Coordination Chemistry Reviews, 14 (1974) 47—66

VIBRONIC SPECTRA OF COORDINATION COMPOUNDS

C.D. FLINT

Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX (England)

(Received December 18th, 1973)

CONTENTS

A. INTRODUCTION

The importance of molecular vibrations in determining the intensities and shapes of the electronic absorption and emission bands in transition metal compounds has been appreciated since the earliest days of crystal field theory[1]. Although there have been many thousands of studies of the electronic spectra of these compounds, few have attempted to identify which specific vibrations are responsible for the intensity of particular bands. It is not possible at present to calculate the contribution of vibrations to the intensity mechanism with any reliability so that it is necessary to use experimental data. Few spin-allowed transitions, however, show a sufficiently well resolved vibrational structure to permit a thorough analysis of the transition. The broadness of these bands is a consequence of the crystal field potential since spin-allowed transitions from or to the ground state must involve the transfer of an electron

from a sigma-nonbonding to a sigma-antibonding orbital or vice versa and hence a change in the equilibrium metal—ligand distance. Spin-forbidden transitions may however occur between states derived from the same strong field configuration and hence may be well resolved but their weakness and proximity to spin-allowed transitions often makes it difficult to obtain good quality absorption spectra. In favourable cases, luminescence spectroscopy may be used to obtain spectra of spin forbidden transitions.

The intensity of *d*—*d* transitions in centrosymmetric and nearly centrosymmetric compounds arises primarily from a mixing of the crystal field states with states involving non-*d*-orbitals under the influence of nuclear vibrations. This interaction of vibrational and electronic motions (or vibronic interaction) is responsible for a variety of other phenomena in spectroscopy and solid state physics, of which the Jahn-Teller[2] and Ham[2–4] effects and radiationless relaxation[5], are of particular interest to inorganic spectroscopists. These topics have been reviewed in the cited references. In this article only the intensity mechanism of *d*—*d* transitions in coordination compounds will be considered.

B. ELECTRONIC TRANSITIONS

(i) Literature

A very readable account of the mechanism of electronic transitions in polyatomic molecules has been given by Herzberg[6]. Ballhausen and Hansen[7] have considered some theoretical aspects in greater detail. These articles do not explicitly consider coordination compounds but the principles are equally applicable to these systems and organic molecules. The most importance difference is that coordination compounds are ususally studied as solids, whereas the most detailed experimental and theoretical studies have been made on gaseous systems. The differences between solid state and gas phase spectroscopy is considered in section C. Ballhausen[8] and Ferguson[9] have given brief treatments of inorganic vibronic spectroscopy. The following summary is intended to establish a terminology and point of reference rather than be a self contained account.

(ii) Electronic transitions and crystal field theory

Crystal field theory considers the effect of an external static electrostatic field on the *d* or *f* electrons of a metal ion. In the pure crystal field limit, it is possible to calculate the dependence of the potential on the positions and nature of the ligands but such calculations are not realistic. It is more usual to determine the crystal field, interelectronic repulsion and other parameters by experiment, often by electronic absorption spectroscopy. In this way a single set of parameters is obtained which relate to a specific set of internuclear distances. For electronic absorption spectroscopy from the ground state these

internuclear distances are approximately those pertaining in the ground state equilibrium conformation. The familiar semi-classical Franck-Condon principle states that electronic transitions occur without any change in the nuclear coordinates. In electronic absorption spectroscopy at low temperature therefore the most probable (i.e., most intense) transitions are to terminal states with approximately the same internuclear distances as the ground state. These internuclear distances will not, in general, be the same as the equilibrium values in the excited state so that the terminal state will correspond to an excited vibrational level of the excited electronic state. The band maxima in an electronic absorption spectrum therefore give the energy separations between electronic states when there is no change in nuclear geometry, just as are calculated by crystal field theory. This, of course, accounts for the ease with which crystal field theory may be applied to absorption spectra. The intensity of electronic transitions and the analysis of vibrational structure, however, require a more detailed analysis.

(iii) Intensity mechanism and selection rules

Electronic transitions occur between states which involve both electronic and vibrational motion. The best approximation to these so-called vibronic states within crystal field theory is the crude adiabatic approximation[7].

$$\Psi_{ev}^{k}(q,Q) = \Psi_{e}^{ko}(q)\,\Psi_{v}^{k}(Q)$$

where Ψ_{ev}^{k} is a vibronic function, Ψ_{e}^{ko} an electronic (crystal field) function and Ψ_{v}^{k} a vibrational wavefunction. q and Q describe all the electron and nuclear coordinates and ^{o} designates the Q values at the reference conformation. This approximation is not able to account for the electronic spectra of polyatomic atoms. A better approximation is to include the variation of the electronic Hamiltonian with Q, i.e.,

$$\mathcal{H}_{e}(Q) = \mathcal{H}_{e}^{o} + \sum_{i} (\partial V/\partial Q_i)_{o} Q_i + \tfrac{1}{2} \sum_{ij} (\partial V^2/\partial Q_i \partial Q_j)_{o} Q_i Q_j + \ldots \qquad (1)$$

where V is the potential energy term. Using the second term perturbation theory gives

$$\Psi_{ev}^{k}(q,Q) = \Psi_{e}^{ko}(q)\,\Psi_{v}^{k}(Q) + \sum_{l \neq k} C_{lk}\,\Psi_{e}^{lo}(q)\,\Psi_{v}^{k}(Q) \qquad (2)$$

where the summation is over *all of the other states* of the molecule and

$$C_{lk} = \langle \Psi_{e}^{ko}(q) | \sum_{i} (\partial V/\partial Q_i)_{o} Q_i | \Psi_{e}^{lo}(q) \rangle$$

This is the Herzberg-Teller adiabatic approximation[7]. Retaining for clarity just one term of the summation in (2) $l = X$ in addition to the other state involved in the transition, we obtain the following expression for the oscillator strength of a transition from vibronic state ev to another e′v′

$$D_{eve'v'} = \langle \Psi_e^o | M | \Psi_e^o \rangle \langle \Psi_v | \Psi_{v'} \rangle + \langle \Psi_e^o | M | \Psi_x^o \rangle [E(e')-E(x)]^{-1} \sum_i \langle \Psi_x^o | (\partial V/\partial Q_i)_o \Psi_e^o \rangle \langle \Psi_v | Q_i | \Psi_{v'} \rangle + \langle \Psi_x^o | M | \Psi_e^o \rangle [E(e)-E(x)]^{-1} \sum_i \langle \Psi_x^o | (\partial V/\partial Q_i)_o \Psi_e \rangle \langle \Psi_v | Q_i | \Psi_{v'} \rangle + \ldots\ldots \quad (3)$$

The coordinates q and Q have been omitted for brevity. The operator M may be the electric dipole, magnetic dipole, or electric quadrupole operator, which transform as x, y, z; R_x, R_y, R_z; and x^2, y^2, z^2, xy, xz, and yz respectively. Theory and experiment show that the squares of the relative magnitudes of the matrix elements of M are $1: 10^{-5} : 10^{-8}$ respectively.

If the first term in (3) is non-zero the transition is said to be allowed*, the second and third terms (often referred to as the forbidden component) will almost** always be non-zero for some coordinate Q and state X.

