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A study of the $F_H(CN^-)$ centre in KCl and CsCl: the potential energy surface and EV energy transfer

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Abstract. Adiabatic potential energy surfaces (APES) of the $F_H(CN^-)$ centre in KCl and CsCl are calculated for the excited and ground states. It is shown that in CsCl the APES of the excited state intersects that of the ground state on the path of de-excitation leading to the quenching of emission. In KCl, the opposite situation is obtained in agreement with experiment. The calculation for CsCl shows a rapid variation of the dipole moment of the CN^- molecule near the crossing region. The electronic-to-vibrational energy transfer (EV transfer) between the F centre and CN^- molecule is discussed in terms of the non-radiative transitions between the two intersecting APES. The dipole-dipole coupling between the F centre and CN^- molecule (Dexter-Förster theory) is also considered to analyse certain aspects of the EV transfer.

1. Introduction

When an electron is trapped at a negative ion vacancy in an alkali halide crystal, a simple defect of cubic symmetry known as the F centre is formed. More complex defects may be produced by the association of the F centre with various neighbouring cationic or anionic defects. Of these, the F_H centres (F-molecule complex), of reduced local symmetry and changed electron-lattice coupling, provide interesting systems for the study of a variety of fundamental energy transfer processes in solids. Among these complex centres, F-centre- CN^- defect pairs ($F_H(CN^-)$) and F-centre- OH^- defect pairs ($F_H(OH^-)$) are of particular interest and have been extensively studied [1–3]. In this paper we shall concentrate on the $F_H(CN^-)$ centres in CsCl and KCl as they represent the contrasting groups.

The most novel and interesting effect appears in the case of $F_H(CN^-)$ in CsCl and CsBr [1]. Electronic excitation of these centres by optical radiation produces an intense CN^- vibrational emission band and at the same time the electronic luminescence is quenched. The F luminescence in undoped Cs halides is not quenched [4]. In contrast, although vibrational fluorescence of the CN^- molecule has been observed for the $F_H(CN^-)$ centre in KCl, the efficiency of the conversion is only about 4%, and the electronic luminescence is hardly reduced [1]. This shows that the perturbation of the CN^- molecule on the F centre is considerably stronger in CsCl. In fact in the case of $F_H(CN^-)$ in CsCl, the original F band is split into two bands, $F_H(1)$ and $F_H(2)$, separated by 0.27 eV, while the F band in KCl is only slightly red shifted and broadened by the presence of CN^- . Indeed, Lüty and co-workers [2, 3] observed that the coupling between the two defects is stronger generally in the CsCl lattice than in the NaCl lattice. They also noted that despite such a difference, the electronic-to-vibrational energy transfer (hereafter EV transfer) process always produces a maximum population in the $\nu = 3-4$ state of the associated CN^- in both types of material.

The first theoretical calculation of the $F_H(CN^-)$ centre in CsCl was made by Gash [5]. The method used was the ion-size approximation, which was developed for F-centre studies in alkali halides. Gash approximated the ion-size parameters of the CN^- molecule by those of the Br^- ion, which has the same number of electrons as CN^- . The electric dipole potential of the CN^- molecule was included and the relaxation of the first-shell atoms was considered. The calculated optical absorption energies were in satisfactory agreement with experiment. The EV transfer and the quenching of the luminescence were not addressed. Recently Halama *et al* [6, 7] employed a 'supermolecule' model to explain the observed anti-Stokes resonance Raman scattering of $F_H(CN^-)$ in CsCl. However, a satisfactory microscopic theory to account for the highly efficient EV energy transfer processes in CsCl has not yet been developed.

In this paper, we attempt to explain some of the observed properties of $F_H(CN^-)$ in CsCl and KCl by performing first-principles calculations of the adiabatic potential energy surfaces (APESs) of the ground and excited states of these defect centres. The configuration coordinates used for the APES are the molecule bond length of CN^- , designated by Q_1 , and the distance separating the F centre and the CN^- molecule (its mid-point), designated by Q_2 . The method employed is the extended-ion method, which has been developed recently by Song and co-workers and applied successfully to the study of self-trapped excitons in alkali halides and other insulators [8]. This method treats the excited electron of the F centre within the extended-ion approximation, while the CN^- molecule is treated by a CNDO code. The two parts are interfaced so that the various parameters, in particular the charges distributed on CN^- and the potential acting on the molecule, are updated consistently during the lattice relaxation. Besides the APES, we have determined the optical transition energies, which are found to be in general agreement with experimental data.

