ON THE INFORMATION CONTENT IN A WEAKLY STRUCTURED ABSORPTION BAND

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ABSTRACT

Electronic absorption bands result from transitions between two electronic states. Associated with these states are vibrational and rotational levels. For inorganic complexes embedded in a lattice, the librations associated with the excited states of the solute molecules may give each vibrational level a breadth of up to several hundred wavenumbers. The vibrational levels of the ground state are populated according to a Boltzmann distribution and the resulting electronic absorption band is a superposition of many individual vibronic transitions. Therefore, the usual broad structureless band in most cases is a result of crowding and overlapping of vibrational levels. However, unresolved structure may sometimes be seen. The dangers of assigning weakly structured bands to partially resolved vibrations, lower symmetry, spin–orbit coupling, Jahn–Teller effects, 'Antiresonances' or a suitable mixing of all are pointed out. Only by using many different experimental techniques is it sometimes possible to sort out the various 'effects'. All parameters derived from weakly structured bands are therefore to be viewed with caution.

INTRODUCTION

Most chemists who do spectroscopy on inorganic complexes have come to the subject via an education in inorganic chemistry rather than one in spectroscopy. Consequently a great deal of background is often lacking. This manifests itself in the theoretical and experimental treatments of many systems. How many times have we been shown a broad, nearly featureless band with a small dent on the red side accompanied by the most detailed interpretation? Spin–orbit coupling, Jahn–Teller distortions and lower symmetry are effects usually introduced to explain the 'unusual' bandshape. Theoretically the phenomenon is then treated, using at least tensors of rank four, with the most astonishingly detailed conclusions being drawn. Indeed, a characteristic feature of the literature is the over-interpretation of a few data and/or the over-elaboration of what was in the beginning an approximate theory. Instead, our aim should be to get a simple physical understanding of the various phenomena. That can, fortunately, be done without much theory.

NATURE OF BROAD UNSTRUCTURED GAUSSIAN BANDS

The questions which I shall try to treat in this lecture are:
(1) Why do the electronic absorption bands of complexes often show up as

broad unstructured Gaussian shaped envelopes? (2) What might the appearance of 'weak' structure on such a band signify?

In contrast to the electronic energy of an atom, the electronic energy of a molecule also depends upon the atomic distances inside the molecule. The immediate consequence of this is that while atomic absorption lines are sharp, the electronic excitations of molecules, reflecting the molecular vibrations and rotations, may take the form of band envelopes. Consider a medium sized molecule. We can to a good approximation write the energy of an electronically non-degenerate state as

$$W = W_{el} + W_{vib} + W_{rot}$$

Defining the length $a \approx 10^{-10}$ m, we have $W_{el} \approx \hbar^2/ma^2$ and $W_{rot} \approx \hbar^2/Ma^2$ where W_{el} and W_{rot} are the electronic and rotational energies of the molecule, respectively; m is the electronic mass and M the total nuclear mass. For the vibrational energy we have $W_{vib} = \hbar(k/M)^{\frac{1}{2}}$ where k is the 'force constant'. We can also write $W_{el} = \hbar(k/m)^{\frac{1}{2}}$ since at equilibrium the same forces act on the electrons and nuclei. Hence

$$W_{vib} = (m/M)^{\frac{1}{2}} W_{el} \quad \text{and} \quad W_{rot} = (m/M) W_{el}$$

As W_{el} for a molecule is a few electron volts, W_{vib} is of the order of magnitude of a few hundred wavenumbers and W_{rot} is a few wavenumbers in magnitude. Our spectral resolution for 'visible' light is such that the rotational quanta cannot be easily resolved but appear as a bandwidth associated with the vibrational levels. If we observe the spectrum of a molecule embedded in a medium, be it a solution or a crystal, additional broadening of the vibrational levels may occur. Following Moffitt and Moscowitz[1], we introduce a 'libration' effect associated with the molecular vibrational levels. The librations refer to a continuum of states, arising from the motions of the solute molecules with respect to the centres and axes of their parent sites. The resulting band is not resolvable and, depending upon how different the excited state geometry is from that of the ground state, may give the vibrational transition a halfwidth of up to a few hundred wavenumbers.