The requirements for an allowed component are then

$$\left.\begin{array}{l} \Gamma(\Psi_e) \times \Gamma(\Psi_{e'}) \text{ contains } \Gamma(M) \\ \text{and} \\ \Gamma(\Psi_v) \times \Gamma(\Psi_{v'}) \text{ contains } \Gamma_1 \end{array}\right\} \quad \text{Rule 1}$$

Usually measurements are made at low temperatures so that $\Gamma(\Psi_v) = \Gamma_1$. Thus for an allowed transition at low temperatures only totally symmetric vibrational levels of the terminal state can be reached.

The requirement for the forbidden component to be nonzero is that $\Gamma(\Psi_e) \times \Gamma(M) \times \Gamma(\Psi_{e'})$ has an irreducible representation in common with $\Gamma(\Psi_v) \times \Gamma(\Psi_{v'})$ and Ψ_v and $\Psi_{v'}$ differ by a single quantum of a non-totally symmetric vibration (Rule 2). When these conditions are satisfied, the transition is vibronically allowed. The intensity of a vibronically allowed transition is often said to be stolen (or borrowed) from the allowed transition $\Psi_e^o \rightarrow \Psi_x^o$. In practice, the ratio of the matrix element between Ψ_e^o and Ψ_x^o to their separation is small so that it is only necessary to consider M as the electric dipole operator.

For a centrosymmetric complex d—d transitions are electric dipole forbidden but may be magnetic dipole allowed and are always electric dipole vibronically allowed. The last two mechanisms may give rise to comparable intensity but more usually the vibronic mechanism predominates. When there is no centre

---

* Herzberg[8] refers to the transition as allowed only if this term is non-zero for the electric dipole operator.

** One example where there is no coordinate which makes these terms non-zero is the $A'_1 \rightarrow A''_1$ transition of a four atom system with D_{3h} symmetry. The third term in (1) must be used to achieve vibronic coupling in this case.

of symmetry, the *d*—*d* transitions become electric dipole allowed but the perturbation of the *d* functions is usually small, so that the electric dipole allowed mechanism may give similar intensity to one or both of the other mechanisms. It is also possible for allowed and vibronically allowed components to appear in (3) with different sign and to partially cancel each other.

The vibronic states corresponding to a vibration belonging to an irreducible representation Γ_v in an electronic state Γ_e will be given by the number and type of irreducible representations in the direct product $\Gamma_v \times \Gamma_e$. If both Γ_v and Γ_e are not spacially one-dimensional, there will be several vibronic states which are degenerate if vibrational—electronic interaction is neglected. Vibronic coupling will relieve this spacial degeneracy so that an adiabatic state will be split into several components each with its own vibronic selection rules but it cannot split degenerate vibronic states or remove Kramers degeneracy. This splitting is likely to be appreciable if the degenerate Γ_v is contained in the symmetric product $[\Gamma_e]^2$ for even electron systems or the antisymmetric product $[\Gamma_8]^2$ for odd electron systems* and the electronic state does not correspond to a filled or half-filled shell or subshell (The Jahn-Teller effect). If the coupling is neither very strong nor very weak, the separation of electronic and nuclear coordinates is no longer even approximately correct and the behaviour of such systems is complex. Although there can be no splitting of vibronic degeneracy, when the coupling is strong there is a splitting of the electronic degeneracy as viewed in the field of the nuclei fixed in one of their positions of lowest energy. The simplest way to treat such systems is to consider the effective point group as the group of symmetry elements common to both initial and terminal states.

(iv) Spin-forbidden transitions

Each term in equation (3) will be zero if the initial and terminal states are of different spin. Spin forbidden transitions become allowed by the mixing of states of different spin via the spin-orbit operator, H_{SO}. The simplest way to handle spin-forbidden transitions is to use the double group formalism. This however obscures the nature of the intermediate states in the intensity mechanism. Very often only the mixing of the terminal (or initial) state with the nearest state to which (or from which) a transition occurs is considered but this is only likely to be a reasonable approximation if the transition from which the intensity derived is strong and other states are well separated. More usually a great many terms can contribute to the intensity. As an example the most important couplings for the intensity of a transition ${}^aA_g \rightarrow {}^bB_g$, where a and b differ by two units, the transition ${}^aA_g \rightarrow {}^aX_u$ is allowed and there are only two other states ${}^bY_u$ and ${}^aC_g$, are illustrated in Fig. 1. In practice there will be many states of the type ${}^aX_u$, ${}^bY_u$ and ${}^aC_g$. The spin orbit coupling matrix elements are typically several hundred wavenumbers in first-row transition

* $\{\Gamma_{6g} + \Gamma_{7g}\}^2$ for T_h.

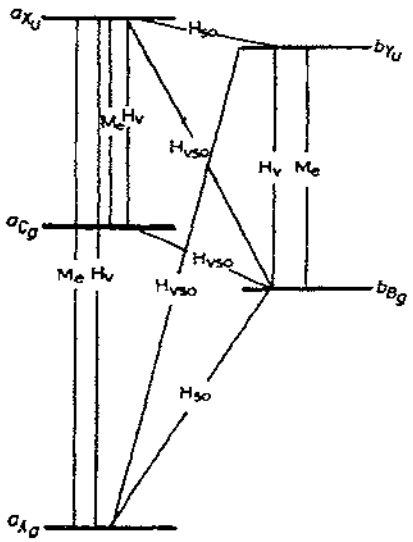


Fig. 1. Simplified coupling scheme for the intensity mechanism of the spin and parity forbidden transition ${}^{a}A_g \rightarrow {}^{b}B_g$. M_e, H_v, H_{SO} and H_{VSO} are the electric dipole, vibronic coupling, spin-orbit coupling and spin-vibronic coupling operators respectively.

elements, so that the mixing of states is sufficient to give measurable intensity to spin forbidden transitions without seriously distorting the potential surfaces involved.

(v) Vibrational structure of allowed transitions

The intensity distribution of the transition ev→e'v' is given by the vibrational overlap (or Franck-Condon) Integral $\langle \Psi_v / \Psi_{v'} \rangle$. There are two limiting cases.

(i) The equilibrium internuclear distances and force constants are similar in the initial and terminal electronic states. The vibrational overlap integrals will be nearly zero (wavefunctions are nearly orthogonal) except when both wavefunctions correspond to the same number of quanta of the same vibrational mode, in which case the integral is nearly unity. Thus the low temperature spectrum consists of a single sharp line corresponding to the pure electronic transition. This is termed an electronic origin, a O—O' line, or (in the solid state) a zero phonon line.

(ii) The equilibrium internuclear distances and/or force constants are different in the two electronic states. The overlap integrals will now be non-zero when the initial and final vibrational wavefunctions differ by any number (including zero) of quanta of totally symmetric vibrations. (The vibrational Hamiltonians are not identical in the two states). Progressions in totally symmetric modes based on the electronic origins are now observed but a general expression for the intensity of the members of the progression cannot be

given in closed form. If the equilibrium internuclear distance is assumed not to change, then the intensity of O—O line relative to the total intensity of the whole progression is

$$\frac{I_o}{\sum_n I_n} = \frac{(\nu\nu')^{\frac{1}{2}}}{\frac{1}{2}(\nu+\nu')} \tag{4}$$

where ν and ν' are the vibrational frequencies in the initial and terminal states. Alternatively, if the internuclear distance is assumed to change (δr) without there being any change in vibrational frequency, then the intensity of the nth line will be

$$I_n = [\tfrac{1}{2}\beta(\delta r)^2]^n I_o/n! \text{ where } \beta = 4\pi^2\nu\, cM/h \tag{5}$$

and M is the mass of the monoatomic ligand. For large δr the envelope of the band will be the familiar Gaussian curve with a maximum corresponding approximately to the transition in which there is no change in nuclear coordinates. β is of the order of 300 when δr is in Å, so that rather large changes in force constant but little change in bond length is necessary to give appreciable intensity to the progressions.