The most significant result in the work is that there is a clear difference in the APES between the $F_H(CN^-)$ centres in KCl and CsCl. (A preliminary report has been made recently [9].) In CsCl, the ground and excited APESs intersect at a region near the relaxed excited state (RES) configuration, while the APESs in KCl do not cross. According to the theory of Dexter and co-workers [10], this accounts for the experimental observation that the $F_H(CN^-)$ luminescence is quenched in CsCl but not in KCl. We have evaluated the dipole moment of the CN^- molecule of the excited and ground states during the de-excitation process and found a large variation near the crossing region. We propose a mechanism of the EV energy transfer based on non-radiative transition (NRT) accompanied by 'hot' transfer near the crossing. This model is able to explain the difference between KCl and CsCl regarding the strength of EV transfer, and is satisfactory in accounting for the relation between the F emission quenching and EV transfer. We also examine the implication of the Dexter-Förster mechanism [11, 12] of energy transfer through dipole-dipole coupling between the two defects. Although a quantitative analysis is not possible, the observed anisotropy in the EV transfer between the $F_H(1)$ and $F_H(2)$ bands [3] is explained in terms of the anisotropic dipole-dipole interaction.

This paper is organized as follows. In section 2, we give a brief description of the method of calculation. In section 3, we present and discuss the results of our calculations. Finally in section 4 we discuss the EV energy transfer process in CsCl (CN^-) based on the results of the APES and dipole-dipole coupling.

2. Method of calculation

The method used in this work is similar to the one used by Song and co-workers in their study of self-trapped excitons in alkali halides. The F-centre electron is treated by the

extended-ion method in which the electron wavefunction is taken as a linear combination of floating 1s Gaussians made orthogonal to all occupied electronic states in a large region in the crystal. This has been proven to be computationally efficient and versatile. The details, in particular the interpolation formulae, which evaluate various short-range electronic energy terms, have been given in [8]. The wavefunctions of K^+ , Cs^+ , C and N^- used in this work are those published by Clementi and Roetti [13]. For Cl^- , we have recalculated the wavefunctions with an SCF code in an approximate ionic lattice to take into account the substantial shrinking of its valence p shell as in our earlier works [8].

The CN^- molecule is treated by a standard CNDO code. The charges on the two atoms of CN^- , as determined by the CNDO calculation, are required for the calculation of both the Coulomb potential experienced by the F-centre electron and the lattice Coulomb energy. At the same time, the CNDO molecular calculation requires the potential produced by the remainder of the crystal including the F centre. This is achieved by constantly updating these parameters during the defect system energy minimization. Also the CNDO molecule energy enters the total energy of the defect system. The short-range potential terms of CN^- acting on the F electron (screened Coulomb, exchange and overlap integrals arising from orthogonalization) have been approximated by those corresponding to N^- and C^0 . These approximated charge states are rather close to the charge distribution obtained in the CNDO calculation (~ -0.3 for C and ~ -0.7 for N)†. The CNDO parameters for C and N are chosen to fit the bondlength of 1.36 Å and the vibrational frequency of 2255 cm^{-1} of the free CN^- molecule. The CNDO parameters for these ions are presented in table 1.

Table 1. CNDO parameters used in this work (energies are in electronvolts and α is in \AA^{-1}).

	I_s	I_p	β	$\alpha_s = \alpha_p$
N	-19.32	-8.72	-16.0	1.95
C	-14.05	-4.12	-12.0	1.62

The total energy of the defect system is the sum of the F-centre electron energy, the CNDO energy of CN^- , the lattice energy and the polarization energy. In this work, the lattice is represented by the usual Born–Mayer pair potentials [14]. The electronic polarization is treated with the approximation of point-polarizable dipoles within the lowest-order Mott–Littleton method. Values of the polarizability of CN^- and those of Cl^- , Cs^+ and K^+ are from [15].

The electronic wavefunction is represented by floating 1s Gaussians. For the ground s-like state and the excited p-like state parallel to the molecular axis, a basis of five Gaussians is used, while a basis of six Gaussians is used for the p-like states perpendicular to the molecular axis. The number of Gaussians is slightly increased near the crossing region of the APESs.