For a non-linear molecule possessing N nuclei, each having three coordinates we can form $3N - 6$ vibrational molecular symmetry coordinates. (The six 'missing' are the three rotational and three translational coordinates which give rise to the librations.) Each vibrational symmetry coordinate is orthogonal upon each of the others. Performing a cut through a multi-dimensional surface we can then picture the energy as a function of a particular vibrational symmetry coordinate, say ξ_i (*Figure 1*). The potential curve gives the electronic energy as a function of ξ_i, and the vibrational energies (that is, the energy of the entire molecule in the vibrational mode ω_i) are indicated as horizontal levels. For the $3N - 6$ multi-dimensional potential surface the energy difference between two electronic states in the harmonic approximation is given by

$$W_{(\text{excited})} - W_{(\text{ground})} = \varepsilon_0 + \sum_j [(n_j' + \tfrac{1}{2})\hbar\omega_j' - (n_j'' + \tfrac{1}{2})\hbar\omega_j''] \qquad (1)$$

Here ω_j is an angular vibrational frequency and n_j', n_j'' refer to the values of the vibrational quantum number in the excited and ground state respectively.

Usually the excited states possess different equilibrium configurations and different sets of force constants from that of the ground state. Formally, this is described as a rotation and translation of the molecular coordinates (the Duschinky effect).

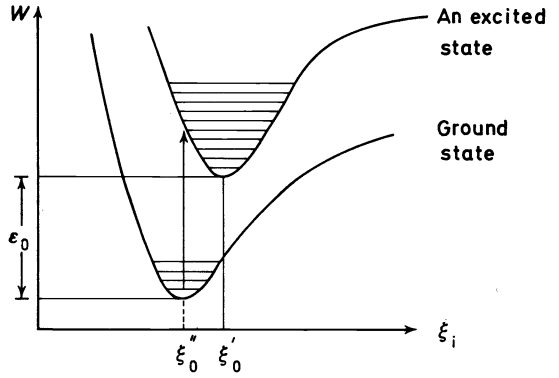

Figure 1. Potential surfaces.

In absorption spectroscopy we observe a narrow range of frequencies. If too many lines, each with a certain spectral width, are congested in that spectral region, no individual levels will be discerned. Clearly, there will be a density of states in the ground potential, and the assembly of molecules will be distributed over these states according to the Boltzmann distribution. At 0 K only the lowest vibrational state will be populated but at higher temperatures the higher lying vibrational states also will become populated. The number of vibrational states as a function of the energy W rises steeply with W. Two excitations of a vibration with energy $\hbar\omega_i$ may for example equal the energy of one excitation $\hbar\omega_j$, giving two states of that energy. With $3N - 6$ vibrations the number of combinations of excitation giving the same energy becomes quite large!

It has been found that, to a good approximation, the total number of states $N(W)$ goes as $N(W) = e^{\alpha W}$. The state density, $dN(W)/dW$ is then $\alpha e^{\alpha W}$. The number of individual transitions contributed by levels in the energy interval W to $W + dW$ therefore is proportional to

$$\alpha e^{\alpha W}\, dW\, e^{-W/k_B T} = \alpha e^{(\alpha - 1/k_B T)W}\, dW \qquad (2)$$

Clearly[2] this becomes independent of W for $T_s = (\alpha k_B)^{-1}$. Therefore for $T > T_s$ each band group between $h\nu$ and $h\nu + \Delta(h\nu)$ will spread out over the entire spectrum. By going to low temperature we may, on the other hand, avoid the crowding and see some structure. However, most frequently some, if not all, of the vibrational structure is still lost. In these cases the relevant degrees of freedom may be treated as quasi-continuous and the situation is analogous to the 'libration' case.

In crystal field theory for a regular octahedron the transitions which depend upon the parameter 10 Dq involve the excitation of a t_{2g} electron to an e_g

antibonding orbital. The excited state is expanded compared to the ground state. The vibrational levels are then associated with a lot of librations and fuse together to form one structureless vibrational band envelope.

