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The Interpretation of Factor-Group Splittings in Weak Crystal Transitions

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The Davydov splitting in weak ultraviolet absorption systems such as those of benzene and naphthalene has been interpreted according to two different theoretical schemes. In the first the benzene crystal spectrum[1] and the naphthalene spectrum[2] were treated in the framework of neutral exciton theory.[3] Then, since the transition dipole moment is too small to give appreciable intermolecular coupling, it is necessary to invoke higher moments of the transition, and to assign values to them to give agreement between measured and calculated Davydov splitting. The required values for naphthalene are $O_3^{3c} = 12$ Å^3 and $O_3^{1c} = -9$ Å^3 which, though within physically possible limits, are somewhat higher than given by molecular orbital wave functions. The alternative proposal[4] ascribes the splitting primarily to coupling between the neutral exciton state and a charge transfer state lying closely above it. In this theory the splitting depends on the separation between the two states, as well as on the properties of the states themselves.

As a contribution to the problem of the correct theoretical description two types of experimental test are considered. Their use to distinguish between the theories is indicated, and matters on which decisive evidence is still lacking are pointed out.

On the charge transfer (CT) theory the Davydov splitting of the lowest (neutral exciton, NE) level being a second-order effect, should alter with a variation in the energy gap separating the CT and NE

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levels. There should in general be a change in separation when deuterium atoms are substituted for hydrogen atoms in a hydrocarbon, insofar as the energy gap on isotopic substitution changes according to the differences of zero-point energies in the two states. On the other hand deuteration leaves the electronic properties of the NE level unaltered, and the splitting on the octupole model or any other describing the splitting as a first-order effect, is not changed. In naphthalene as example the gap between the ground state and the first excited state in the free molecule changes by ~ 118 cm^{-1} in perdeuteronaphthalene. The shift is to higher energies. In the CT state there will also be an isotope shift, the magnitude of which depends upon quite different dynamical factors, and is unlikely to be equal to that of the lowest excited neutral exciton level. The isotope shift now depends upon the averaged zero-point energy of positive and negative ions, which cannot be obtained from presently available data. However, we can readily estimate from the matrix elements given in Ref. 4 how large a change in spacing would be needed to give a change in the splitting of magnitude outside limits of experimental error. For a separation of 500 cm^{-1} between the NE and CT states one can estimate that a change of 15 cm^{-1} would give a detectable splitting change.

Measurements of the splitting in a number of deuteronaphthalenes were reported by Sheka[5] at 20°K. In naphthalene h_8, α-d_1, α-d_4, β-d_4 and d_8 the splittings are all equal, 147–148 cm^{-1}. New measurements of the absorption spectrum of perdeuteronaphthalene crystals have been made at the temperature of liquid helium under conditions as nearly as possible identical with those used for naphthalene itself.[6] Crystals grown by sublimation were mounted over a pinhole drilled in a brass disk. The disk was held in a brass crystal holder and, after microscopic examination for locating the crystal axes, the assembly was screwed into a block in the liquid helium cryostat. The spectra of nine crystals of thickness between 0.7 and 1.3 μ were recorded photographically and measured by comparison with the iron arc spectrum. The mean value of the ac and b polarized absorption frequencies are recorded in Table 1 and are compared with those for naphthalene taken from Ref. 6.

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TABLE 1 Crystal Splittings in the Spectra of Naphthalene and Perdeuteronaphthalene (cm^{-1})

Compound	Transition	*ac* Component	*b* Component	Splitting
Naphthalene	0–0	$31,475 \pm 2$	$31,626 \pm 2$	151 ± 4
	1–0[a]	$32,231 \pm 2$	$32,259 \pm 2$	28 ± 4
Perdeutero-naphthalene	0–0	$31,591 \pm 2$	$31,742 \pm 4$	151 ± 6
	1–0[a]	$32,278 \pm 2$	$32,304 \pm 4$	26 ± 6

[a] Transition to the 1-quantum level of the a_g vibration of frequency 702 cm^{-1} in naphthalene-h_8 and 638 cm^{-1} in d_8.