3. Results and discussion

3.1. The ground-state APES

As we described above, two configurational coordinates are chosen to represent the APES of the system. One is the molecular bondlength Q_1 of the CN^- molecule, and the other

† An *ab initio* Hartree–Fock calculation using Gaussian 88 code gave similar charges and bondlength.

is the distance Q_2 between the F centre and the mid-point of the CN^- molecule. For a complex defect system, choosing the configuration coordinates is not always evident. One could think of the breathing mode of the F centre as a possible one. However, because of the lowered symmetry this would be complex and requires more coordinates than we can manage. The Q_2 mode partly represents this coordinate and at the same time is an important one as will be shown below.

For a given set of values (Q_1, Q_2), the total energy of the system is minimized with respect to the displacements of about two dozen surrounding ions. These optimized energies are used to construct the APES. For both the ground s-like and the excited p-like APES, we have assumed in accordance with experiment that the CN^- molecule is aligned along the $\langle 110 \rangle$ and the $\langle 100 \rangle$ axes in KCl and CsCl respectively. We have, however, studied both orientations of the CN^- molecule relative to the F centre, namely the $\text{F}(\text{CN}^-)$ and $\text{F}(\text{NC}^-)$ orientations, corresponding respectively to the case where the C or N atom is close to the F centre. For both KCl:CN and CsCl:CN we have found no significant difference between the ground state total energies for these two orientations. The total energy differences are about 0.04 eV, which is beyond the precision of the present computation. Therefore we have to conclude that the present work is unable to distinguish between the $\text{F}(\text{CN}^-)$ and $\text{F}(\text{NC}^-)$ orientations. Also, since there are only minor differences between the APESs for these two orientations, we have chosen to present only the APES for the $\text{F}(\text{CN}^-)$ orientation.

At the minimum-energy configuration, the equilibrium bond length (Q_1) is 1.36 Å in both KCl and CsCl, which is close to the fitted value of the free CN^- molecule. The equilibrium value for Q_2 is found to be 4.45 Å for KCl and 4.62 Å for CsCl. These values should be compared with the values of the distance between the F-centre site and the closest regular anion site in a perfect lattice. These are 4.45 Å and 4.11 Å for KCl and CsCl respectively. From this comparison, it is apparent that there is an overall short-range repulsion between the F centre and the CN^- molecule. This will become clearer when compared to the excited-state APES presented below. It is interesting to note that this situation is similar to that observed in the off-centre self-trapped exciton (STE) in alkali halides. In the STE, the excited electron occupies a vacant anion site to become a primitive F centre and at the same time the V_k centre (a halogen molecule-ion X_2^-) is expelled axially.

3.2. The excited-state APES

For the excited 2p-like states, both p_y (parallel to the CN^- molecular axis) and p_x (perpendicular to the CN^- molecular axis) are studied. In the case of the $\text{F}_H(\text{CN}^-)$ centre in CsCl, the system has C_{4v} symmetry and the two p-like states perpendicular to the CN^- molecular axis are degenerate. In the case of KCl(CN), which has C_{2v} symmetry, the x -axis, chosen along the $\langle 1\bar{1}0 \rangle$ axis, and the z -axis are inequivalent. Nevertheless, our calculations have shown that the p_x - and p_z -like states in KCl(CN) are quite indistinguishable. Henceforth we shall only be concerned with the p_y - and p_x -like states for both KCl and CsCl.

The APESs for the excited p_y -like and p_x -like states in the $\text{F}(\text{CN}^-)$ orientation are presented in figure 1 for KCl and in figure 2 for CsCl. For later discussion of luminescence and the EV energy transfer, the Franck-Condon ground-state APESs are also presented within the same figures. We note that the Franck-Condon ground-state APES is different from that of the relaxed ground-state APES discussed in subsection 3.1. Comparison of figures 1 and 2 shows that the most important feature is the intersection of the excited-state APES with that of the ground-state in CsCl but not in KCl. Although it may not be clearly visible in the figures presented, the crossing occurs at $Q_2 \simeq 2$ Å for the entire range of Q_1 shown. This point will be useful when discussing the EV transfer. For both the p_y - and p_x -like