Often a molecule has several totally symmetric vibrations. In this case we can get not only progressions in each mode based on the origin but also progressions based on every member of the other progressions. Fortunately, in coordination compounds there are usually only one or two internuclear distances for which δr is appreciable.

(vi) Vibrational structure of vibronically allowed transitions

The selection rule 2 shows that the electronic origin is forbidden by this mechanism but there will be one or more vibronic bands corresponding to the transition $O \rightarrow O' + \nu'_u$ where ν'_u is a non-totally symmetric fundamental vibration satisfying the selection rule. These bands are termed vibronic origins (false origins) and ν'_u an enabling vibration. There is no simple way of evaluating the intensity of different vibronic origins, although some approximate calculations have been carried out[12,13]. Clearly however they will depend on the intensity and position of the transition, $\Psi_e^o \rightarrow \Psi_x^o$, the magnitude of $\langle\Psi_v/Q_i/\Psi_v'\rangle$, as well as the magnitude of $(\delta V/\delta Q_i)_o$. This last term is not expected to be large if Q_i does not involve bond distances or angles near the metal atom. $\langle\Psi_v|Q_i|\Psi_v'\rangle$ may be separated into $\langle\Psi_u|Q_u|\Psi_u'\rangle\langle\Psi_a|\Psi_a'\rangle$ where u is a nontotally symmetric vibration and a is a totally symmetric vibration. Thus if the potential surfaces in the two states are different along the totally symmetric coordinates, there will be a progression or progressions involving the totally symmetric modes based on the vibronic origins. The intensity distribution in these progressions will be similar to that in a progression in an allowed transition.

At higher temperatures, transitions of the type $O + \nu_u \rightarrow O' + (p \pm 1)\nu'_u + q\nu'_a$ may occur and an approximate calculation shows that the intensity (oscillator strength) of a vibronically allowed transition should be proportional to Coth $(h\nu'_u/2kt)$. In real systems, there may be many different enabling vibrations as well as an allowed component for the transition. Since the experimental data and approximations in the theory are not sufficiently good for the extraction of more than one parameter the best that can be done in cases where the vibrational structure is not resolved is to determine a weighted average of the various ν'_u.

The temperature dependance of the intensity of vibronically allowed transitions has often be used to distinguish allowed and vibronically allowed electronic transitions but in view of the complexities, this is not completely reliable.

C. SOLID STATE EFFECTS

(i) The site model

Incorporation of the molecule into a lattice site has two important effects. Firstly, the symmetry of the site may be lower than that of the idealised gas phase molecular geometry which will cause splittings of the vibronic states. If the crystal structure (or often only the space group) of the lattice is known, the site symmetry can be determined from the International Tables of Crystallography or from Halford's Tables[10]. The relating of the idealised and actual symmetries and selection rules is facilitated by the use of correlation tables. Secondly, the molecule is held in a fixed orientation relative to the crystal axes so that if non-cubic single crystals are used, the spectra are anisotropic. In favourable cases, the use of polarized light and various crystal orientations (i.e., the differentiation of the x,y and z directions of the transition moment vectors) enables much more detailed information concerning the vibronic states and intensity mechanism to be obtained. It may happen that there are several non-equivalent sites in a given lattice. Comparison of absorption, excitation and luminescence spectra and the measurement of luminescence decay curves can greatly assist the unravelling of the resulting complex spectra.

(ii) The unit cell model

In this model two additional effects occur that are not present in the site model. There will be several vibrations involving motion of the complex molecule as a whole and of the other molecules or ions in the unit cell. The calculation of the number and symmetries of these lattice vibrations has been discussed many times[11,12]. In the absence of any interaction between the internal and lattice vibrations, the intensity of electronic transitions involving excitation of lattice vibrations in molecular complexes will be relatively small since these motions neither give a a large value of $(\delta V/\delta Q)_o$ (Equation 3) nor

have appreciably different frequencies in the two electronic states. This experimental distinction of internal and external vibrations is not possible by IR and Raman spectroscopy. There may be low frequency bending modes of the coordination complex which have similar frequency and the same symmetry as one or more external modes. Mixing of internal and external vibrational coordinates may then be strong and the "lattice" vibrations appear strongly in the vibronic spectrum.

If there are two or more crystallographically identical molecules in the unit cell then a Davydov splitting[13] of the electronic states and a correlation field splitting[14] of the internal vibrational states will occur. These effects arise from an electrostatic interaction between the molecules and is quite distinct from any magnetic coupling[15]. The Davydov splitting will be larger for the electronic origin than for the vibronic bands based on them[16] but the vibronic bands will also be subject to correlation field effects. These splittings are small in coordination compounds because the transition metal ions are well separated and are seldom resolved. One possible example is the $^2E \rightarrow {}^4A$ transition in $NaMgCr(C_2O_4)_3.9H_2O$[17] but there is uncertainty as to the nature of the smallest unit cell in this compound.

(iii) The space group model

The electronic and vibrational spectra of coordination compounds are usually determined using crystalline (or microcrystalline) samples. These crystals have translational symmetry (at least locally) and it is necessary to consider this symmetry in order to explain some of the details of the observed spectra of coordination compounds. The translational properties of crystal wavefunctions forms a major part of the subject of solid state physics. An account of these properties is given in most textbooks dealing with the solid state, a detailed account is given in reference 18. The following account is intended merely as a summary of the results necessary for the interpretation of experimental spectra.

In an extended crystal, the ground state crystal wavefunctions may be written

$$\phi^0 = \prod_j^N \Psi_j^0$$

where j goes over the N molecules of the crystal and the Ψ_j^0 are the ground state functions of the isolated molecule. For simplicity, only one molecule per unit cell is assumed. Unit cell functions may replace molecular functions. Similarly, one excited wavefunction may be written

$$\phi_r' = \Psi_r' \prod_{j \neq r}^N \Psi_j^0$$

where the molecule at the point r has been raised to an excited vibronic state,

Ψ'_r. These wavefunctions are N-fold degenerate and it is necessary to form linear combinations of these degenerate wavefunctions to obtain functions which have the translational symmetry of the crystal. The resulting excited state functions have the form

$$\Phi'(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{r}^{N} e^{i\mathbf{k}\mathbf{R}_r} \Psi'_r \prod_{j \neq r}^{N} \Psi_j^o$$

where $\mathbf{R}_r$ is the position vector for the point r and $\mathbf{k}$ is termed the wavevector. This procedure is analogous to the representation of molecular wavefunctions as linear combinations of atomic functions having the correct point group symmetry. The vector $\mathbf{k}$ is used to classify crystal states in much the same way as the characters of the representations of point group operations are used to classify molecular states. The main difference is that $\mathbf{k}$ is continuous for an infinite crystal. $\mathbf{k}$ may be regarded as describing the phase relationships of the elementary excitations in the unit cells.

The behaviour of $\Phi'(\mathbf{k})$ will repeat for values of $\mathbf{R}_r$ which differ by one primitive lattice translation so that it is only necessary to consider a range of values of $\mathbf{k}$. This range of $\mathbf{k}$ defines a volume of $\mathbf{k}$ space termed the (First) Brillouin zone. The maximum range of $\mathbf{k}$ in this zone will be $\pm \pi/a$ where a is the primitive lattice translation and this will be of the order of 10^8 cm^{-1}.

