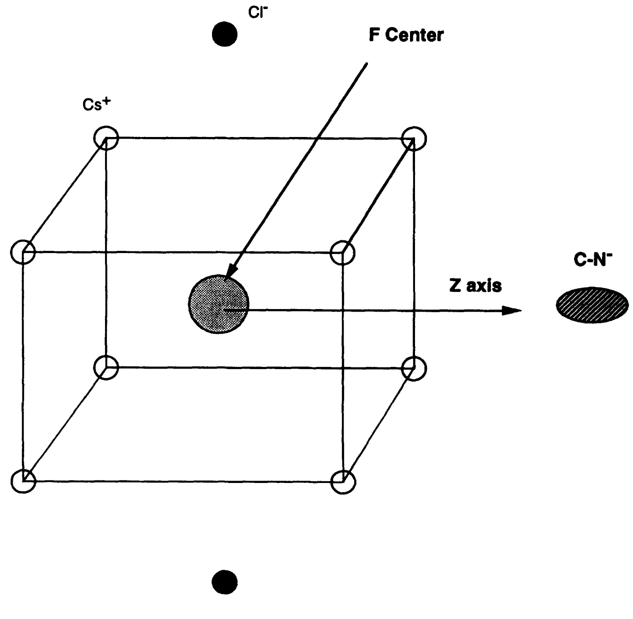

FIG. 4. A diagram of the $F_H(\mathrm{CN}^-)$ defect pair in CsCl, which clearly demonstrates the V_{4v} symmetry of the defect pair.

configuration and polarization of the host crystal anions due to the replacement of the second Cl^- anion by the CN^- molecule. It also includes interaction of the F electron via spin-orbit and electron-phonon interactions. These interactions are decomposed as follows:

$$H' = H'_1(T) + H'_2 + H'_3 \ , \tag{1}$$

where $H'_1(T)$ includes effects of replacing the Cl^- anion by the CN^- molecule, which has axial symmetry, as well as the odd parity A_1 phonon modes, which transform as z. We explicitly indicate the temperature dependence of this interaction, since the position of the center of mass of the CN^- molecule may depend on the temperature. H'_2 includes spin-orbit interaction as well as interactions with the A_2 and B_2 phonon modes. H'_3 represents the electron-phonon interactions involving the even parity A_1 phonon modes (i.e., those transform like x^2+y^2 and z^2) and the B_1 phonon modes (which transform as x^2-y^2).[42] These are responsible for the large widths observed in both the F center and $F_H(CN^-)$ absorption spectra and shifts in peak positions due to lattice expansion.[44,45] The results of the application of the perturbations $H'_1(T)$, H'_2, and then H'_3 are shown to scale in a simple level diagram in Fig. 5. The spin-orbit coupling, contained in H'_2, has the potential to mix $|z\rangle$ with $|x\rangle$ or $|y\rangle$, as well as to mix $|x\rangle$ with $|y\rangle$. However, because the measured value of the spin-orbit interaction is much smaller than the splitting induced by $H'_1(T)$,[19] the spin-orbit coupling of $|z\rangle$ with $|x\rangle$ or $|y\rangle$ will be ignored, and only the spin-orbit coupling of $|x\rangle$ with $|y\rangle$ will be considered. Similarly, the contributions of the A_2 and B_2 phonon modes to H'_2 have only off-diagonal elements in $|x\rangle$ and $|y\rangle$. The combined magnitude of these phonon interactions is less than that of the spin-orbit splitting,[23] and the major effect of these modes is to increase the width of the $|x\rangle$ and $|y\rangle$ states. This additional broadening is found to be negligible in comparison to that produced by the even phonon modes in H'_3 (see Fig. 5). The influence of the A_2 and B_2 phonon modes are therefore not included in the calculations. The effects of E symmetry modes, which weakly mix $|x\rangle$ or $|y\rangle$ with $|2s\rangle$ or $|z\rangle$, are also neglected in comparison with the large splitting introduced by $H'_1(T)$.