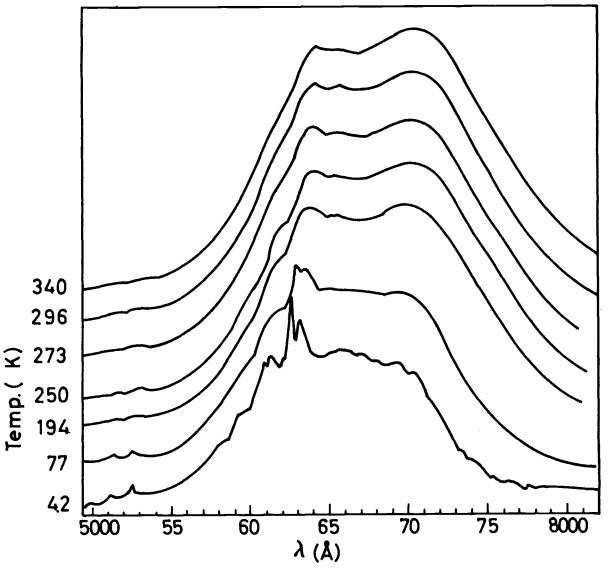

Figure 2. Low resolution spectra of the $^3A_{2g} \Rightarrow {}^3T_{1g}$(a) band in $Ni(H_2O)_6 \cdot SiF_6$ at various temperatures.

Let me illustrate these points by showing the appearance at different temperatures of the 'red' Ni(II) band, assigned as $^3A_{2g} \rightarrow {}^3T_{1g}$ (*Figure 2*). It is immediately obvious how the details emerge more and more clearly, without completely getting rid of the absorption background, as the temperature is lowered. It has been possible[3], by studying the $Ni(H_2O)_6^{2+}$ cluster embedded in sixteen different crystal-surroundings, at 5 K to follow in detail the nature of the non-crossing of the $^3T_{1g}$ and ^1E_g levels, and at the same time to account for the resulting bandshape.

CALCULATION OF BAND SHAPE

The bandshape of a structureless absorption band may be calculated from 'first principles' as follows. Let $M_{ba}(\xi)$ be the electric dipole matrix element between the initial and final electronic state $\Phi_a(r, \xi)$ and $\Phi_b(r, \xi)$, where r denotes the electronic and ξ the molecular symmetry coordinates. The absorption intensity $I_{ba}(h\nu)$ as a function of wavelength is proportional to

$$I_{ba}(h\nu) \simeq \mathrm{Av}_{n''} \sum_{n'} \left| \int \chi_{bn'}(\xi) M_{ba}(\xi) \chi_{an''}(\xi)\, \mathrm{d}\xi \right|^2 \delta(W_{bn'} - W_{an''} - h\nu) \qquad (3)$$

χ stands for the vibrational wavefunctions, and $\mathrm{Av}_{n''}$ is to be understood as a

Boltzmann distribution over the initial states. M_{ba} is the electronic transition moment. In the so-called semi-classical approximation in which one neglects a few commutators[10] this expression can be reduced to

$$I_{ba}(h\nu) = \frac{1}{\gamma\sqrt{\pi}} \int e^{-(\xi^2/\gamma^2)} M_{ba}^2 \, \delta(\Delta V(\xi) - h\nu) \, d\xi \tag{4}$$

where $\gamma^2 = \hbar\omega \coth(\hbar\omega/2k_B T)$ and $\Delta V(\xi)$ stands for the potential energy difference of a and b.

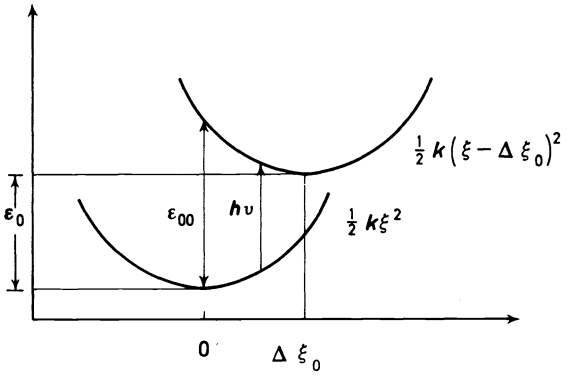

Figure 3. Displaced potential surfaces.