If there is no interaction between unit cells, the energy corresponding to $\Phi'(\mathbf{k})$ will be independent of $\mathbf{k}$ but the presence of an interaction removes this degeneracy. Using the crude adiabatic approximation enables the energy of a vibronic state to be written as the sum of a vibrational and electronic contribution

$$E_{ev}(\mathbf{k}) = E_e(\mathbf{k}_e) + E_v(\mathbf{k}_v) \text{ where } \mathbf{k} = \mathbf{k}_e + \mathbf{k}_v$$

The energies of crystal field states are virtually independent of $\mathbf{k}_e$ since the d-orbitals on different ions do not overlap appreciably. Similarly, the internal vibrational frequencies will not depend strongly on $\mathbf{k}_v$ (i.e., will exhibit little dispersion) since these modes in different complexes do not couple strongly. The dispersion of lattice modes may however be large, although reliable calculations have only been carried out on the simplest lattices. It can be shown that $\mathbf{k}$ is conserved during an electronic, vibrational or vibronic transition. The $\mathbf{k}$ value of the photon will be 10—10^5 cm^{-1} and therefore small compared to the range of $\mathbf{k}$ in the Brillouin zone. Excitation of a single quantum of a vibration during an IR or Raman experiment must therefore involve only the frequency near $\mathbf{k} = 0$. On the other hand, excitation of a vibrational combination mode or of a vibronic transition may involve vibrational frequencies corresponding to any value of $\mathbf{k}$.

$$\mathbf{k}_{photon} = \mathbf{k}_v + \mathbf{k}_v \doteq 0$$
$$\mathbf{k}_{photon} = \mathbf{k}_e + \mathbf{k}_v \doteq 0$$

The importance of this is that when $\mathbf{k} = 0$, the electronic and vibrational

functions have the same symmetry as is given by unit cell analysis but if $\mathbf{k} \neq 0$, the symmetries are lower, until for a general $\mathbf{k}$ the effective symmetries are C_1. Thus, *any vibrational mode can appear in a vibronic spectrum and the vibrational frequencies may have a range of values.*

The vibronic spectrum will then consist of a vast number of closely spaced transitions, the intensity of a given band will, amongst other factors, depend on the number of crystal vibrational states per unit frequency interval (i.e., the density of states). When dispersion is small the density of states is high; this will occur generally for interval vibrational modes and often for lattice vibrations at certain special values of $\mathbf{k}$. The most important of these special values is $\mathbf{k} = 0$. Thus if we exclude all values of $\mathbf{k}$ other than $\mathbf{k} = 0$ we reobtain the vibronic spectrum predicted by the unit cell model. There will however be contributions to the spectrum from vibronic transitions involving vibrational functions for which $\mathbf{k} \neq 0$. This will result in a broadening of the internal vibrations and a general smearing of the lattice vibrations. An intensity maximum in the lattice vibration region may represent a $\mathbf{k} = 0$ vibrational mode but it may also represent a vibration for some special value of $\mathbf{k}$ which cannot be observed in the IR or Raman spectrum (except possibly as a combination).

This summary neglects the interaction of the lattice with the radiation field. The most important consequence of this is the splitting of certain degenerate vibrational modes into two components even at $\mathbf{k} \doteq 0$. These are termed the transverse and longitudinal components.

The fundamental problem facing the coordination chemist is to decide whether an observed vibronic spectral feature which cannot be easily explained using unit cell analysis, is due to an incorrect assumption in the analysis (such as the incorrect identification of the electronic or vibrational states involved, a difference in geometry between the electronic states, incorrect crystal structure, etc.), or is caused by a contribution from $\mathbf{k} \neq 0$ selection rules. For a complex system, there is unlikely to be any guidance from theoretical treatments of the lattice dynamics and it is necessary to proceed empirically. For systems such as V^{2+} in MgO, where there are no "internal" vibrations, it is clear that $\mathbf{k} \neq 0$ effects are essential in understanding the observed spectrum[19]. Similarly, the ${}^3A_{1g} \rightarrow {}^3T_{2g}$ transition in $KNiF_3$, whilst showing[20] the four vibronic origins predicted by unit cell analysis has many more bands which must involve $\mathbf{k} \neq 0$ vibrations. However for K_2MnF_6, where the Mn—F interaction is much stronger than the F—K interaction, unit cell analysis can explain most of the more intense features (see below).

D. SOME EXPERIMENTAL STUDIES

(i) MX_6^{n-} Systems

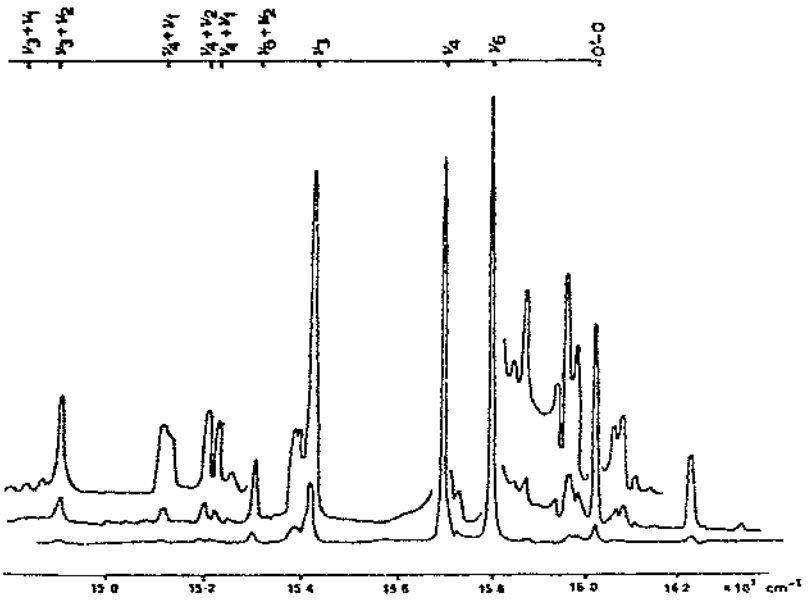
One of the most extensively studied complex ions is the octahedral MnF_6^{2-}

ion in which the $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^2T_{1g}$ and $^4A_{2g} \leftrightarrow {}^2E_g$ transitions show extensive vibrational structure. The selection rules show that the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition is electric dipole forbidden, magnetic dipole allowed and electric dipole vibronically allowed with enabling vibrations of α_{1u}, ϵ_u, τ_{1u} symmetry. The internal vibrational modes of the isolated MnF_6^{2-} are the $\nu_1(\alpha_{1g})$, $\nu_2(\epsilon_g)$ and $\nu_3(\tau_{1u})$ Mn-F stretches and the $\nu_4(\tau_{1u})$, $\nu_5(\tau_{2g})$ and $\nu_6(\tau_{2u})$ F—Mn—F bends. It would be expected therefore that this transition should consists of four electronic origins (the $^4T_{2g}$ state splits into $2\Gamma_8$, Γ_7 and Γ_6 when spin orbit coupling is included) with three vibronic origins based on each electronic origin. On each of these sixteen origins there will be a progression in the α_{1g} mode and since there will be a considerable difference in the equilibrium internuclear distance between the $^4A_{2g}(t_{2g}^3)$ and $^4T_{2g}(t_{2g}^2 e_g)$ states, the intensity of the progressions will pass through a maximum.