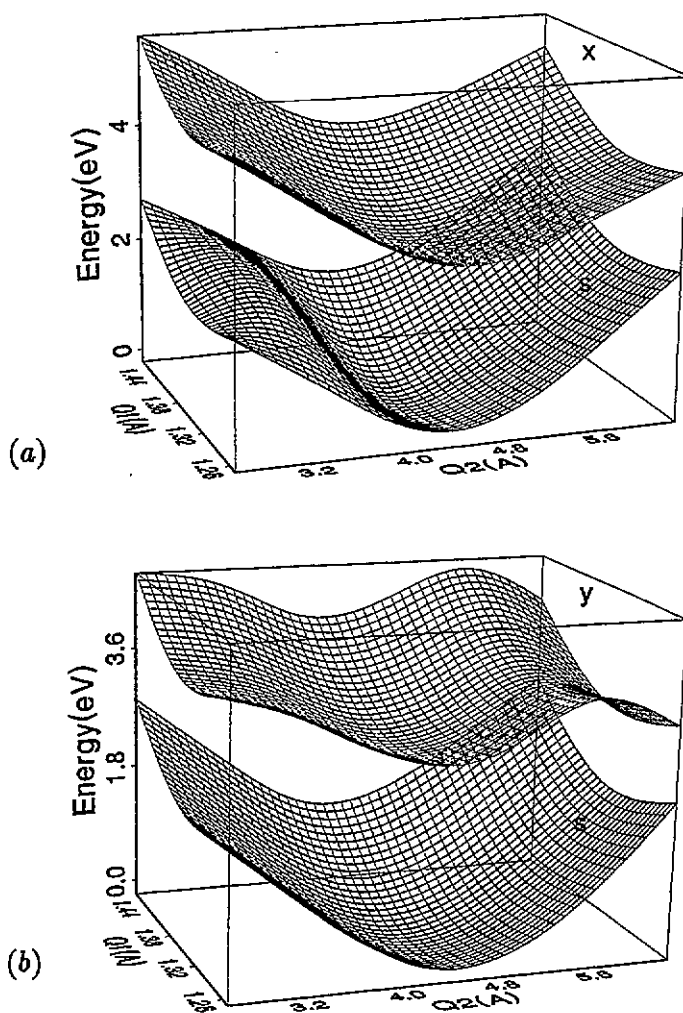


Figure 1. Adiabatic potential energy surfaces (APES) of the $F_H(\text{CN}^-)$ system in KCl with the F centre in (a) p_x and (b) p_y states (respectively perpendicular and parallel to the CN^- axis). Franck-Condon ground-state APES are also shown. Q_1 represents the molecule bondlength and Q_2 the distance between the F centre and the CN^- molecule (mid-point). (The theoretical results obtained over the same grid of Q_1 - Q_2 as in table 3 have been plotted using a 3D-spline smoothing process.)

excited states in CsCl (corresponding to optical excitation in the $F_H(1)$ and $F_H(2)$ bands respectively), it is fairly clear that the $F_H(\text{CN}^-)$ -centre luminescence is quenched in CsCl. We recall that the F luminescence band is observed in all Cs halides [4] (in CsCl, it is at 1.255 eV). As discussed below, the crossing of the APES should be associated with the observed EV transfer leading to efficient vibrational fluorescence. By contrast, there is no crossing of the APES in KCl(CN). These results are in agreement with experimental observation regarding the luminescence quenching of the $F_H(\text{CN}^-)$ centre.

We have commented earlier on the short-range repulsive interaction between the F centre and the CN^- in the ground state. This repulsive interaction is somewhat modified in the excited state and as a result Q_2 reaches a new equilibrium value on the excited APES.

