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Annotationes

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Group-Theoretic Criterion for Selection Rules in the Vibronic Mechanism and Applications to Copper Acetylacetonate

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In a recent publication, Dijkgraaf [*1*] proposed an exciton interpretation of the crystal spectra of copper acetylacetone. Although it is possible that the bands observed in molecular crystals of some metal chelates do show Davydov splitting, as Dijkgraaf believes, several considerations make it unlikely that copper acetylacetone is such a case. Ferguson [*4*] discusses some of these considerations; in this paper we point out another. Furthermore, there are some other features of Dijkgraaf's treatment which require clarification.

In this paper, we begin by showing that the group-theoretic vibronic selection rules given by Dijkgraaf [*1*] are equivalent to those used by Piper and Belford [*6*]. We then discuss some features of the energy level scheme and spectra.

Group-Theoretic Discussion of Vibronic Selection Rules for a Point-Group

One is given the following wavefunctions and perturbations.

φ_0: Ground-state wavefunction, associated with representation (rep) Γ_0, having character $\chi_0(R)$ for element R of the point group of the problem.

φ_1: Excited-state wavefunction, with rep Γ_1.

V_q: Vibrational perturbation operator produced by distortion along normal coordinate q, associated with rep Γ_q.

E_r: Perturbation operator owing to interaction of the system with linearly r-polarized radiation associated with Γ_r.

Attacking the problem by first-order perturbation theory, one asks that some other states be mixed into φ_1 by V_q, such that transitions to these admixed states from φ_0 will be allowed by E_r. That is, one asks for at least one state, φ_j, associated with irreducible rep Γ_j, such that both the following conditions are satisfied:

$$(\varphi_j, V_q \varphi_1) \neq 0 \tag{1}$$

$$(\varphi_j, E_r \varphi_0) \neq 0\,. \tag{2}$$

These are the conditions of Dijkgraaf, which he points out cannot be satisfied unless

$$\Gamma_j^* \times \Gamma_q \times \Gamma_1 \text{ contains the identity rep } (A_{1g}), \tag{3}$$

and

$$\Gamma_j^* \times \Gamma_r \times \Gamma_0 \text{ contains } A_{1g}\,. \tag{4}$$

(Note that we have throughout corrected the original equations of both DIJKGRAAF and PIPER and BELFORD to take account of the possibility that φ_j and some elements of Γ_j are complex.)

Conditions (3) and (4) hold *if and only if* $\Gamma_q \times \Gamma_1$ and $\Gamma_r \times \Gamma_0$ contain at least one irreducible rep, namely Γ_j, in common. (See, for example, HAMERMESH [*5*], p. 172.)

Note that for any rep Γ_j, there are always associated eigenfunctions of the Hamiltonian, since the eigenfunctions form a complete set. Thus we do not have to be concerned lest (3) and (4) be satisfied but (1) and (2) be impossible. (Of course, group theory can never guarantee that an integral is not negligibly small.)

Now, $\Gamma_r \times \Gamma_0$ and $\Gamma_q \times \Gamma_1$ contain at least one irreducible rep in common *if and only if*

$$(\Gamma_r \times \Gamma_0) \times (\Gamma_q \times \Gamma_1)^* \text{ contains } A_{1g}\,, \tag{5}$$

i.e.,

$$\sum_R \chi_0(R)\,\chi_r(R)\,\chi_q^*(R)\,\chi_1^*(R) \neq 0\,. \tag{6}$$

(See, for example, HAMERMESH [*5*], p. 106, 132.) This, except for the aforementioned correction for complex bases, is the prescription of PIPER and BELFORD [*6*]. Thus DIJKGRAAF's general group-theoretic conditions are precisely equivalent to ours. (DIJKGRAAF's comment to the contrary is based on his neglect of an infinite number of excited states (φ_j) on physical, rather than group-theoretic, grounds.)