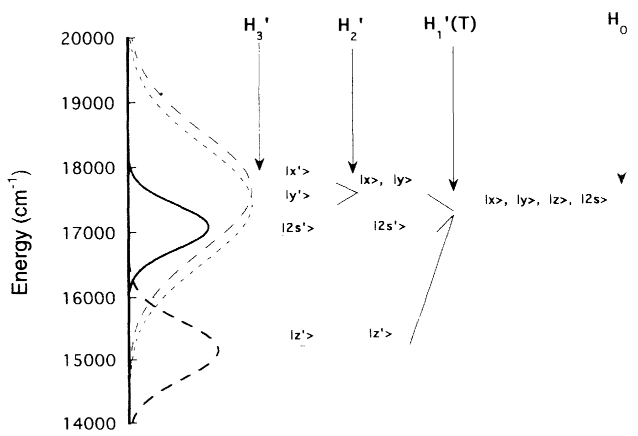

FIG. 5. A level diagram, drawn to scale for $T=20$ K, showing, from right to left, the successive effects of $H'_1(T)$, H'_2, and H'_3 on the F-center states $|2s\rangle$, $|x\rangle$, $|y\rangle$, and $|z\rangle$. It is seen that $H'_1(T)$ produces states of three energies, with $|x\rangle$ and $|y\rangle$ remaining degenerate. H'_2 then lifts the degeneracy of these two states, and H'_3 introduces a large width to each of the states due to electron-phonon coupling.

The interactions with $H'_1(T)$ will be considered in detail first. These interactions can be separated into two parts: one is the interaction of the F electron with the CN^- dipole moments and the other is the interactions of the F electron with the odd parity A_1 phonon modes and the configurational changes in the host crystal that are due to the replacement of the Cl^- ion by the CN^- molecule. Explicitly, $H'_1(T)$ can be written as

$$H'_1(T) \equiv H'_{CN}(T) + H'_z \ ,$$

where

$$H'_{CN}(T) \equiv \left[\frac{qe}{|\mathbf{r}-\mathbf{R}(T)+\mathbf{d}|} - \frac{qe}{|\mathbf{r}-\mathbf{R}(T)-\mathbf{d}|} \right] + \left[\frac{e^2}{|\mathbf{r}-\mathbf{R}(T)|} - \frac{e^2}{|\mathbf{r}-\mathbf{R}_0|} \right] . \tag{2}$$

The origin is taken to be at the F-electron lattice site, and e is the charge of an electron. The position vector $\mathbf{R}_0$ describes the location of the Cl^- lattice site, which is now occupied by the CN^- molecule, and $\mathbf{R}(T)$ is the position vector of the center of mass of the CN^- molecule. Both vectors are assumed to lie along the positive z axis. The terms inside the first set of parentheses of Eq. (2) represent the interaction of the F electron with the intrinsic dipole moment of the CN^- molecule, which is modeled as two equal and opposite electric charges of magnitude $q=e/20$ separated by 1.2 Å, $\mathbf{d}$ has a magnitude of 0.6 Å and is along the positive z axis.[17] Calculations by ourselves and Gash[41] indicate that this intrinsic dipole moment alone is about a factor of 5 too small to account for the amount of spectral separation of the $F_H(1)$ and $F_H(2)$ absorption bands. To explain this significant spectral separation, the center of mass (and therefore the center of charge) of the CN^- molecule is allowed to be displaced from the lattice site;[18] and, to account for the temperature dependence of the spectral separation, the displacement is allowed to be temperature dependent so that $R=R(T)$. The above consideration leads to the addition of the terms in the second set of brackets in Eq. (2), referred to by Gash[18] as the displacement dipole moment. The interaction Hamiltonian $H'_{CN}(T)$ predominantly determines the separation of the $F_H(1)$ and $F_H(2)$ bands in the absorption spectra. A comparison of the measured absorption spectra with calculations using the hydrogenlike wave functions of Sivasankar, Sankar, and Whippey[34] for the F electron and straightforward perturbation theory gives $R=4.382$, 4.381, 4.364, 4.358, 4.350, and 4.330 Å for $T=20$, 40, 60, 80, 100, and 130 K, respectively. From this analysis, we find that the spectral separation of the $F_H(1)$ and $F_H(2)$ bands is very sensitive to the position of the center of mass of the CN$^-$ molecule. The Hamiltonian H_z' includes the interactions of the F electron with the odd parity A_1 phonon modes and the induced changes in the host crystal due to the replacement of the Cl$^-$ ion by the CN$^-$ molecule, so that H_z' transforms like z. Such an interaction has only off-diagonal terms in $|2s\rangle$ and $|z\rangle$, and so tends to increase the degree of mixing between these states. Strictly speaking, there would be a broadening associated with the interactions with the odd parity A_1 modes, but the small amount of structure in the F center spectra indicates that the effects of these modes are at least an order of magnitude smaller than those of the CN$^-$ dipole moments. This is consistent with the results of Moran,[24] and this source of broadening is neglected in our analysis.