In the simplest case, *Figure 3*, we have

$$\Delta = \varepsilon_0 + \tfrac{1}{2}k(\Delta\xi_0)^2 + \xi k\Delta\xi_0 \tag{5}$$

$$= \varepsilon_{00} + \xi k\Delta\xi_0 \tag{6}$$

From the δ function in expression 4 we immediately get

$$I_{ba}(h\nu) \simeq \exp\{-(\varepsilon_{00} - h\nu)^2/\gamma^2 k^2 (\Delta\xi_0)^2\} \tag{7}$$

The band is seen to be Gaussian, with a temperature dependent halfwidth.

In cases where weak structure is seen superimposed on a smooth 'background', one possible explanation is that single lines may 'come through' because of a favourable vibrational overlap (compare equation 3). This is partly so in the Ni(II) band already discussed.

ORIGINS OF WEAK STRUCTURE

Weak absorption band structure may, as is well known, also arise from the superposition of two or more electronic transitions. The resolution of a weakly structured absorption into the anticipated electronic transitions is a process beset with danger. Indeed, the proposed resolution is usually governed by what 'one would expect'. In other words, what one wants to prove is put into the procedure. The result is then taken as a proof of one's theories. The resolution of composite bands into components, even when these components are real,

cannot in practice be done in a unique way. The composite curves of Vandenbelt and Henrich[4] offer proof enough (*Figure 4*). Unless one can separate the components of a composite band through some *physical* measurements, attempts to do so are only numerology.

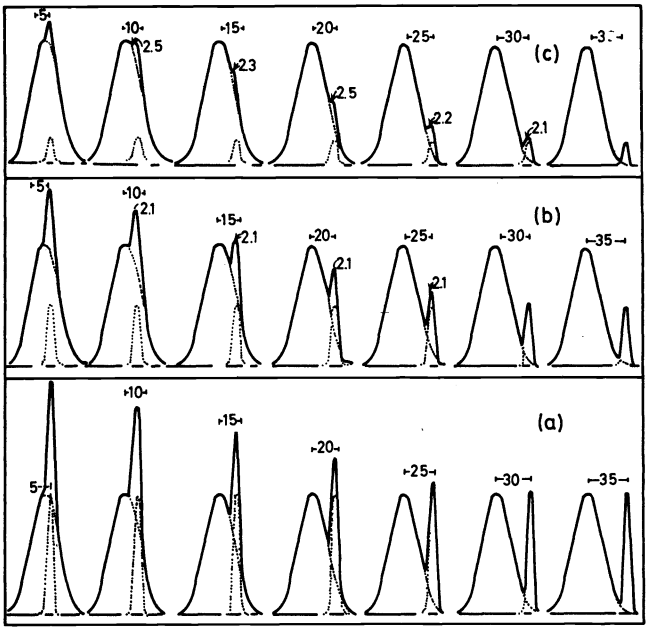

Figure 4. Composite Gaussian curves after Vandenbelt and Henrich[4].

Even if the observed structure is well documented experimentally as a 'band splitting', one should be aware that an extraction of parameters is a tricky process. From the Wigner–Eckart theorem in connection with the variational principle we know that provided the orbital ψ_i transforms correctly, the calculated quantity $w_i = \int \psi_i^* \mathcal{H} \psi_i \, d\tau$ will be proportional to the 'true' energy, ε_i. We do not, however, know the proportionality constant, which will be different for each system and for each electronic configuration.

