

to be never more than ~ 1 kHz. At such low frequencies and a lattice temperature $\sim 1^\circ\text{K}$ induced currents seem unlikely to be a problem.

¹⁸I am grateful to Professor M. Goldman for pointing out this effect to me.

¹⁹Numbers quoted are the maximum variations of energy as a function of angle. The quoted value of (4b) is valid for $1-f \ll 1$ and is in general an upper limit on the order of magnitude. The term (4a) involves shape-dependent demagnetization factors; the value quoted is for a sphere deformed ellipsoidally by the tetragonal

anisotropy, but by suitable shaping of the sample this term can in principle be made very small (or to compensate some of the others).

²⁰It is at first sight tempting to use instead of a single crystal a poled ceramic (Ref. 7, pp. 127, 532); this would eliminate effect (4b) altogether, and reduce all other class (B) effects by a factor proportional to the degree of 90° domain rotation, while A' would be reduced at most by a factor of $\frac{1}{2}$. Unfortunately it seems doubtful whether the "solid-effect" polarization technique would work in such a material.

Exciton Structure of Crystalline K^+CN^-

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In the ionic molecular crystal K^+CN^- , excitonic properties characteristic of both ionic and molecular crystals are observed at different photon energies. Various molecular exciton interactions are manifested in the low-energy part of the spectrum. A resolved Davydov-type splitting is observed for the first time in an ionic crystal and is explained by a weak-interaction model. Charge-transfer excitons occur at higher energies.

The electronic structure of both ionic and molecular crystals has attracted continuous interest over many decades. In this Letter we discuss a unique system which exhibits excitonic features typical of both molecular and ionic crystals. Crystalline KCN manifests many other fascinating properties related to the simple nature of the diatomic CN^- molecule. The phase transitions at 168 and 83 K are examples of, respectively, ferroelastic^{1,2} and antiferroelectric³ ordering of the molecules due to their associated elastic and electric dipoles.

In contrast to ordinary crystals the binding energy of K^+CN^- is comparable to the dissociation energy of the CN^- molecule. Hence crystalline KCN can be best described as a "pseudo alkali halide" in which *both* molecular and ionic excitons should be observed. Since CN^- is isoelectronic with the molecules N_2 and CO which form simple crystal structures in the solid phase, their spectra^{4,5} and the molecular part of the spectrum of KCN should be similar. Alkali-halide-like excitons should be observable because of the interaction of CN^- with the cation. We report for the first time that in a ionic crystal both charge-transfer and resolved Davydov-type excitons⁶ are

observed. Experimental results ^{<labs>} which explains the molecular-crystal-like spectrum are presented in this paper.

The reflectivity of KCN single crystals has been measured in an oil-free vacuum-ultraviolet spectrometer system.⁷ The samples have been cleaved *in situ* in a vacuum better than 10^{-7} Torr. Liquid-He temperature is achievable in 10 min after cleaving by means of a continuous-flow evaporation cryostat, in which the temperature can be varied between 3 and 400 K. The reflectivity has been measured at near-normal incidence and no angular or polarization dependence can be expected as the crystal undergoes the phase transition at 168 K where multidomain formation is observed. The crystals under investigation have been grown by either Bridgman or Czochralski technique. KCN crystals are hygroscopic and therefore all preparation steps were carried out under rare-gas atmosphere.

The experimental results displayed in Fig. 1 exhibit a broad band between 9 and 10 eV due to a charge-transfer exciton. The structure in the region of 7 eV is due to the electronic $A^1\Pi - X^1\Sigma^+$ transition of the CN^- molecule and consists of a progression of combined electronic and vibration-

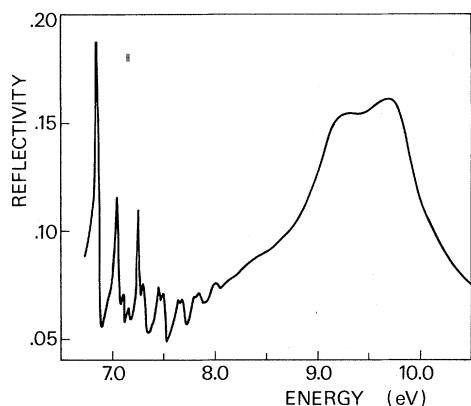


FIG. 1. Reflectivity of KCN at 5 K. Molecular-crystal-like exciton with vibrational structure at 7 eV; charge-transfer exciton at 9 eV.

al transitions, each band exhibiting a splitting. This splitting is due to the *resonance* interaction between the molecules and therefore a Davydov-type splitting.⁶ The progression of split bands shows a systematic variation of the intensity ratio and is interrupted by a weak band at 7.13 eV, which must be assigned to a so-called two-particle state.⁸ In the quantitative interpretation of the spectrum we first treat the resonance splitting of the electronic transition separately from the vibrational problem. We introduce the following assumptions:

(1) The CN^- molecule is only weakly perturbed by the crystalline environment such that an effective electronic transition energy T_e of the molecule can be defined which includes all effects due to the surroundings. The crystal-field splitting of the degenerated $A^1\Pi$ state is neglected.