The action of $H_1'(T)$ is therefore to leave the $|x\rangle$ and $|y\rangle$ states degenerate and purely p like, and to remove the near degeneracy of the $|2s\rangle$ and $|z\rangle$ states (see Fig. 5). The new $|2s\rangle$ and $|z\rangle$ states are written as[37]

$$\begin{aligned} |z'\rangle &\equiv \beta|z\rangle + \sqrt{(1-\beta^2)}|2s\rangle \ , \\ |2s'\rangle &\equiv \sqrt{(1-\beta^2)}|z\rangle - \beta|2s\rangle \ , \end{aligned} \tag{3}$$

where β is a parameter, which measures the mixing of the two electronic states: $|2s\rangle$ and $|z\rangle$.

Next, we consider the effects of H_2'. The only nonzero elements of H_2' are off-diagonal elements connecting $|x\rangle$ and $|y\rangle$. If the angular part of the electronic states are expressed in terms of a $|J,Jz\rangle$ basis,[46] the spin-orbit interactions are easily evaluated using

$$H_{\text{s.o.}} \propto \frac{1}{r}\left[\frac{\partial V}{\partial r}\right](\mathbf{S}\cdot\mathbf{L}) \ ,$$

or (4)

$$H_{\text{s.o.}} \equiv \tfrac{2}{3}\Delta(\mathbf{S}\cdot\mathbf{L}) \ ,$$

where $\Delta = 390$ cm^{-1}. The magnitude of the spin-orbit parameter Δ has been measured in F_H(OH$^-$) defect pairs in CsCl by Dierolf, Paus, and Luty.[19] The fact that this value is very close to that measured in the pure F-center defect system indicates that it is primarily host dependent.[23,43] We therefore chose $\Delta = 390$ cm^{-1} for F_H(CN$^-$) defect pairs in our model calculations. Surprisingly, the elements connecting the $|x\rangle$ and $|y\rangle$ states involve basis states with the *same* spin-state component only. Since all other interactions in H' are incapable of mixing states with different spin-state components, it is not necessary to specify the spin-state components of our electronic states. The effect of H_2' is to mix the $|x\rangle$ and $|y\rangle$ states, and form the new states: $|x'\rangle$ and $|y'\rangle$, where

$$|x'\rangle \equiv \frac{|x\rangle + |y\rangle}{\sqrt{2}} \quad \text{and} \quad |y'\rangle \equiv \frac{|x\rangle - |y\rangle}{\sqrt{2}} \ . \tag{5}$$

These two new states are still purely p like, and split in energy by $2\Delta/3 = 270$ cm^{-1}. The purely p-like $|x'\rangle$ and $|y'\rangle$ states continue to contribute their original strength to the absorption process. Due to the $|2s\rangle$ component in $|z'\rangle$; however, the contribution of $|z'\rangle$ to the absorption spectra is reduced by a factor of β^2 relative to those of $|x'\rangle$ or $|y'\rangle$. In addition, the previously forbidden $1s \rightarrow |2s\rangle$ transition, as in the pure F-center case, is now dipole allowed as $1s \rightarrow |2s'\rangle$, with a strength of $(1-\beta^2)$ relative to that of the $|x'\rangle$ or $|y'\rangle$ state. The value of β^2 therefore sets the ratio of the $F_H(2)$ and $F_H(1)$ absorption bands.