For a t_{2g} and e_g orbital in O_h we can therefore write:

$$\varepsilon(t_{2g}) = \alpha w(t_{2g}) \tag{8}$$

$$\varepsilon(e_g) = \beta w(e_g) \tag{9}$$

We can further define a zero of energy by completely filling the two orbitals with electrons and taking the orbital energy of that state to be zero

$$W = 6\alpha w(t_{2g}) + 4\beta w(e_g) = 0 \tag{10}$$

In spectroscopy we deal with energy differences. Hence we can define the

energy separation

$$\varepsilon(e_g) - \varepsilon(t_{2g}) = \alpha w(e_g) - \beta w(t_{2g}) = 10\,Dq \tag{11}$$

Using the equations 10 and 11 we can therefore from the definition of an energy difference, defining a particular system, calculate the orbital energies, ε_i.

$$\varepsilon(t_{2g}) = -4\,Dq, \qquad \varepsilon(e_g) = 6\,Dq \tag{12}$$

Consider now the case where we have a lower symmetry than O_h, say D_{4h}

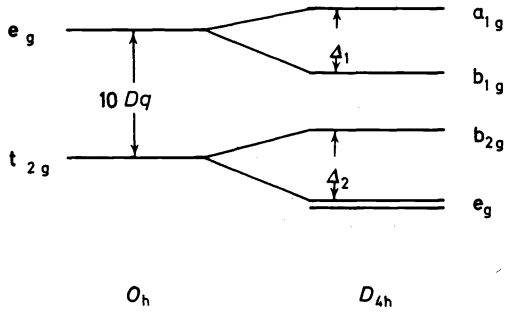

Figure 5. Tetragonal splitting parameters.

(*Figure 5*). We may define:

$$\left.\begin{aligned}\varepsilon(a_{1g}) &= 6\,Dq + \tilde{\alpha} w(a_{1g})\\ \varepsilon(b_{1g}) &= 6\,Dq + \tilde{\beta} w(b_{1g})\end{aligned}\right\} \Delta_1 = \tilde{\alpha} w(a_{1g}) - \tilde{\beta} w(b_{1g})$$
$$\left.\begin{aligned}\varepsilon(b_{2g}) &= -4Dq + \tilde{\gamma} w(b_{2g})\\ \varepsilon(e_g) &= -4\,Dq + \tilde{\delta} w(e_g)\end{aligned}\right\} \Delta_2 = \tilde{\gamma} w(b_{2g}) - \tilde{\delta} w(e_g). \tag{13}$$

As before we take our zero of energy to be the filled shell

$$2\tilde{\alpha} w(a_{1g}) + 2\tilde{\beta} w(b_{1g}) + 2\tilde{\gamma} w(b_{2g}) + 4\tilde{\delta} w(e_g) = 0 \tag{14}$$

The tetragonal splitting for the system is defined by Δ_1 and Δ_2. Using the definitions of Δ_1 and Δ_2 in equations 13 we get

$$\Delta_1 + \Delta_2 + 2\tilde{\beta} w(b_{1g}) + 3\tilde{\delta} w(e_g) = 0 \tag{15}$$

It is therefore not possible to find a unique expression for the orbital energies of the tetragonal complexes in terms of the characteristic splitting parameters Δ_1 and Δ_2. A characterization of the orbital energies in terms of Δ_1 and Δ_2 can only be done provided some assumptions for the bonding scheme are introduced.

The state energy differences, hv, can of course be written as $hv = f(Dq, \Delta_1, \Delta_2, J_{ij}, K_{ij})$ where J and K are functions of the electronic repulsions. Here Dq and the electronic repulsions are slowly varying from one system to the

next, whereas Δ_1 and Δ_2 vary greatly. Naturally the worth of parameters depends upon how slowly they vary.

Consider the molecular orbital for the complex

$$\Psi = \alpha\psi_M + \beta\psi_L \tag{16}$$

where ψ_M is a metal orbital and ψ_L is a combination of ligand orbitals. Using a suitable Hamiltonian, $\mathscr{H}$, this leads to the secular equation:

$$\begin{vmatrix} H_{MM} - \varepsilon & H_{ML} - \varepsilon S_{ML} \\ H_{ML} - \varepsilon S_{ML} & H_{LL} - \varepsilon \end{vmatrix} = 0 \tag{17}$$

where

$$H_{MM} = \int \psi_M^* \mathscr{H} \psi_M \, d\mathbf{r}, \qquad H_{LL} = \int \psi_L^* \mathscr{H} \psi_L \, d\mathbf{r},$$

$$H_{ML} = \int \psi_M^* \mathscr{H} \psi_L \, d\mathbf{r} = \int \psi_L^* \mathscr{H} \psi_M \, d\mathbf{r}, \quad S_{ML} = \int \psi_L^* \psi_M \, d\mathbf{r}.$$