(2) The transition dipole moment is responsible for the splitting (resonance splitting, Davydov splitting). We assume a point-dipole lattice which is invariant with respect of the CN^- - NC^- orientation. Consequently a primitive cell with only one molecule is used.

(3) Six nonequivalent orthorhombic domains are arranged in such a way that each orientation occurs with the same probability.⁹ Furthermore, the sizes of the domains are distributed such that there is an equal number of molecules for each possible orientation. Therefore a cubic overall symmetry can be assumed. For the computation of the short-range dipole-dipole interaction, the crystal structure within one domain is taken into account. It is presumed that the number of the molecules within one domain is large enough that molecules at the domain inter-

face play an inferior role. For long-range dipole-dipole interaction we consider the cubic overall symmetry.

With these assumptions we calculate the resonance splitting and the corresponding intensity distribution. As the molecules are oriented along the b axis of the orthorhombic unit cell the transition dipole moments can be taken as perpendicular to the b axis. With cell dimensions given in Table I, the summation of the dipole-dipole interactions leads to two electronic resonance energies $\epsilon_a = -0.0101P^2$ and $\epsilon_c = 0.0024P^2$, where P is the transition dipole moment and the numerical factors are given in inverse volume units. These energies are modified by the macroscopic dipole sum which in the case of cubic crystals is $-4\pi(\epsilon_0 + 2)P^2/9V$ for dipoles perpendicular, and $8\pi(\epsilon_0 + 2)P^2/9\epsilon_0V$ for dipoles parallel, to the direction of the propagating light.^{10,11} Here ϵ_0 stands for the dielectric constant and V for the volume of the unit cell. As an equal distribution of the six possible domain orientations is assumed one-third of the transition dipoles is parallel to each axis of the cubic overall cell.

TABLE I. Molecular and crystal constants of KCN.

	a	4.22 Å ^a
Dimension of the unit cell	b	5.07 Å ^a
	c	6.13 Å ^a
Dielectric constant	ϵ_0	1.8 ^b
Effective electronic transition energy	T_e	6.951 eV ^c
Vibrational constants in the electronic excited state	ω_e'	198.3 meV ^c
	$\omega_e'x_e'$	2.2 meV ^c
Vibrational constants in the electronic ground state	ω_e''	256.6 meV ^d
	$\omega_e''x_e''$	1.8 meV ^d
Molecular interatomic equilibrium distances	r_e'	1.28 Å ^c
	r_e''	1.17 Å ^d
Transition dipole moment	P	0.57 D ^c
Oscillator strength	f	0.20 ^e
Resonance splitting	ϵ_-	-272 meV ^f
	ϵ_+	-13 meV ^f
Coupling constant between one- and two-particle states	$\langle\epsilon\rangle$	109 meV ^c
Intensity ratio	I_-/I_+	2.7 ^c

^aFrom Ref. 9.

^bFrom the Kramers-Kronig analysis of the measured spectrum.

^cFrom the fit of the synthetic to the experimental spectrum.

^dG. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N. Y., 1950).

^eComputed using P .

^fComputed applying P and Eq. (1).

Now the resonance splittings of the transverse mode can be derived:

$$\epsilon_{\pm} = \frac{\epsilon_a + \epsilon_c}{2\epsilon_0} \left(\frac{\epsilon_0 + 2}{3}\right)^2 - \frac{8\pi P^2}{9V} \frac{\epsilon_0 + 2}{3} \pm \left[\left(\frac{\epsilon_a - \epsilon_c}{2\epsilon_0}\right)^2 \left(\frac{\epsilon_0 + 2}{3}\right)^4 + \left(\frac{8\pi P^2}{9V}\right)^2 \left(\frac{\epsilon_0 + 2}{3}\right)^2 \right]^{1/2}. \quad (1)$$

After solving the 2×2 problem, the intensity ratio corresponding to the two eigenvalues ϵ_{\pm} is given by $I_-/I_+ = 94$, independent of the dipole moment. A dielectric correction factor^{11,12} $(\epsilon_0 + 2)^2/9\epsilon_0$ has been applied for short-range dipole-dipole interaction in Eq. (1).

We now treat the vibrational problem within the weak-coupling model which is appropriate in the case where the time of the delocalization of the electronic excitation is in the range of the internal vibrational period. The wave functions of a localized vibronic excitation represent an adequate basis set for the description of the delocalized vibronic states and weakly perturbed progressions of vibrational levels can be expected. This is opposite to the strong-coupling case where the electronic resonance interaction is very strong, the electronic excitation is almost delocalized, and a short progression of heavily perturbed vibrational bands appear.

One-particle, two-particle, and multiparticle states can be distinguished in the weak-coupling case.⁸ One-particle states occur if one molecule is electronically and vibrationally excited and both types of excitation delocalize together as a single particle (vibronic exciton). Two-particle states are excitations where one molecule is vibronically excited and a second purely vibrationally excited. Cooperative transitions from the ground state to two-particle states are forbidden and two-particle bands borrow their intensity

through the coupling with one-particle states. Similarly three-particle states occur if one molecule is vibronically excited and two other molecules vibrationally excited. These states couple with two-particle, but not with one-particle, states.