The remaining H_3' term represents the interactions of all of the states with the even parity A_1 phonon modes, often referred to as "breathing" modes due to their high degree of symmetry, and the B_1 phonon modes. H_3' has nonzero diagonal elements in each of the electronic states $|x'\rangle$, $|y'\rangle$, $|z'\rangle$, and $|2s'\rangle$, and interacts very strongly with them, dominating the electron-phonon interactions, and producing the large widths observed in the spectra of F and F_H centers.[47,48] If the coupling is assumed to be linear in the phonon coordinate, then it is possible to apply previous theoretical results for band-shape functions to the analysis of absorption spectra.[16]

B. Band-shape functions

Because the vibronic interactions can be approximated as diagonal, the phonon contributions to the energy of the states are additive, indicating that the wave functions of the electron-phonon system may be written as the *product* of diagonalized electronic components, $|\Phi\rangle$, and a vibrational (phonon) component, $|\Theta\rangle$, so that the complete wave function is $|\Psi\rangle = |\Phi\rangle|\Theta\rangle$. This is the adiabatic approximation, and allows the application of previous theoretical results on the subject of absorption-band-shape functions. Utilizing the Condon approximation, the absorption coefficient of a single band may be written as[16]

$$\alpha_{ab}(\omega) \equiv \frac{\omega|\boldsymbol{\mu}_{ab}|^2 4\pi^2}{3\sigma\hbar c} F(\omega) \ , \tag{6}$$

where $\boldsymbol{\mu}_{ab} \equiv \langle\Phi_a|e\mathbf{r}|\Phi_b\rangle$, and σ is the cross-sectional area of the sample, c is the speed of light, and $\hbar \equiv h/2\pi$, where h is Planck's constant. The subscript "a" refers to the $1s$-like electronic ground state, the subscript "b" refers to the excited electronic state involved in the absorption process (i.e., $|x'\rangle$, $|y'\rangle$, $|z'\rangle$, or $|2s'\rangle$), and ω is the frequency of the incident light. The function $F(\omega)$ is the band-shape function, given by

$$\begin{aligned} F(\omega) &\equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} \sum_{v',v''} P_{av'}|\langle\Theta_{av'}|\Theta_{bv''}\rangle|^2 e^{i(\omega_{bv'',av'}-\omega)t}\,dt \ , \\ \omega_{bv'',av'} &\equiv (E_{bv''} - E_{av'})/\hbar \ , \end{aligned} \tag{7}$$

where v' and v'' refer to the phonon occupation numbers, and $P_{av'}$ is the Boltzman factor for the phonon occupation number of the $1s$ state. We assume that the vibrational states are purely harmonic, and that they are thermalized before the optical process occurs. It is further assumed that the frequencies of the phonon modes involved in the absorption process are the same in both the $1s$ state and in the excited electronic state to which the system is excited (displaced oscillator model). The band-shape function is then written

$$F(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i(\Delta\omega)t}\prod_i e^{-f_i(t)}dt\ ,$$

where

$$f_i(t)\equiv S_i\{\coth(\Gamma_i)-\mathrm{csc}h(\Gamma_i)\cosh[\Gamma_i+i(\omega_i')t]\}\qquad(8)$$

and

$$\Gamma_i\equiv\frac{\hbar\omega_i'}{2kT},\quad S_i\equiv\frac{\omega_i'(d_i')^2}{2\hbar},\quad \Delta\omega\equiv\frac{E_b-E_a}{\hbar}-\omega\ .$$

S_i is commonly known as the Huang-Rhys factor, or coupling constant, d_i' is the normal coordinate displacement of the ith phonon mode in the excited electronic state relative to that of the 1s state during the optical transition. The electronic energy of the 1s state is E_a, and E_b is the electronic energy of the bth excited state, in the relaxed excited state configuration of the lattice. In an exact treatment, interactions of all of the modes of A_1 symmetry with each of the electronic states would have to be considered. As a general rule, however, it is a good approximation to replace all of the modes interacting with a particular electronic state by a single mode.[48–50] This mode has a single effective frequency, and single effective-coupling constant: $\{\omega_i'\}\equiv\omega'$ and $S=\sum S_i$. The process of lattice reconfiguration following the absorption process is then viewed as the excitation of S phonons of effective frequency ω' in the host crystal.[50]