Pfie![21] has measured this spin allowed transition in a single crystal of Cs_2MnF_6. This compound belongs to the $Fm3m$-O_h^5 space group with $Z = 1$ so that the Mn^{4+} ion occupies a site of O_h symmetry. Unfortunately the spectrum is not sufficiently well resolved to permit a complete analysis but it is clear that there are progressions in *two* modes of frequencies 575 and 482 cm^{-1} and based on a number of vibronic origins. These are probably the α_{1g} and ϵ_g vibrational frequencies in the $^4T_{2g}$ state, the corresponding ground state frequencies being 592 and 508 cm^{-1}. The appearence of progressions in the ϵ_g mode indicates that the potential minima of the excited states are displaced along the ϵ_g coordinates relative to the ground state, probably as a result of a Jahn—Teller effect in the $^4T_{2g}$ state. If this is the case, then it would be expected that the overall splitting of the origins will be less than the ca. 200 cm^{-1} predicted by first-order spin orbit coupling due to a Ham effect. Unfortunately the electronic origins have not been definitely located in either the absorption or excitation spectra.

Turning to the spin-forbidden transitions, the ^2E_g state is not split by spin orbit coupling $[^2E_g(O_h) \rightarrow \Gamma_{8g}(O_h^*)]$ but the $^2T_{1g}$ state splits into two components $[^2T_{1g}(O_h) \rightarrow \Gamma_{6g}(O_h^*) + \Gamma_{8g}(O_h^*)]$. The intensity of the electronic origins arises primarily from a mixing of the doublet states with the $^4T_{2g}$ state and they are magnetic dipole allowed. The double group selection rule shows that all vibrations may be vibronically active for both $\Gamma_8(^4A_2) \rightarrow \Gamma_8(^2E \text{ or } ^2T_1)$ and $\Gamma_8(^4A_2) \rightarrow \Gamma_6(^2T_1)$ transitions. The three transitions should therefore each consist of a weak electronic origin with τ_{2u} and two τ_{1u} vibronic origins but the α_{1g} progressions on these origins will be weak since there is no change of strong field configuration during the transitions. Whilst it is feasible to measure the $^4A_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$ transitions in absorption, the low intensity of the absorption and the high efficiency of the $^2E_g \rightarrow {}^4A_{2g}$ transition makes it far easier to measure the $^2E_g \rightarrow {}^4A_{2g}$ transition in emission and the $^4A_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$ transitions in excitation.

The spectra (Figs. 2 and 3) are superficially in good agreement with these predictions based on the site symmetry. Closer examination, particularly of the luminescence spectra[22], where the sensitivity is particularly high, shows that there are many lines which are not readily accounted for by this model.



'ig. 2. The luminescence spectrum of Cs_2MnF_6 at 80 K (ref. 22).

n addition to the weak progressions in the $\nu_1(\alpha_{1g})$ mode there are stronger ırogressions in the 508 cm^{-1} $\nu_2(\epsilon_g)$ vibration. Whilst a Jahn—Teller effect in ny of the intermediate states (Fig. 1) could produce these progressions, comıarison with the luminescence of the CrF_6^{3-} ion strongly suggests that $^4T_{2g}$ tate is the important one. Between the origin and $\nu_6(\tau_{2u})$ at least five weak

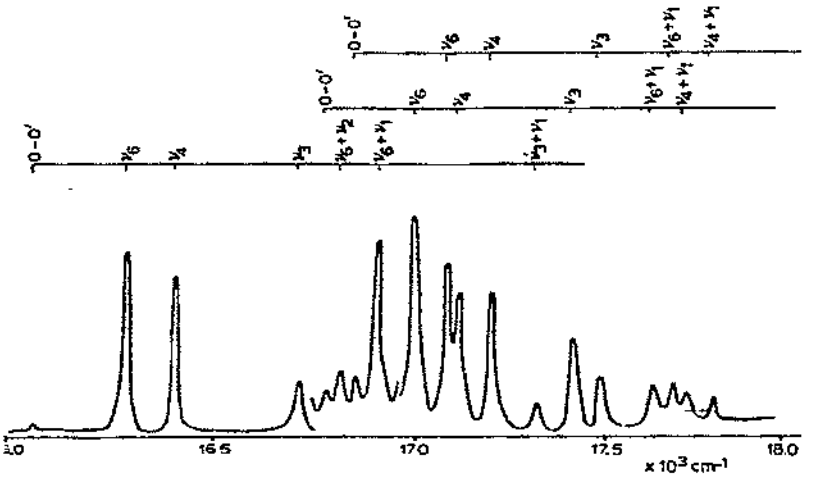


Fig. 3. The $^4A_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$ excitation spectrum of Mn^{4+} in Cs_2SiF_6 at 80 K (ref. 23).