An additional comment should be made. The roles of φ_0 and φ_1 in the preceding discussion may be interchanged, and produce another possibility, i. e.

$$(\varphi_j,\, V_q\,\varphi_0) \neq 0 \tag{1'}$$

and

$$(\varphi_j,\, E_r\,\varphi_1) \neq 0\,. \tag{2'}$$

Following the development through, we see that the transition is not symmetry-forbidden in polarization r if either (6) or (6′).

$$\sum_R \chi_1(R)\,\chi_r(R)\,\chi_q^*(R)\,\chi_R^*(R) \neq 0\,. \tag{6'}$$

Combining (6) and (6′), we have

$$\sum_R \chi_r(R)\,\chi_q^*(R)\,[\chi_0(R)\,\chi_1^*(R) + \chi_1(R)\,\chi_0^*(R)] \neq 0\,. \tag{7}$$

Application to Copper Acetylacetone

In the pseudo-symmetries considered for copper acetylacetone, D_{4h} and D_{2h}, the characters of all reps are real (as they will be in most cases). Thus the equations originally used by PIPER and BELFORD (Sec. 4.1 of Ref. [*6*]) to obtain vibronic selection rules are correct versions of (7). DIJKGRAAF correctly assigned $x^2 - y^2$ as the highest-energy d orbital, but mislabelled it as a_g. It is rather b_{1g} [*6*]. The ground state and the nature of the transitions and arrangement of orbitals, as labelled by their irreducible reps, are thus not those given by DIJKGRAAF. The point of confusion is that the in-plane two-fold symmetry axes in DIJKGRAAF's model must be the lines $x = y$ and $x = -y$, whereas in most works on applied group theory $x = 0$ and $y = 0$ are taken as the two-fold axes.

Charge-Transfer Transition

Correct labelling of the ground state actually tightens DIJKGRAAF's argument that the charge transfer transition in which an electron jumps from $x^2 - y^2$ (σ^*) to a ligand — and — p_z orbital b_{1u} (π^*) is expected to be of low intensity, and therefore might be assigned to the 26 kK shoulder. Instead of the transition's being ${}^2B_{1u} \leftarrow {}^2A_g$ [1], which would be allowed in z polarization, it is actually ${}^2B_{1u} \leftarrow {}^2B_{1g}$, which is symmetry forbidden in the electric-dipole mechanism in the absence of crystal perturbations and distortions, spin-orbit mixing, or vibronic mixing. [Note that E_r belongs to B_{1u}, B_{2u}, or B_{3u} (z, $x \pm y$); ($B_{1u}^* \times B_{1,\,2,\,3u} \times B_{1g}) = B_{1,\,2,\,3g}$, which does not contain A_g.] However, it is clear that the transition in an isolated molecule would be made allowed through *gerade* vibrations B_{1g}, B_{2g}, B_{3g}, each one corresponding to a different polarization.

In the crystal, static distortions may provide sufficient perturbation to make the 26 kK band allowed. However, there is little reason to expect that the molecule in solution has symmetry lower than D_{2h}; thus the vibronic mechanism would be a likely source of intensity and could produce rather severe sensitivity of the band intensity to temperature. Experiments to test this point are now in progress in these laboratories.

Davydov Splitting

Does the crystal spectrum of undiluted copper acetylacetone show clear evidence of Davydov splitting? We think it does not. Consider the argument of DIJKGRAAF that there are two solution bands ($\sim$15.4 kK and $\sim$18.35 kK) that show up at noncoincident frequencies in the $\parallel b$ and $\perp b$ spectra of the (101) crystal face (15.6 $\parallel$, 16.1 $\perp$; 18.0 $\parallel$, 18.5 $\perp$). We suggest that the absorption bands are composite and so broad that one cannot determine whether there are really differences in position. Highly resolved spectra would be necessary to settle the question. However, a more serious objection is that the previously published crystal spectra at 30 °K [3], which show better resolution than the previous spectra of FERGUSON [2] and the later spectra of DIJKGRAAF [1] taken at higher temperatures, clearly show that there are two components in the vicinity of 15 kK, each of which appears in *both* $\parallel$ and $\perp$ polarizations ($\sim$14.5 kK and 16.3 kK). Therefore, they *cannot* be Davydov-split ($\perp$ and $\parallel$) components of the same transition, as suggested by DIJKGRAAF. (This conclusion is predicated on the assumption that there was little polarization-mixing in the spectra reported by FERGUSON, BELFORD, and PIPER [3], but sufficient experimental error to alter the conclusions is unlikely.)

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