Due to the symmetry of the electronic states, it is expected that there would be a common effective mode, with a common coupling strength, for $|x'\rangle$ and $|y'\rangle$. Likewise, we expect a common effective mode frequency for $|2s'\rangle$ and $|z'\rangle$. As a double check on the self-consistency of the model, the effective mode frequencies for the $|2s'\rangle$ and $|z'\rangle$ electronic states are determined independently, and then compared with each other. We do not, however, generally expect the values of $S_{2s'}$ and $S_{z'}$ to be the same. This is due to the fact the final relaxed lattice configuration may depend strongly on the detailed nature of the excited electronic state.[26]

An approximate expression for the band-shape function can be obtained by utilizing the short-time approximation. Using this approximation, the resulting band shape is Gaussian and given by[16]

$$F_j(\omega)\equiv F[D_j(T),\omega_j(T),\omega]=\frac{\exp\left[-[\omega_j(T)-\omega]^2/D_j^2(T)\right]}{[\pi D_j^2(T)]^{1/2}}\ ,\qquad(9)$$

where

$$\omega_j(T)\equiv(E_j-E_a)/\hbar+S_j\omega_j'\ ,$$

$$D_j^2(T)\equiv 2(2n+1)S_j(\omega_j')^2$$

and

$$n\equiv 1/(e^{(\hbar\omega_j')/(kT)}-1)\ .$$

The transitions are from the ground electronic state to the jth excited state ($j=x'y'$, z', or $2s'$). The parameter, $\omega_j(T)$, corresponds to the position of the band-shape function, and is a function of temperature through E_a and E_j, which, in turn, are functions of temperature through $H_1'(T)$. Using Eqs. (1), (5), (6), (9), the absorption coefficient may be written as

$$\alpha(\omega)\equiv\alpha_{x'y'}(\omega)+\alpha_{2s'}(\omega)+\alpha_{z'}(\omega)\ ,\qquad(10)$$

where

$$\alpha_{x'y'}(\omega,T)\equiv\frac{|\mu_{\mathrm{sp}}|^2 4\pi^2\omega}{3\sigma\hbar c}\times\left\{F\left[D_{x'y'}(T),\left[\omega_{x'y'}(T)+\frac{\Delta}{3}\right],\omega\right]+F\left[D_{x'y'}(T),\left[\omega_{x'y'}(T)-\frac{\Delta}{3}\right],\omega\right]\right\},$$

$$\alpha_{2s'}(\omega,T)\equiv\frac{|\mu_{\mathrm{sp}}|^2 4\pi^2\omega}{3\sigma\hbar c}(1-\beta^2)F[D_{2s'}(T),\omega_{2s'}(T),\omega],$$

and

$$\alpha_{z'}(\omega,T)\equiv\frac{|\mu_{\mathrm{sp}}|^2 4\pi^2\omega}{3\sigma\hbar c}(\beta^2)F[D_{z'}(T),\omega_{z'}(T),\omega]\ .$$

IV. ANALYSIS AND DISCUSSION

The functions defined by Eq. (10) were fit to the data using seven adjustable parameters for each temperature: $D_j(T)$, and $\omega_j(T)$ for $j=1$ (or $x'y'$), 2 (or $2s'$), 3 (or z'), and β^2. The theoretical fits, and the decomposition of the absorption band-shape functions into $|2s'\rangle$, $|z'\rangle$ and $|x'\rangle+|y'\rangle$ components, are shown in Figs. 6 and 7 for $T=20$ K and $T=100$ K, respectively. The values of $D_j(T)$, $\omega_j(T)$, and β^2, obtained from the fits at $T=20$, 40, 60, 80, 100, and 130 K, are listed in Table I. It is in-