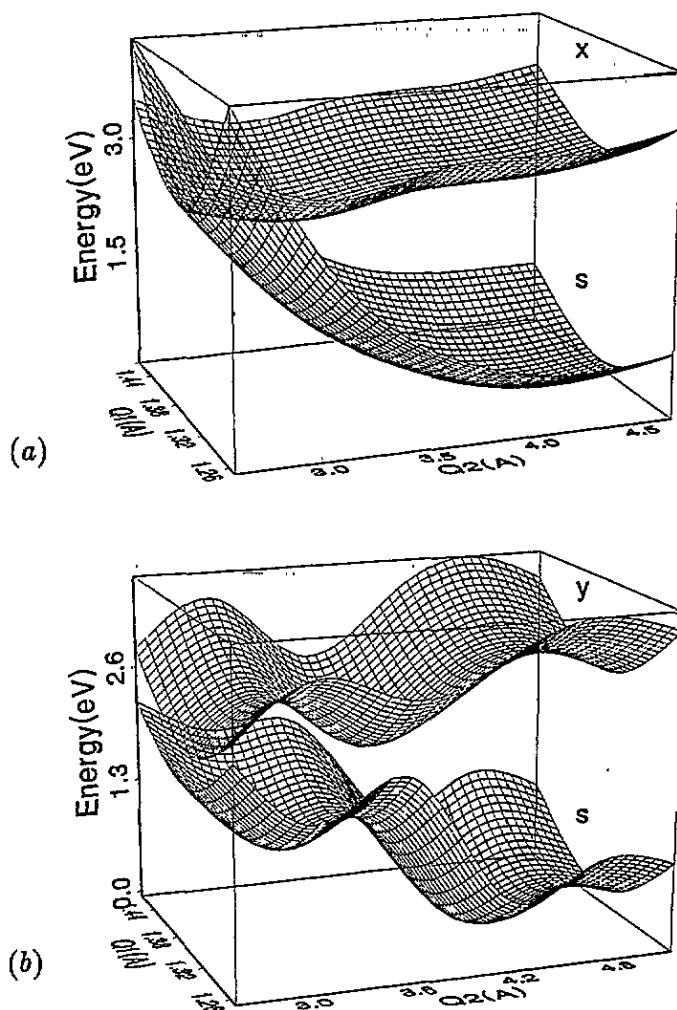


Figure 2. Adiabatic potential energy surfaces (APES) of the $F_H(CN)$ system in CsCl with the F centre in (a) p_x and (b) p_y states (respectively perpendicular and parallel to the CN^- axis). Franck-Condon ground-state APES are also shown. Q_1 and Q_2 are defined as in figure 1. (The theoretical results are plotted using a smoothing process as in figure 1.)

This is in fact the situation in CsCl(CN) and leads to the crossing of the APES in CsCl. Obviously, the situation is different in KCl. This very fundamental difference is attributable to the lattice structure difference, which exerts subtle influences on the interaction between the excited F electron and the nearby molecule. Finally there is also some difference in the shape of the APES between the p_y - and the p_x -like states, which is due partly to the difference between their overlaps with the CN^- molecule.

3.3. The absorption and emission energies

Using the equilibrium lattice configurations obtained for the ground-state APES of the $F_H(CN^-)$ centres in KCl and CsCl the optical absorption energies are readily evaluated. These values are presented in table 2 together with the experimental data. For the case of

Table 2. Absorption energies of $F_H(CN^-)$ in KCl and CsCl.

	$ p_y\rangle$	$ p_x\rangle$	Experiment
KCl ($F(NC^-)$)	2.41	2.51	(2.30)
CsCl ($F(CN^-)$)	2.30	3.21	(1.85, 2.12)
($F(NC^-)$)	1.90	2.04	

CsCl(CN), both the $F(CN^-)$ and $F(NC^-)$ orientations are studied, and as shown in table 2, slightly better agreement with experiment is obtained for the $F(NC^-)$ configuration. In general, the calculated absorption energies are in reasonable agreement with experiment for both KCl(CN) and CsCl(CN). In particular the observed splitting of the absorption band in CsCl(CN) is qualitatively reproduced. At the same time, the calculated smaller splitting between the p -like levels in KCl(CN) is quite consistent with the observed broadening of the absorption band (about 0.1 eV). The emission is quenched in the case of CsCl(CN), as discussed above. In KCl(CN), we obtain luminescence energy in the range of 1.0–2.5 eV from the lower-lying p_x state. These rather divergent values are due to the difference in the lattice relaxation in the RES, which is quite sensitive to the Gaussian basis functions and the size of the relaxing ion cluster. For comparison, the observed luminescence energy in KCl(CN) is 1.03 eV.

4. Electronic-to-vibrational (EV) energy transfer in CsCl

The efficient transfer of electronic excitation energy of the F centre to vibrational energy of the CN^- molecule in the $F_H(CN^-)$ centre in CsCl is the most interesting subject and has been actively investigated. At present, there is no satisfactory theory that explains this outstanding phenomenon. In this section we investigate this subject on the basis of the results presented above. The following are some of the questions that have to be addressed.

(i) Which basic feature distinguishes the two different groups of materials, CsCl and KCl, regarding the EV transfer efficiency and the luminescence quenching?

(ii) What is the precise mechanism of the EV energy transfer?

(iii) How can we account for the experimental observation that in all materials the strongest EV transfer occurs to $\nu = 3-4$ of the CN^- molecule?