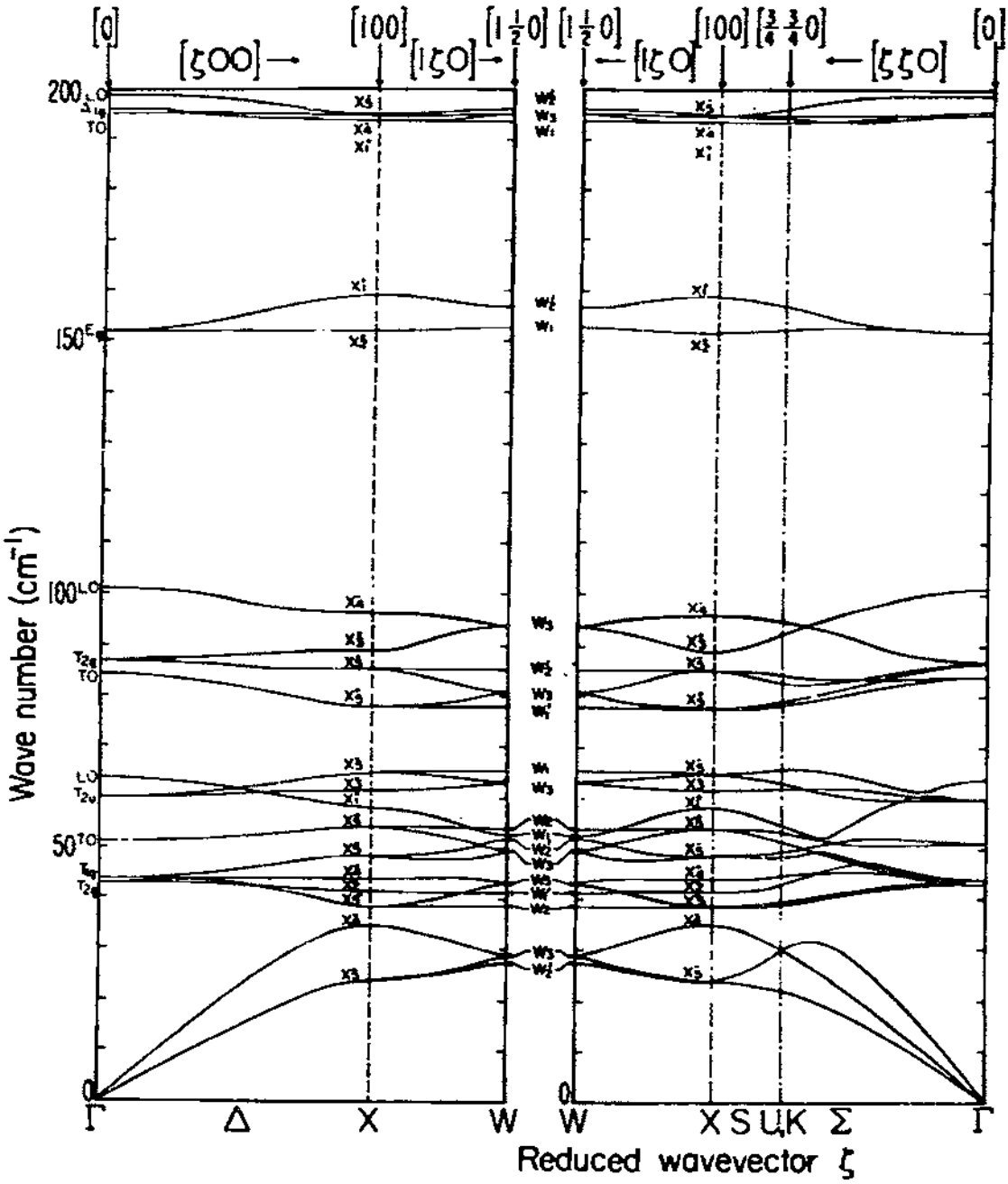
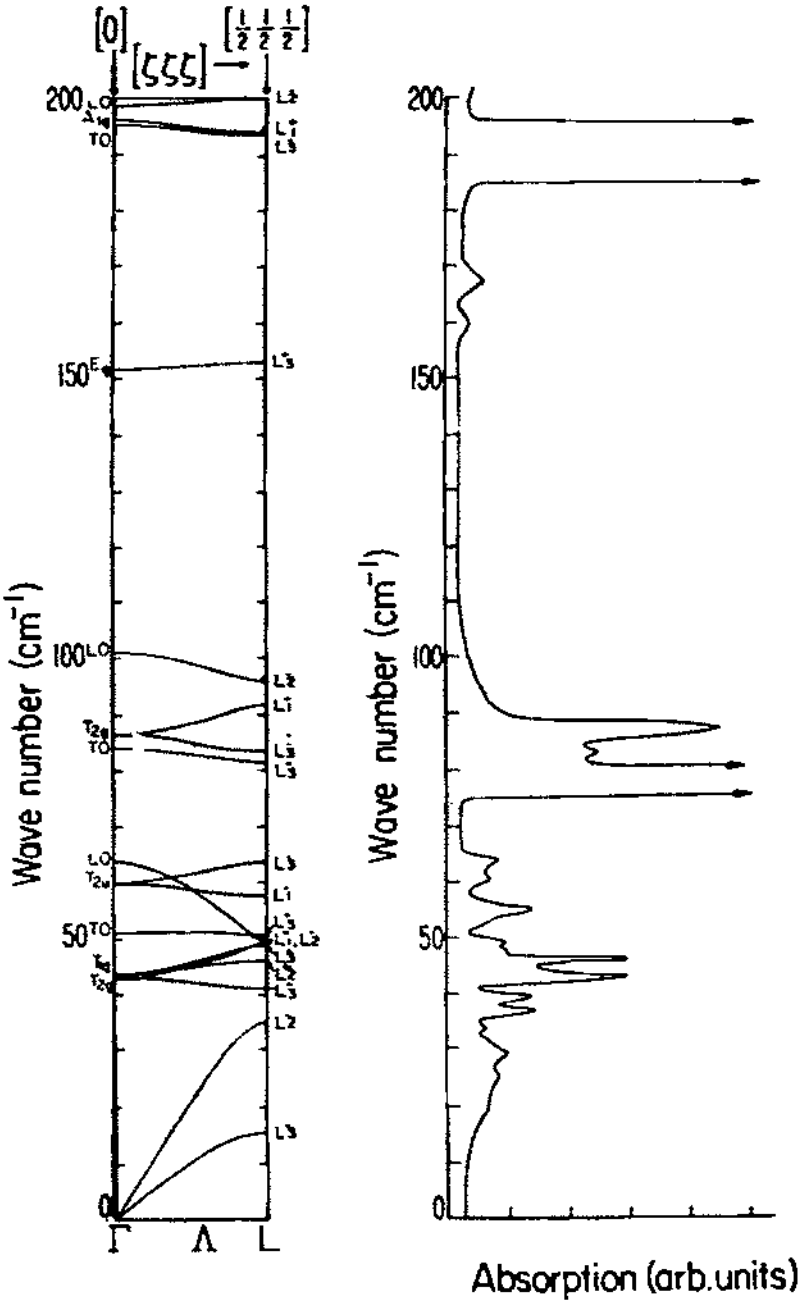


Fig. 4. Calculated dispersion curves for Cs_2UBr_6 and the absorption spectrum of Cs_2UBr_6 in the region of the Γ_{1g} electronic origin at 14,692 cm^{-1}. For this transition the τ_{2u} vibration is not an enabling mode in the unit cell approximation. (Reproduced by permission from ref. 26).


[0]
[555]
[½ ½ ½]
200
150
100
50
0
Wave number (cm⁻¹)
Γ
Λ
L
Absorption (arb.units)

bands can be detected which at 80 K can also be observed with the expected intensity in the anti-Stokes emission. A similar set of bands can be observed in the luminescence spectra of Mn^{4+} in other $Fm3m$ lattices[23]. Unit cell group analysis predicts the presence of lattice modes of τ_{1u}, τ_{2g} and τ_{1g} symmetry. One of the five bands (at 92 cm^{-1}) is coincident with a strong infrared absorption band and is assigned as the transverse optic (τ_{1u}) fundamental. A second band (at 68 cm^{-1}) is coincident with a strong Raman band and is presumably the τ_{2g} mode but there seems to be no mechanism in the unit cell model which can account for the τ_{2g} mode appearing in the vibronic spectrum with an intensity comparable to the τ_{1u} mode. Of the remaining three bands, one may be the τ_{1g} mode, but the other two bands cannot be $\mathbf{k} = 0$ modes. Thus it seems necessary to consider vibronic coupling at $\mathbf{k} \neq 0$ to explain four of the observed low frequency modes. Similarly in the higher frequency region there are a number of weak features which are not readily explained by the $\mathbf{k} = 0$ model.

Even more detailed studies have been made by Satten et al.[24,25] on the $5f^2$ ions UCl_6^{2-} and UBr_6^{2-}. The visible absorption spectrum consists of a large number of electronic transitions, each with well resolved vibronic structure. The overall appearance of the spectra is in good agreement with the vibronic selection rules for the octahedral anion, and this has been used to identify the terminal electronic states. Under high resolution the vibronic origins split into at least three components with a total separation of about 25 cm^{-1}. Vibronic interaction in the unit cell approximation cannot by itself explain this splitting since the ground state is Γ_{1g} and all terminal vibronic states must be Γ_{4u}. Satten and Pollack[24] attribute the splitting to a combination of vibronic coupling and the splitting of the optical branches away from $\mathbf{k} = 0$.

The only case in which an attempt has been made to calculate the vibrational frequencies of a coordination compound as a function of $\mathbf{k}$ is the work of Chodos[26] on Cs_2UBr_6 (Fig. 4). Whilst the model employed is of necessity rather crude the agreement with experiment is satisfactory.

Some other MX_6^{n-} systems, for which vibronic analyses have been carried out, are CrF_6^{3-} (ref. 27), $ReCl_6^{2-}$, (ref. 28), $ReBr_6^{2-}$ (ref. 29), $OsBr_6^{2-}$ (ref. 30), IrF_6 (ref. 31) and MoF_6^- (ref. 32).