Within experimental limits the splitting is not changed by complete deuteration. This result is also found for phenanthrene, for which the results in Table 2 apply, taken from Ref. 7. In principle an even more sensitive test concerns the effects on the 1–0 band in the spectrum, with a one quantum excitation of the totally symmetrical vibration of 701 cm^{-1} in the upper state. This level is either below and nearer to the *CT* level, or may lie closely above it, and in either case the influence of a deuteration shift if one existed should be profound in the *CT* theory, whereas in the octupole theory no influence at all is expected.

TABLE 2 Crystal Splittings in the Spectra of Phenanthrene and Perdeuterophenanthrene (cm^{-1})

Compound	Transition	*ac* Component	*b* Component	Splitting
Phenanthrene	0–0	$28,597 \pm 2$	$28,656 \pm 2$	59 ± 4
Perdeutero-phenanthrene	0–0	$28,687 \pm 2$	$28,745 \pm 2$	58 ± 4

Experimentally (Table 1) there is again no observed change in splitting nor in other features of the 1–0 band pair. The polarization ratio (b/a) in the 1–0 bands is less than that in the 0–0, but greater than in the vibrationally induced 438–0 bands, and is estimated as 5–10:1.

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It is of course quite clear that other contributions to the splitting, such as intermolecular electron exchange, would also be insensitive to deuteration, and therefore that the octupole model is not unique in this respect. The distinction is essentially between theories describing the splitting as first-order in the intermolecular perturbation, as for octupole and electron exchange effects, and second-order theories depending on the energy separations of different electronic states. The special feature of the CT theory is the extremely small energy separation of the NE and CT states that must be assumed to explain the splitting; this leads to the sensitivity to small changes in the separation just discussed.

A second test of the nature of the crystal levels depends on the band structure of the exciton band. Let us suppose that levels have energies $e(\mathbf{k})$, $\mathbf{k}$ being the wave vector. In a monoclinic crystal like that of naphthalene, the two optically accessible levels are $e(0a)$ and $e(0b)$, both belonging to $\mathbf{k}=0$ and excited in transitions polarized along the a and b monoclinic axes for light incident normal to the ab face. In the presence of low concentrations of impurity molecules new optical levels are formed outside the band, and transitions are made to some extent allowed to levels within the band. The intensities of these transitions provide a sensitive index of the band structure. Rashba[8] showed that for a transition in a mixed crystal to a level of energy E, the ratio of the intensity of light polarized along the a and b axes (the polarization ratio PR') is given in terms of the intensity ratio for the optical levels of the pure crystal (PR) by the relation

$$PR' = \left\{\frac{E-e(0a)}{E-e(0b)}\right\}^2 PR$$

depending on the separation of the observed level from the pure crystal levels. Since for impurities acting as shallow traps, such as perdeuteronaphthalene, the lowest optically accessible level closely coincides with the bottom of the band, we can use the measured polarization ratio to estimate the quantities $E-e(0a)$ and $E-e(0b)$ in the equation above. In this way Broude *et al.*[9] found that the level of energy $e(0a)$ lies very close to, if not coincident with, the

bottom of the band. It remains to test methods of calculating the band structure by reference to this conclusion.

The calculation on the basis of an octupole–octupole coupling has recently been reported.[10] Table 3, taken from Ref. 10, lists the energies of levels corresponding to extrema of the first Brillouin zone. It will be seen that the calculation does give the result that the a polarized level coincides with the lower limit of the exciton band.

TABLE 3 Energies of Levels in the Lowest Naphthalene Band (cm^{-1}) (octupole–octupole model)

k[a]	ac-branch	b-branch
(000)	−113.6[b]	59.5
(00π)	−111.5	90.4[c]
(π00)	−7.9	−7.9
(π0π)	11.6	11.6
(0π0)	−5.3	−5.3
(0$\pi\pi$)	−0.8	−0.8
($\pi\pi$0)	10.3	10.3
($\pi\pi\pi$)	28.9	28.9

[a] For extrema of the first Brillouin zone.
[b] Lowest level of exciton band.
[c] Highest level of exciton band.

It is concluded that the octupole–octupole coupling model gives general agreement with experiment both in the insensitivity of splitting to deuteration, and in the structure of the lower limit of the exciton band. It seems important that further calculations by the CT model should be made in order that its performance may be checked in these respects.

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