The lowest 'bonding root' to good approximation is given by

$$\varepsilon^b = H_{LL} - (H_{ML} - H_{MM}S_{ML})^2/(H_{MM} - H_{LL}) \tag{18}$$

and the 'antibonding root' as

$$\varepsilon^a = H_{MM} + (H_{ML} - H_{LL}S_{ML})^2/(H_{MM} - H_{LL}) \tag{19}$$

Most inorganic complexes will have

$$H_{MM} - H_{LL} \gg |H_{ML} - H_{LL}S_{ML}| \tag{20}$$

Solving for α and β in equation 16 then leads to

$$\psi^b = \psi_L \tag{21}$$

and

$$\psi^a = (1 - S_{ML}^2)^{-\frac{1}{2}} (S_{ML}\psi_L - \psi_M) \tag{22}$$

correct to second order in S_{ML}.

The orbitals used in crystal field theory are the ψ^as, and we notice that only by arbitrarily putting $S_{ML} = 0$ do we get ψ^a to be a pure metal orbital. We can of course in accordance with the Wigner–Eckart theorem use a pure d-orbital as a 'variational' function. In that case, but in that case only, the Hamiltonian can be expanded in a few spherical harmonics, and we can calculate a, b and c in an expression for the orbital energies,

$$\varepsilon(\psi^a) = a\,Dq + b\,Ds + c\,Dt \tag{23}$$

Knowing b and c, Ds and Dt can then be related to Δ_1 and Δ_2. But, the above partitioning of the energy on three parameters is a consequence of putting $S_{ML} = 0$. To do so is completely unrealistic. We must conclude that an ordering of the orbital energies in some set of a 'tetragonal series' is physically meaningless.

Effects other than the two already treated may also give rise to dents in an otherwise smooth absorption curve. The electronic origin of a formally

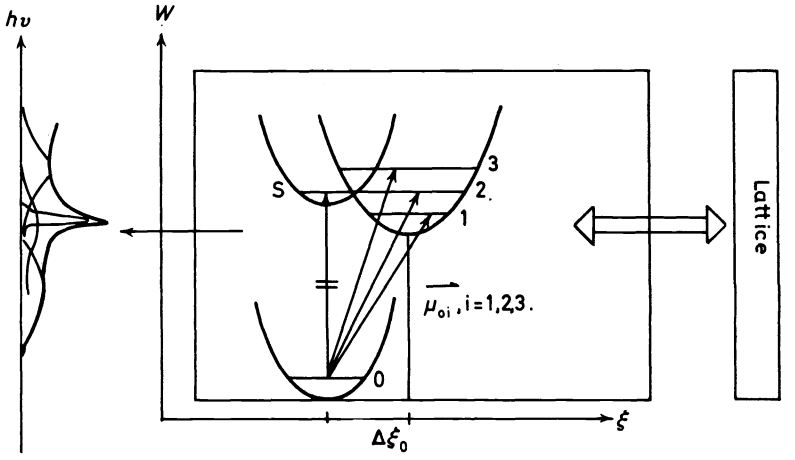

Figure 6. Idealized potential surfaces for octahedral d^3 systems. Ground state $^4A_{2g}$, excited states ^2E_g and $^4T_{2g}$.

forbidden, but vibronically allowed transition could produce a dip, and so might the presence of a dynamic Jahn–Teller effect in the excited state. However, due to the presence of librations or of other active vibrations these anticipated effects may not be observable.