(ii) Ammino and aquo complexes

The most thoroughly studied[33,34] complex ion in this category is $Cr(NH_3)_6^{3+}$. Assuming free rotation of the ammino groups and O_h symmetry for the ion there are seven τ_{1u} and four τ_{2u} vibrational modes that can act as vibronic origins for the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^2E_g$ transitions. The vibrational structure of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition is not resolved (this is not surprising with four electronic origins, forty-four vibronic origins and six potential progression forming modes!) but the ${}^4A_{2g} \rightarrow {}^2E_g$ transition of $Cr(NH_3)_6(ClO_4)_3$ in which the Cr^{3+} ion occupies an O_h site is well resolved, both in absorption and emission (Fig. 5). At least ten of the eleven internal vibronic origins and the first

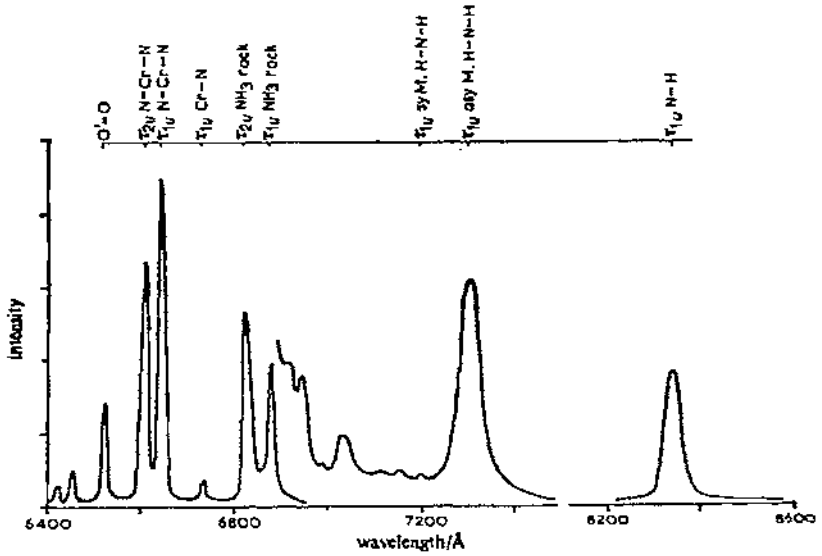


Fig. 5. The 80 K luminescence spectrum of $Cr(NH_3)_6(ClO_4)_3$ (ref. 34).

members of progressions in two ϵ_g modes have been identified[33,34]. The intensity of the origin relative to the vibronic origins is much higher than in Cs_2MnF_6, which may indicate that the chromium ion is subject to a non-centrosymmetric field due to hydrogen atoms. The vibronic origins involving N—Cr—N and Cr—N—H bending are an order of magnitude stronger than the Cr—N stretching modes. There is little definite evidence for the failure of the unit cell approximation, although the structure near the origin and certain weak bands remain unexplained.

The $^2E \rightarrow {}^4A$ luminescence spectrum of the $Cr(OD_2)_6{}^{3+}$ ion in alums[35,36] and other salts[37], has an overall similarity to that of $Cr(ND_3)_6{}^{3+}$ and can be assigned similarly (Fig. 6). The alums are however not very convenient for detailed vibronic analysis because of the low site symmetry of the Cr^{3+} ion, the large number of low energy lattice vibrations and the possibility of phase transitions. In addition, many alums are disordered[38] and energy transfer between non-equivalent sites occurs[35].

An analysis of the magnetic circular dichroism of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition of the $Ni(OH_2)_6{}^{2+}$ ion in $Ni(BrO_3)_3.6H_2O$ has been given by Harding et al.[39]. This transition shows little structure in the absorption spectrum but the MCD spectrum can be interpreted as a progression in a totally symmetric mode, based on a single vibronic origin involving a τ_{1u} vibration. This is in marked contrast to the behaviour of the spin forbidden transitions in ammino and aquo complexes of chromium (III). MCD absorption spectra are usually better resolved than conventional absorption spectra and it is probable that the measurement of MCD spectra will become increasingly important in the study of vibronic spectra.

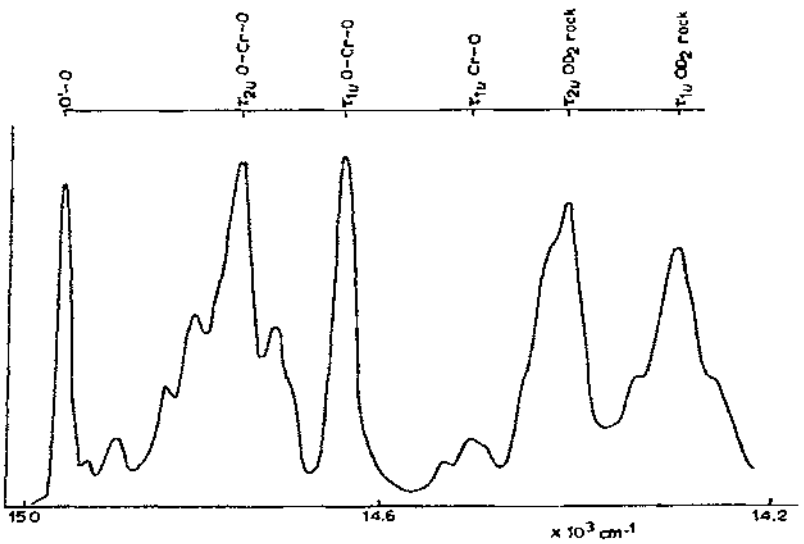


Fig. 6. The 80 K luminescence spectrum of deuterated thallium chromium alum

One of the rare cases where a spin-allowed transition in a complex with polyatomic ligands does show vibronic structure in absorption is the $^1A_1 \rightarrow {}^1T_1$ (O) transition of $2[Co(en)_3Cl_3].NaCl.6H_2O$, reported by Ballhausen and Dingle[40]. They were able to locate an electronic origin and three vibronic origins. To high energy of these origins there are progressions in a totally symmetric mode, of which one to four members may be resolved. Clearly, this is a case where the electric dipole vibronic mechanisms make a comparable contribution to the band intensity.

Some other molecules with oxygen or nitrogen donors, for which fairly detailed analyses have been carried out, are $Cr(NH_3)_5X^{2+}$ (X = Cl, Br, I, ONO_2, ONO, CF_3COO, H_2O)[41] and $Cr(en)_3{}^{3+}$ (ref. 42).

(iii) The hexacyanochromate (III) ion

The combination of a high value of D_q and relatively small values of B and C causes the first spin-allowed transition to lie well above the third spin-forbidden ($t_{2g}{}^3 \rightarrow t_{2g}{}^3$) transition in this ion, so that three well resolved transitions are observed. The only compounds that have been studied in detail are $K_3Cr(CN)_6$ and $K_3(Cr{:}Co)(CN)_6$, which are structurally similar. The cobalt compound and possibly the chromium compound exhibit polytypism[43] but this probably does not influence the band positions in the observed spectra (at a resolution of of ca. 1 cm^{-1}) so that it is convenient to assume the smallest monoclinic unit cell ($C_{2h}{}^5$, $Z = 2$) for analysis of the spectra. In this lattice the chromium ions occupy sites of C_i symmetry, which splits the $^2T_2$, $^2T_1$ and ^2E states into 3, 3 and 2 Kramers doublets respectively. Each of these eight electronic origins

have been found in the absorption spectrum of $K_3Cr(CN)_6$ but none of them shows splittings which can be attributed to Davydov effects. The vibrational modes of the $Cr(CN)_6^{3-}$ entity are $2\alpha_{1g}$, $2\epsilon_g$, τ_{1g}, $4\tau_{1u}$, $2\tau_{2g}$ and $2\tau_{2u}$. In the $z = 2$ lattice, the τ_{1u} and τ_{2u} modes are split into three unit cell group pairs, all of which can act as vibronic origins. In the $^4A_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$ and $^2T_{2g}$ absorption spectra[44], the lowest energy τ_{1u} and τ_{2u} modes have not been observed owing to their low intensity. The next lowest τ_{1u} and τ_{2u} modes clearly show the splitting into three components but the unit cell group splitting is not resolved.