The answer to the first question seems the most clear in view of the APES calculated. Our model considers the NRT between the two states as the key element. In our preliminary report [9], we argued that the efficient EV energy transfer is related to the F-emission quenching. The criterion formulated by Dexter and co-workers [10] predicts quenching of the F emission in CsCl and no quenching for KCl. We propose here that the energy transfer is controlled by the two APES intersecting in the Q_1 – Q_2 configurational space, as shown in figure 2 for CsCl(CN). It has been shown in several works dealing with NRT [10, 16, 17] that when the excited state reached by optical absorption is above the point where the excited and ground states intersect, there is an efficient NRT to the ground state while the system is relaxing toward the RES. This is efficient not only at the crossing point, but also above that energy over a fairly large energy interval [17]. In order to have an efficient NRT, the two states should be found close enough in the configuration coordinate (CC) space. This is trivial to visualize when only one coordinate is explicitly employed, as in the F centre. In our present case with the Q_1 and Q_2 coordinates, a certain caution is needed. The best way to do this is to plot the APES as we did in figures 1 and 2. When such APES are projected

on a plane, points that are actually separated in the CC space may appear to cross (as in figure 2 of [3]). Lüty and Dierolf [3] proposed 'hot transfer' during the rapid relaxation along the *lattice mode* (similar to our Q_2 coordinate) as one of the possible mechanisms. The process we have just described above is indeed equivalent to the 'hot transfer' and we consider it as an important aspect of the problem.

This brings us to the second question enumerated above. Regarding the mechanism responsible for the EV transfer, there have been several recent studies [6, 7]. In their study of certain aspects of EV transfer in $\text{F}(\text{CN}^-)$ and $\text{F}(\text{OH}^-)$ centres, Halama *et al* [7] have adapted the Dexter-Förster theory originally formulated to treat EE transfer in sensitized luminescence. According to this theory, the transition of the system from $|i\rangle = |p; \nu = 0\rangle$ to $|f\rangle = |s; \nu = n\rangle$ occurs as the result of the dipole-dipole coupling given by

$$H' = [\mu_A \cdot \mu_D - 3(\mathbf{R} \cdot \mu_A)(\mathbf{R} \cdot \mu_D)/R^2]/\epsilon R^3. \quad (1)$$

Here, A and D represent CN^- and F centre respectively, separated by R . ϵ is the dielectric constant. To obtain the transition probability of the EV transfer, the matrix element of the above operator H' has to be evaluated between the initial and final states. A numerical evaluation of the matrix element $\langle i|H'|f\rangle$ would be complex. For the dipole μ_D (the F centre), it is in principle straightforward. However, that of μ_A (CN^-) would be complex. The CN^- molecule in the free state has a permanent dipole moment (0.3 Debye [18]). What is needed here is the matrix element of μ_A between the initial and final states. Halama *et al* have assumed that the electronic state of CN^- does not change between the two states and assumed instead a linear dependence of μ_A on Q_1 in their study [7]. Along this line, Fowler has found that the probability of transition for the process ($\nu : 0 \rightarrow 4$) of the CN^- molecule in CsCl was too small by several orders of magnitude to explain the experimental observation [19].

Table 3. The dipole moment μ_A of the CN^- molecule evaluated as a function of Q_1 and Q_2 coordinates with the excited F-centre electron in the p_y and p_x states. For each case, the ground-state μ_A is also shown in brackets (μ is in units of Debye).

Q_2 (Å)	Q_1 (Å)		
	1.25	1.36	1.47
$ p_y\rangle$			
3.67	1.38 (1.14)	1.70 (1.44)	1.98 (1.69)
3.19	1.56 (1.26)	1.76 (1.50)	1.91 (1.69)
2.72	1.08 (1.26)	1.31 (1.44)	1.55 (1.76)
2.26	1.02 (1.14)	1.24 (1.44)	1.41 (1.62)
1.76	0.78 (1.44)	1.04 (1.83)	1.34 (2.12)
$ p_x\rangle$			
4.14	1.38 (1.32)	1.63 (1.56)	1.98 (1.83)
3.67	1.43 (1.21)	1.67 (1.43)	1.93 (1.67)
3.19	1.38 (1.07)	1.63 (1.26)	1.88 (1.47)
2.72	1.30 (0.76)	1.54 (0.91)	1.79 (1.07)
2.31	0.44 (1.22)	0.41 (1.46)	0.49 (1.69)

In an attempt to understand the relation between the NRT processes discussed above and the dipole-dipole coupling between the two defects that is the triggering mechanism of Dexter-Förster theory, we have evaluated the dipole moment of CN^- on the excited-state