Finally, let us take a brief look at what may happen provided we have two states of different spin-multiplicity located on top of one another, as for example found in octahedral Cr^{3+} complexes, *Figure 6*. The ground state is a $^4A_{2g}$ state, the excited states ^2E_g and $^4T_{2g}$. It is a characteristic situation that $^4A_{2g}$ and ^2E_g, having approximately the same electronic configuration, have their minima nearly on top of each other whilst $^4T_{2g}$ is displaced towards a greater equilibrium distance.

The situation here is that ^2E_g 'borrows' spin-quartet character from $^4T_{2g}$ via the spin–orbit coupling. The transition from the ground state $^4A_{2g} \Rightarrow {}^2E_g$ is thereby made spin-allowed. The combined system will further have to 'steal' some intensity from a parity allowed transition.

Consider the following idealized situation for the interaction of the ^2E_g and $^4T_{2g}$ excited states. A level ψ_s associated with ^2E_g interacts with three vibrational levels, ψ_1, ψ_2 and ψ_3 associated with $^4T_{2g}$ (*Figure 7*).

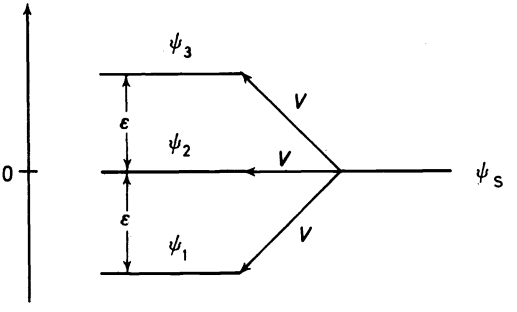

Figure 7. Interacting levels.

The combined wavefunction for the system is

$$\Psi = \alpha_1\psi_1 + \alpha_2\psi_2 + \alpha_3\psi_3 + \alpha_4\psi_s \tag{24}$$

and the secular equation is given by:

$$\begin{vmatrix} -\varepsilon - W & 0 & 0 & v \\ 0 & -W & 0 & v \\ 0 & 0 & \varepsilon - W & v \\ v & v & v & -W \end{vmatrix} = 0 \tag{25}$$

Assume further that in zeroth order, transitions from the ground state are allowed to ψ_1, ψ_2 and ψ_3 with the same transition moment μ_{0i}, $i = 1, 2, 3$ but that the transition to ψ_s is forbidden; $\mu_{0s} = 0$.

Provided $\varepsilon \gg v$ we obtain

$$W^2 = \begin{cases} \varepsilon^2 + 2v^2 \\ v^2 \end{cases} \tag{26}$$

The intensity of the levels is given by

$$I(W) = |\mu_{0i}|^2 \frac{v^2(\varepsilon^2 - 3W^2)^2}{2W^2(\varepsilon^2 + W^2)v^2 + (\varepsilon^2 - W^2)^2(v^2 + W^2)} \tag{27}$$

Putting $|\mu_{0i}|^2 = 1$ we find to first approximation:

$$I(\pm\sqrt{\varepsilon^2 + 2v^2}) = 1 + 2v^2/\varepsilon^2 \tag{28}$$

$$I(\pm v) = \tfrac{1}{2} - 2v^2/\varepsilon^2 \tag{29}$$

Equations 28 and 29 lead to an increase in intensity at high and low absorption frequencies with a decrease in I at intermediate frequencies as shown in *Figure 6*. Notice how intensity is pressed 'out on the wings'. A more refined calculation[5,6] gives the same result.

Now consider *Figure 6* again. A transition to ψ_s excites no vibrations in the system. The excited electronic state and the ground state are not rotated or translated with respect to each other. Hence the associated librations will be superimposed upon each other and the transition $\psi_0 \rightarrow \psi_s$ produces a sharp, nearly atomic-like line. If, on the other hand, we compare ψ_0 with ψ_i, $(i = 1, 2, 3)$ the librational coordinates of the excited electronic state will be translated and rotated relative to that of the ground state. Hence the Franck–Condon overlap factors in the librational coordinates will lead to a broad line. The situation for $\varepsilon \gg v$ is pictured to the left in *Figure 6*.