It has not proved possible to obtain a high resolution luminescence spectrum from pure $K_3Cr(CN)_6$ but the $Cr(CN)_6^{3-}$ ion in $K_3Co(CN)_6$ gives a very well resolved emission from the ^2E_g state[45]. In the region between the origin and 250 cm^{-1} about sixteen bands are observed, all of which are electric dipole transitions. Comparison with the IR spectra shows that most of these band maxima correspond to ($k = 0$) fundamentals. The six components of the τ_{1u} and τ_{2u} C—Cr—C bending vibrations are expected to occur in this region but the vibronic intensity from these motions is distributed over a number of bands, i.e., the mixing of internal and lattice modes is strong.

Each of the remaining vibronic origins can be identified in the luminescence spectrum. Based on each of these vibronic origins, progressions of four members of the α_{1g} Cr—C stretching vibration are observed. Use of Eqn. (5) shows that their relative intensity corresponds to a change in Cr—C distance of about 0.05 Å between ^2E_g and $^4A_{2g}$ states.

(iv) Concluding remarks

The vibronic analysis of electronic transitions in coordination compounds can give very detailed information concerning the nature of the electronic states involved and the shape of their potential surfaces. The selection rules may be different from those in IR and Raman spectroscopy, so that it is possible to locate vibrational frequencies that are not readily identified by ground state spectroscopies. This is particularly valuable when a normal coordinate analysis of a coordinate complex is to be carried out, since the number of approximations made in setting up the force field may be reduced. In very favourable cases it may even be possible to identify $k \neq 0$ frequencies of relatively simple lattices. The greatest difficulty facing the electronic spectroscopist is that relatively few electronic transitions show well resolved vibrational structure, even at the lowest temperature. However when such structure is observed, its high information content makes the search for suitable systems worthwhile.

ACKNOWLEDGEMENT

I wish to thank the Science Research Council and the University of London Central Research Fund for financial support of this work.

REFERENCES

1 J.H. Van Vleck, *J. Phys. Chem.*, 41 (1937) 67.
2 R. Engleman, *The Jahn-Teller Effect in Molecules and Crystals*, Wiley-Interscience, New York, 1972.
3 F.S. Ham, *Phys. Rev.*, 166 (1968) 307.
4 M.D. Sturge, *Solid State Phys.* 20 (1967) 91.
5 B.R. Henry and M. Kasha, *Annu. Rev. Phys. Chem.*, 19 (1968) 161.
6 G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrand, New York, 1967.
7 C.J. Ballhausen and Aa. E. Hanson, *Annu. Rev. Phys. Chem.*, 23 (1972) 15.
8 C.J. Ballhausen, in C.N.R. Rao and J.R. Ferraro (Eds.), *Spectroscopy in Inorganic Chemistry*, Academic Press, 1970.
9 J. Ferguson, in S.J. Lippard (Ed.), *Progress in Inorganic Chemistry*, Vol 12, Interscience, 1970.
10 R.S. Halford, *J. Chem. Phys.*, 14 (1946) 8.
11 D.M. Adams and D.C. Newton, *Tables for Factor Group Analysis*, Beckman-RIIC, (1970).
12 S. Bhagavantam and T. Venkatarayudu, *Theory of Groups and its application to physical problems*, Academic Press, New York, 1969.
13 A.S. Davydov, *Theory of Molecular Excitons*, (Translated by M. Kasha and M. Oppenheimer) McGraw Hill, New York, 1962.
14 S.S. Mitra, in S. Nudelman and S. S. Mitra (Eds.), *Optical Properties of Solids*, Plenum Press, New York, 1969.
15 C.D. Flint and P. Greenough, *J. Chem. Soc. Faraday II*, 69 (1973) 1469.
16 D.S. McClure, *Solid State Phys*, 8 (1959) 1.
17 O.S. Mortensen, *J. Chem. Phys.*, 47 (1967) 4215.
18 See for example, J.M. Ziman, *Electrons and Phonons*, Clarendon Press, Oxford 1960.
19 G.F. Impush, W.M. Yen, A.L. Schawlow, D.E. McCumber and M. D. Sturge, *Phys. Rev.*, 133 (1964) A1029.
20 J. Ferguson, H.J. Guggenheim and D.L. Woods, *J. Chem. Phys.*, 40 (1964) 822.
21 A. Pfeil, *Theor. Chim. Acta*, 20 (1971) 159.
22 C.D. Flint, *J. Mol. Spectroscopy*, 37 (1971) 414.
23 A.M. Black and C.D. Flint, to be published.
24 S.A. Pollack and R.A. Satten, *J. Chem. Phys.*, (1962) 804.
25 R.A. Satten, D.J. Young and D.M. Gruen, *J. Chem. Phys.*, 33 (1960) 1140.
26 S.L. Chodos, *J. Chem. Phys.*, 57 (1972) 2712.
27 J. Ferguson, H.J. Guggenheim and D.L. Wood, *J. Chem. Phys.*, 54 (1971) 504.
28 P.B. Dorain in R.L. Carlin (Ed.), *Transition Metal Chemistry*, Vol. 4., Marcel Dekker, New York, 1968.
29 H.H. Patterson, J.L. Nims and C.M. Valencia, *J. Mol. Spectrosc.*, 42 (1972) 567.
30 A.R. Reinberg, *Phys. Rev.*, 13 (1971) 341.
31 J.L. Nims, H.H. Patterson, S.M. Khan and C.M. Valencia, *Inorg. Chem.*, 12 (1973) 1602.
32 J.C.D. Brand, G.L. Goodman and B. Weinstock, *J. Mol. Spectrosc.*, 37 (1971) 464.
33 J.L. Nims, H.H. Patterson, S.M. Khan and C.M. Valencia, *Inorg. Chem.*, 12 (1973) 1602.
34 C.D. Flint and P. Greenough, *J. Chem. Soc. Faraday II*, 68 (1972) 897.
35 C.D. Flint, unpublished work.
36 G.J. Goldsmith, F.V. Shallcross and D.S. McClure, *J. Mol. Spectrosc.* 16 (1965) 296.
37 F.D. Camassei and L.S. Forster, *J. Mol. Spectrosc.*, 31 (1969) 129.
38 C.D Flint, unpublished work.
39 M.J. Harding, S.F. Mason, D.J. Robbins and A.J. Thomson, *J. Chem. Soc. A.*, (1971) 3047.
40 R. Dingle and C.J. Ballhausen, *Kgl. Dan Vidensk. Selsk., Mat. Fys. Medd.*, 35 (1967) 12.
41 C.D. Flint and A.P. Matthews, *J. Chem Soc. Faraday II*, 69 (1973) 419.
42 P.J. McCarthy and M.T. Vala, *Mol. Phys.*, 25 (1973) 17.
43 J.A. Kohn and W.D. Towns, *Acta Crystallogr.*, 14 (1961) 617.
44 R.K. Mukherjee, S.C. Bera, A. Bose and M. Chowdhury, *J. Chem. Phys.*, 56 (1972) 3720.
45 C.D. Flint and P. Greenough, *J. Chem. Soc. Faraday II*, 70 (1974) 815.