

### *Annotationes et Errata*

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## **Davydov Splitting and the Absorption Spectra of Transition Metal Ion Crystals**

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It is usual for the interpretation of transition metal ion crystal spectra to neglect interactions between metal ions in the crystal and to consider the crystal as an oriented gas. As this is a starting approximation, one must be careful to bear it in mind when attempts are made to interpret crystal spectra. Such is the case for aromatic crystals and this led DAVYDOV [3] to extend FRENKEL's theory [8] of excitons to these crystals. The theory has been developed further and explored by a number of workers and exciton phenomena are reasonably well understood [2, 10]. This theory has not so far been applied to the spectra of transition metal ion crystals because of the lack of experimental evidence to support a breakdown of the oriented gas model. However, DIJKGRAAF [4] has recently introduced exciton theory into the interpretation of some metal chelate spectra and has bypassed the usual methods of treating these data.

When considering electrostatic interactions between aromatic molecules in crystals, it is possible to divide the interaction matrix elements into those which involve excitation transfer on the one hand, and both excitation and electron transfer (exchange) on the other. The former are responsible for the crystal splitting observed in many singlet-singlet absorption bands in aromatic crystals while the latter dominate the similar processes involving triplet states. A similar distinction can be made for transition metal ion crystals with the addition that the exchange-type interactions can involve both direct and super-exchange mechanisms.

For the purpose of the present note only those interaction matrix elements which do not involve electron exchange are considered. These have a larger range and are responsible for the singlet exciton bands in aromatic crystals. The number of bands is equal to the number of molecules in the primitive cell and the theory has been developed most completely for crystals which have two molecules per cell such as anthracene. Each excited electronic energy level of the free molecule gives rise to two bands in the crystal which can occur at different frequencies in polarized light. However, this frequency difference or splitting has been observed for pure electronic transitions or vibronic transitions which involve only totally symmetric vibrations. Those electronic transitions which are vibrationally perturbed so that one quantum of a nontotally symmetric vibration is excited are not split and the reasons have been discussed by CRAIG and WALMSLEY [1].

Consider now the spin-allowed  $d - d$  bands of transition metal complexes in crystals where the metal ion lies at an inversion center of the lattice. In most

cases the bands are then forbidden electric dipole transitions and a dynamic perturbation of the  $g \leftrightarrow g$  selection rule is required for absorption of light to take place. This is achieved by a mechanism which involves the absorption or emission of one quantum of a nontotally symmetric vibration of the correct symmetry to break down the selection rule. The process is analogous to that occurring in aromatic molecules. For the same reasons, the splitting of the energy levels would be experimentally indistinguishable from zero. The very low intensities of the bands also argues against any measurable effects even for many cases where the ion does not lie at a point of inversion symmetry.

In order to substantiate these arguments it is, of course, possible to make order of magnitude calculations of splittings using observed oscillator strengths and the most favorable orientation factors for nearest neighbor interactions, based on a dipole-dipole approximation. However, the question of the existence of exciton states associated with spin-allowed bands of metal chelates is best resolved by turning to experiment. This can be done by observing the absorption spectra of different crystal sections to determine whether the frequency of a band changes according to the symmetry properties of the space group. It is not sufficient to observe the spectrum of a section which contains the symmetry axis of a monoclinic crystal as DIJKGRAAF has done for the copper complexes of  $\alpha$ -amino acids and acetylacetone [4]. The absorption spectrum of the section normal to the symmetry axis must also be observed. If the bands are exciton bands then no splitting will be observed in the two spectra taken with polarized light incident normal to this face. Further, the frequencies observed in this (010) section should be identical with the  $\perp b$  component of a spectrum of a section which contains the symmetry axis.

In the earlier work [5] on the copper acetylacetonate crystal spectrum different crystal sections were used to establish that the oriented gas model applies. Two sections containing the  $b$  axis ((101) and  $(10\bar{1})$ ) and the one normal to the  $b$  axis ((010)) were used. If the absorption bands represent transitions to exciton states of the crystal then the (010) spectrum should have maxima whose frequencies (for both extinction directions) coincide with the  $\perp b$  spectra of the other two faces, as they would all correspond to a transition to the  $k = 0$  level of the  $ac$  exciton band. This is not observed and in fact the polarized spectra of the  $(10\bar{1})$  and (010) faces are very similar as would be expected from the simple oriented gas model, because the projections of the molecules on both of these faces are very similar. The interpretation of DIJKGRAAF is therefore not correct. Although the analogous experiments have not been done for the copper complexes of the  $\alpha$ -amino acids there are no new additional features in their spectra which would suggest that the oriented gas model breaks down there either.

Some of the problems in the analysis of metal chelate spectra have been discussed recently [9, 6]. The prime problem is the understanding of the polarization of the crystal bands. Studies of the spectra of more simple copper coordination compounds such as  $\text{CuF}_2 \cdot 2 \text{H}_2\text{O}$  and  $\text{Cu}(\text{HCOO})_2 \cdot 4 \text{H}_2\text{O}$  by the author [7] show none of the polarization problems peculiar to the chelates. It seems that the answer lies in the nature of the odd states which are mixed in through the effect of the perturbing vibrations, and not in the introduction of exciton theory.

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