Should $v \gg \varepsilon$ the situation changes drastically. In that case

$$W^2 = \begin{cases} 3v^2 + \frac{2}{3}\varepsilon^2 \\ \frac{1}{3}\varepsilon^2 \end{cases} \tag{30}$$

and $I(\pm\sqrt{3v^2 + \frac{2}{3}\varepsilon^2}) = \frac{3}{2}$; $I(\pm\sqrt{\frac{1}{3}}\varepsilon) = 0$.

Figure 8 shows how a 'dip' or a so-called 'antiresonance' appears in the band contour. Considering inorganic complexes, this effect has been claimed

for V^{+2} in $KMgF_3$ by Sturge[7,8] and for $Cr(en)_3Cl_3 \cdot 3\frac{1}{2}H_2O$ by McCarthy and Vala[9].

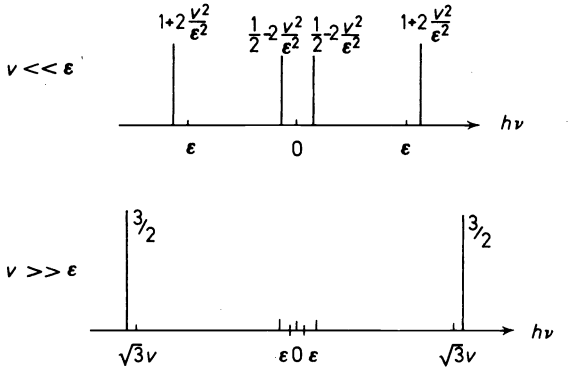

Figure 8. Intensity distribution for the situation pictured in *Figure 7.*

Taking $\mathscr{H}^{(1)}_{s-0}$ as the perturbing operator for the spin–orbit coupling, we obtain

$$v = \iiint \psi_i(r, \xi)\chi_i(\xi)\mathscr{H}^{(1)}_{s-0}\psi_s(r, \xi)\chi_s(\xi)\, d\tau_{spin}\, dr\, d\xi \tag{31}$$

$$i = 1, 2, 3.$$

$$v \simeq \zeta_M \int \chi_i(\xi)\chi_s(\xi)\, d\xi \tag{32}$$

where ζ_M is the spin–orbit coupling for the central atom. Hence, v^2 contains a Franck–Condon factor which will be much smaller than unity, provided the potential curves are displaced from each other. On the other hand, v is likely to be a semi-constant, since the overlap of χ_s with the 'tails' of χ_i must vary slowly. A typical value of ζ_M is $\sim 300\,cm^{-1}$ for $Cr(en)_3^{3+}$ leading to a value of v of perhaps $30\,cm^{-1}$. This is less than the totally symmetric stretching frequency $\varepsilon \approx 300\,cm^{-1}$. Over an energy gap of say $100\,cm^{-1}$, the intensity is then expected to be diminished by about five per cent. Under favourable circumstances, a dip in the absorption curve might be observed.

CONCLUSIONS

Weak structure in an absorption band may be due to one or more of the following causes:

(1) Poorly resolved vibrational structure.
(2) Overlapping bands; 'lower symmetry'.
(3) Vibronic 'forbidden' bands.
(4) Jahn–Teller dynamics.
(5) Spin–orbit coupling or 'antiresonances'.

Only by doing a very careful analysis, using as many different experimental techniques as are available, is it possible to sort out these various 'effects'. However, the model used in defining parameters is often too simple, and the experimental details usually not sufficient to give a reliable answer. It is therefore recommended that chemists refrain from extracting parameters from weakly structured bands. In order to reach a band assignment it should be sufficient to know orders of magnitude for the parameters involved. To try to elaborate upon the basic parameters of crystal and ligand field theory is bound to end in frustration.

Unfortunately, many chemists do not realize this. They are impressed by the mathematical superstructures with the associated parameter variations one can build upon any model. However, the connections to chemistry disappear and they get lost in the maze of the model. Indeed, a parallel which springs to mind is the many futile attempts made by scholars in trying to establish a chronological sequence for the cases of the late Mr Sherlock Holmes. It may be fun but it is hardly to be taken seriously.

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