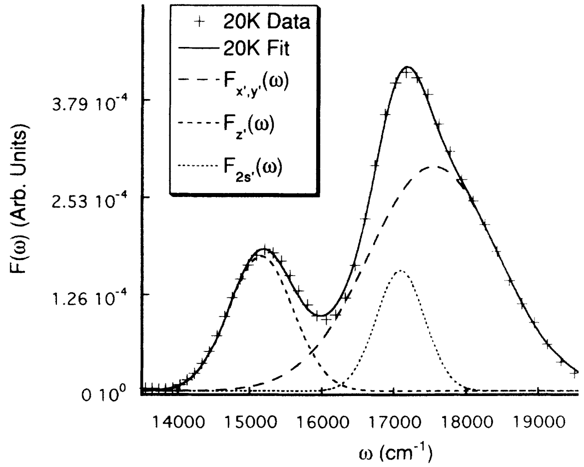

FIG. 6. Comparison of the absorption-band-shape function of $F_H(\mathrm{CN}^-)$ in CsCl obtained from experiment (crosses), with theory (solid line) at $T=20$ K. It is noted that the theoretical line reproduces all of the relevant features. The theoretical band-shape function has also been decomposed into its $|2s'\rangle$, $|z'\rangle$, and $|x'\rangle+|y'\rangle$ contributions, each indicated by the appropriate dashed line.

TABLE I. The best-fit values of $D_{x'y'}$, $D_{2s'}$, and $D_{z'}$ together with the energies of the maxima of the band-shape functions for the 1s to various excited electronic state transitions in the $F_H(CN^-)$ defect pairs are shown. The value $\omega_0(T)$, which is the average energy of the F-center defect transition, is listed for comparison. The values obtained for β^2, which determines the amount of mixing of the $|2s\rangle$ and $|z\rangle$ states, are also shown. The maximum degree of mixing is obtained for $\beta^2=0.5$.

T (K)	$D_{x'y'}$ (cm^{-1})	$D_{2s'}$ (cm^{-1})	$D_{z'}$ (cm^{-1})	$\omega_{x'y'}(T)$ (cm^{-1})	$\omega_{2s'}(T)$ (cm^{-1})	$\omega_{z'}(T)$ (cm^{-1})	$\omega_0(T)$ (cm^{-1})	$\omega_0(T)$ (cm^{-1})	β^2
20	1280	480	635	17 545	17 085	15 155	17 200	17 200	0.60
40	1280	510	701	17 545	17 015	15 165	17 200	17 200	0.61
60	1298	564	765	17 525	16 930	15 190	17 200	17 200	0.58
80	1321	603	856	17 500	16 840	15 215	17 150	17 150	0.57
100	1350	676	860	17 470	16 745	15 245	16 980	16 980	0.52
130	1425	770	930	17 415	16 650	15 275	16 870	16 870	0.49

teresting to note that, as the temperature increases, the degree of *mixing* of $|2s\rangle$ and $|z\rangle$ states increases (β^2 approaches 0.5). Under the same conditions, the *separation* of the absorption peaks from the $|z'\rangle$ and $|2s'\rangle$ components decreases (see Table I). The values of the important parameters S_j and ω'_j are determined from the temperature dependent relationship: $D_j^2(T)=[D_j^2(T=0\text{ K})]\times[2n(\omega'_j,T)+1]$, which holds for each excited electronic state j. The results of this analysis are summarized in Table II. As expected, the values of ω'_j obtained for $j=2$ (or $2'_s$) and $j=3$ (or z') agree with each other to within the uncertainty of the fitting routine (69±3 and 72±4 cm^{-1}, respectively).

The formalism of this paper is directly applicable to $F_H(OH^-/CN^-)$ defects in the other closely related CsBr and CsRb (NaCl structure) host crystals. The most obvious extension of the analysis presented in this paper would be to that of the absorption spectra of $F_H(OH^-)$ defect pairs in CsCl as obtained by Luty and coworkers.[1,19] The OH^- molecule differs substantially from the CN^- molecule in size, magnitude of the intrinsic dipole moment, vibrational frequency and vibrational lifetimes. Comparing the absorption properties of the two defect pairs, it is found that the width of the $F_H(1)$ (due to interactions of the even parity phonon modes with $|z'\rangle$) band in $F_H(OH^-)$ is much smaller than that observed in $F_H(CN^-)$. This suggests that the large differences in the nature of the two dipole molecules significantly affect the electron-phonon interactions. The ratio of oscillator strength $F_H(1){:}F_H(2)$ as measured in $F_H(OH^-)$ in CsCl also differs significantly from 2:1,[51] suggesting that the presence of the OH^- molecule produces a strong mixing of the $|2s\rangle$ and $|z\rangle$ states, similar to that found for $F_H(CN^-)$ in CsCl in this study.