To keep the number of unknown parameters small and to make the computation transparent we introduce the following simplifications:

(i) Morse potentials are taken for intramolecular potentials.

(ii) The molecular transition moment is taken to be independent of the intramolecular coordinate, so that the modulation of the transition moment by the vibration is given by the vibrational overlap integrals.

(iii) Multiparticle states are neglected. Two-particle states are represented by single energy levels as suggested by Craig and Walmsley¹³ which is appropriate in the weak-coupling case and long vibrational progressions where the structure of two-particle bands is not resolved.^{14,15} Individual interaction matrices for each electronic state are reasonable since two-particle states are only weakly perturbed by the interaction with one-particle states.

(iv) Vibronic exciton-phonon coupling is simplified and represented by a linewidth.

With these assumptions we are able to build up the following vibronic interaction matrices:

$$H_{pp'qq'}(\epsilon_{\pm}) = [T_e + G'(p) + G''(q) - 2G''(0)] \delta_{pp'} \delta_{qq'} + \epsilon_{\pm} \xi_0^p \xi_0^{p'} \delta_{q0} \delta_{q'0} + \langle \epsilon \rangle [\xi_0^p \xi_q^{p'} \delta_{q'0} + \xi_q^p \xi_0^{p'} \delta_{q0}]. \quad (2)$$

The first term in this equation represents the energy of a transition from the ground state to an excited state. $G'(p)$ and $G''(q)$ are vibrational-energy progressions for the electronic excited and ground states and p, q are the corresponding vibrational quantum numbers. The second term describes the interaction between one-particle states ($q = q' = 0$) where ξ_q^p is the vibrational overlap integral:

$$\xi_q^p = \langle \chi'(p) | \chi''(q) \rangle, \quad (3)$$

where χ'', χ' are vibrational wave functions of the electronic ground and excited state. The interaction between one- and two-particle states is given in the third term, where $\langle \epsilon \rangle$ is a mean electronic resonance energy. The transition mo-

ments corresponding to the eigenvalues of the vibronic-interaction matrices can be derived applying the eigenvector elements for the linear combinations of unperturbed one-particle vibronic transition moments. From these a complex susceptibility can be computed which can be used for the calculation of an energy-dependent reflectivity. This has been done by taking available molecular constants from the literature and fitting parameters to the experimental reflectivity.

The synthetic spectrum in Fig. 2 fits largely the experimental features. All parameters listed in Table I are reasonable except the fitted intensity ratio which is much smaller than the predicted value. This deviation may be due to in-

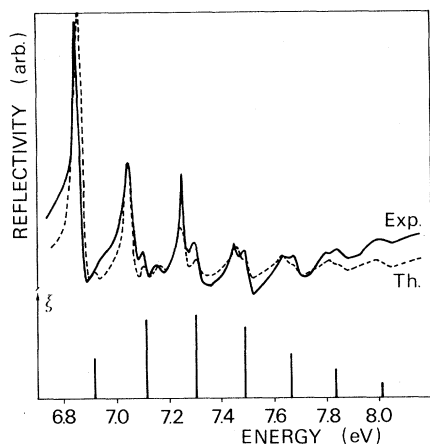


FIG. 2. Measured and computed reflectivity spectra of the molecular $A^1\Pi \leftarrow X^1\Sigma^+$ transition in crystalline KCN. ξ represents the Franck-Condon distribution.

homogeneity or stress within the crystal. A more probable reason for the deviation is the omission of the static splitting of the $A^1\Pi$ state by the crystal field. The large theoretical intensity ratio arises because the term due to the long-range dipole-dipole interaction dominates in the root in Eq. (1) and the short-range dipole-dipole interaction contributes little to the splitting. A static splitting would enhance the contribution of the short-range dipole-dipole interaction and the mixing of the two electronic states by the long-range dipole-dipole interaction would be less pronounced and a smaller theoretical intensity ratio would result. The static splitting should be observable in the upper bands where it dominates because the resonance interaction is small. However, a determination of the static splitting from the experiment is difficult and a further adjustable parameter would arise.

The calculation explains the two separate energy progressions of vibrational energy levels with rather different intensity distributions and reflects the meaning of the electronic resonance energy in Eq. (2). The large negative element shifts the intensity versus lower bands which can be seen if the reflectivity of the "negative" progression is compared with the unperturbed Franck-Condon factors displayed in Fig. 2. The interaction between one-particle states influences significantly the final spectrum whereas the coup-

ling with two-particle states causes a red shift of the lowest band and intensifies the lowest two-particle state at 7.13 eV, but otherwise its contribution to the spectrum cannot be recognized.

We point out that KCN is probably the simplest ionic molecular system exhibiting resolved vibronic structures which can be understood from a weak-vibronic-coupling model. CN is abundant in the universe and our results may contribute to a better understanding of the electronic structure of CN and its ions.

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