APES. We obtained the charges q on C and N in the form of a Mulliken population from the CNDO code. It is possible therefore to follow the variation of the dipole moment μ of CN^- in a qualitative way. μ is defined [20] here as $\delta q Q_1$, where $\delta q = (q_C - q_N)/2$. The variation of μ is shown in table 3 with the F electron in both $|p_x\rangle$ and $|p_y\rangle$ states for CsCl(CN) over a range of $Q_2 \simeq 2\text{--}4 \text{ \AA}$, and $Q_1 = 1.25\text{--}1.47 \text{ \AA}$. The variation of μ is monotonic especially for $|p_x\rangle$ until the crossing region ($Q_2 \cong 2 \text{ \AA}$) is reached. For $|p_y\rangle$ the variation of μ is more complex. In both cases, for any given value of Q_2 , μ varies approximately linearly in Q_1 . However, the dipole moment μ varies abruptly for both the excited and ground states near the crossing region of the APES because of the rapid variation of the effective charges q . This means that there is a substantial change in the internal electronic structure of CN^- near the crossing region even if it is the F-centre electron that undergoes the transition from a p-like to an s-like state. The charge distribution on the molecule varies depending on the bondlength Q_1 even in the free state. In the crystal it depends also on the crystal potential acting on the molecule, in particular the Madelung potential. It is obvious from table 3 that it also depends on the F-electron state when the two centres are close.

From the above observations, it seems possible to put forward the following arguments. When the system undergoes NRT near the crossing region ($Q_2 \cong 2 \text{ \AA}$), the dipole moment of CN^- changes quite substantially as can be seen in table 3. It is speculated that the dipole moment undergoes a fast fluctuation between the old and new values after reaching the ground-state APES, which appears as an excitation of the Q_1 mode, the bondlength. This interpretation of vibrational excitation seems to be another way of describing the transition mediated by the dipole-dipole coupling of Dexter-Förster. On the other hand, it is possible to make several remarks about the coupling between the two dipoles. (1) shows that H' becomes stronger as the system relaxes toward the crossing region where R is smaller than when the system has just been excited. Another interesting point is the anisotropy, which is indicated by H' . We expect the vector of $\langle i|\mu_A|f \rangle$ to be along the molecular axis. It is seen that with the excitation of the $F_H(2)$ band (the p_x state in this work), μ_D of the F-electron would be perpendicular to μ_A , resulting effectively in $H' = 0$ (R is also along the molecular axis). With the $F_H(1)$ band (here, excitation to the p_y state), on the other hand, there would be μ_D parallel to μ_A , thereby resulting in $H' \neq 0$, and we expect a stronger EV transfer. For the geometries of F-centre- CN^- other than those studied, the resulting anisotropy of EV transfer would be weaker. This analysis is in agreement with the experimental observation in CsBr [3] that the $F_H(1)$ band excitation leads to a stronger EV transfer. Based on the present model, we can conclude that the EV transfer would be much weaker in KCl as there is no close approaching of the two APESs, as well as no strong variation of μ_A .

There remains the last question of why in all cases, of both NaCl and CsCl structure, the strongest transfer occurs to $\nu = 3\text{--}4$. At present we do not have a reliable argument, and further studies are needed. We have shown through our theoretical APES that the efficiency of the EV transfer in the $F_H(\text{CN}^-)$ centres is closely related to the intersection of the excited and ground states. We have also argued in favour of the model of 'hot transfer' accompanying the NRT near the crossing of the two APESs. We argued that the vibrational excitation of the CN^- might be attributable to the substantial changes found in the calculated dipole moment μ_A as the system undergoes NRT to the ground-state APES. We have noted some interesting aspects of the dipole-dipole coupling to explain the anisotropy in the EV transfer observed in CsCl.

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- [20] This definition of the dipole moment μ is very approximate. In the *ab initio* Hartree-Fock calculation of free CN^- , we found that the bondlength is 1.22 Å with charges $\text{C}^{0.40}-\text{N}^{0.60-}$, fairly close to our CNDO data. The Gaussian 88 code also gives μ to be 0.37 Debye, which is smaller than the 0.58 Debye one would obtain using the simplistic definition used to obtain table 3. On the other hand, the experimental value of μ is 0.3 Debye according to [18]. We should consider therefore the values of μ in table 3 to merely indicate the trend as a function of Q_1 and Q_2 .