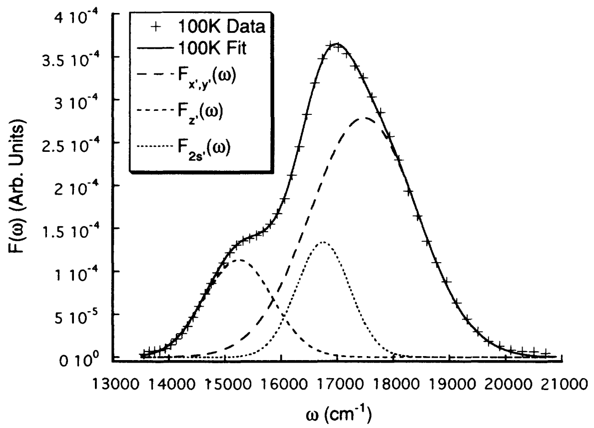

FIG. 7. Comparison of the absorption-band-shape function of $F_H(CN^-)$ in CsCl obtained from experiment (crosses), with theory (solid line) at $T=100$ K. The theoretical band-shape function has also been decomposed into its $|2s'\rangle$, $|z'\rangle$, and $|x'\rangle+|y'\rangle$ contributions, each indicated by the appropriate dashed line. Even though the characteristics of the experimental data are noticeably different than at $T=20$ K, the theoretical line is still able to reproduce all of the relevant features.

V. CONCLUSION

A systematic study of the temperature dependence of the absorption spectra of $F_H(CN^-)$ defect pairs in a CsCl host crystal has been presented. The experimental results have been explained satisfactorily with a simple absorption-line-shape model, which includes the mixing of the 2s and 2p_z electronic states. In particular, we were successful in obtaining the coupling constants and effective phonon mode frequencies, which are involved in

TABLE II. The values of D_j ($T=0$ K), the coupling constant and effective phonon-mode frequency of each electronic states involved in the absorption process are presented. Note in particular that the effective mode frequencies of the $|z'\rangle$ and $|2s'\rangle$ states agree with each other to within the uncertainty of the fitting.

j	D_j ($T=0$ K) (cm^{-1})	S_j	$\omega'j$ (cm^{-1})
1 (or $x'y'$)	1285	19.8	204±5
2 (or $2s'$)	473	20.5	72±4
3 (or z')	636	41.2	69±3

the absorption process. In addition, the peak positions were obtained for each temperature, as well as information about the degree of mixing of the $|2s\rangle$ and $|z\rangle$ states. Because this analysis of absorption spectra fixes several parameters used as adjustable parameters in our previous model calculations,[13–15] the information obtained from this work is very important in a rigorous test of the models proposed for the e-v energy transfer process of $F_H(\mathrm{CN}^-)$ defect pairs in CsCl.

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[*] Also at Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan, R.O.C.

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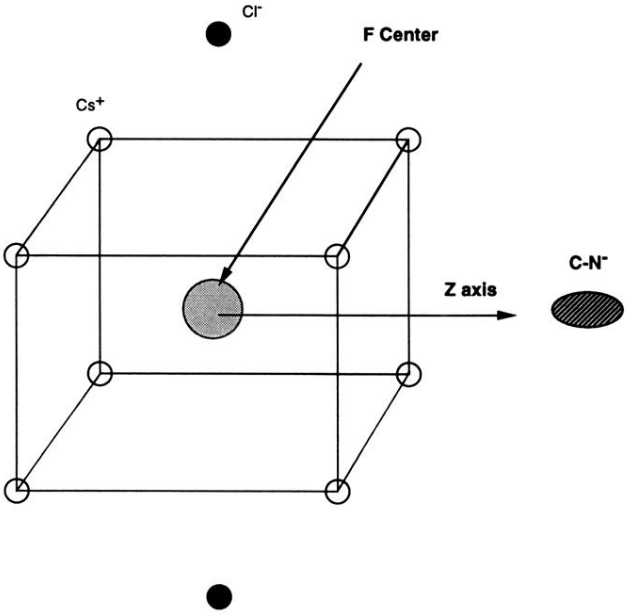

FIG. 4. A diagram of the $F_H(\mathrm{CN}^-)$ defect pair in CsCl, which clearly demonstrates the V_{4v} symmetry of the defect pair.