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VIBRATIONAL FINE STRUCTURE IN THE ELECTRONIC SPECTRA OF TRANSITION METAL COMPOUNDS. AN EXPERIMENTAL SURVEY

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CONTENTS

A. INTRODUCTION

This review is concerned with the electronic spectra of transition metal, d-electronic compounds with observable vibrational structure. The general problems connected with the theory of vibronic spectra have recently been reviewed by Flint [1] and Stephens [2]. This paper devotes much more attention to the experimental material present in the literature, mainly in the period 1970—1978. We decided also to collect some MCD data, as this technique complements conventional absorption and emission spectroscopy in a way which makes possible a full analysis of the electronic structure of a molecule.

For a more detailed discussion on magnetic circular dichroism we refer to the review of Stephens and the references therein [2]. The present paper does not consider the Jahn-Teller and Ham effects. These important topics, very closely related to the subject of the article, have recently been widely reviewed [1,2,4—8].

B. ELECTRONIC-VIBRATIONAL TRANSITIONS

Unlike transitions in atoms, electronic transitions in molecules cover broad areas of energy because electronic excitations are accompanied by vibrations and rotations not present in atoms. Thus the appearance of a particular band in the spectrum is the result of a transition between two sets of vibronic states. The observation of structured spectra gives an important and unique source of information about the structure of molecules.

The molecular state involving both electronic and nuclear motion may be described within the Born—Oppenheimer approximation which separates both motions

$$\psi_{ev}(q, Q) = \psi_e(q,Q)\ \psi_v(Q) \tag{1}$$

where ψ_{ev} is a vibronic function, ψ_e and ψ_v are electronic and vibrational functions respectively, and q, Q are electron and nuclear coordinates. The electronic function ψ_e for a given state is obtained as a solution of the Schrodinger equation

$$H\psi_e(q, Q) = E(Q)\ \psi(q, Q) \tag{2}$$

The Born-Oppenheimer (BO) approximation is valid in the cases where the non-degenerate electronic state ψ_e is well separated from other states; otherwise a coupling occurs between different electronic states giving rise to the well known Jahn—Teller and Renner effects. On the other hand, the approximation is also valid when the coupling is very strong. Some effects of a breakdown of the BO approximation have recently been discussed by Strickler [9].

The electronic transition between the initial vibronic state ψ_{ev} and the final vibronic states $\psi_{e'v'}$ may contain many lines. The intensity of absorption is distributed among them in a particular way [10—13].

Let us consider first a transition between two vibronic states $\psi_{ik} \to \psi_{jl}$. The intensity of the spectrum observed is proportional to the square of the matrix element

$$D_{ik \to jl} \approx \langle \psi_{ik}(q, Q) | M | \psi_{jl}(q, Q) \rangle \tag{3}$$

where M is the sum of the electric dipole, magnetic dipole and electric quadrupole operators. In the Herzberg—Teller adiabatic approximation

$$\psi_i(q, Q) = \psi_i^0(q) + \sum_{l \neq i}^{\infty} c_{il}\psi_l^0(q)$$

and

$$c_{il} = [\epsilon_i(Q_0) - \epsilon_l(Q_0)]^{-1} \left\langle \psi_i^0(q) | \sum_\eta \left(\frac{\partial V}{\partial Q_\eta}\right)_{Q_0} Q_\eta + \ldots | \psi_i^0(q) \right\rangle \tag{4}$$

where ϵ_i, ϵ_l are the eigenvalues of the electronic Schroedinger equation. In this approximation $\psi_i(q, Q)$ are expanded about some reference value of Q denoted by Q_0.

For a given state ψ_x^0 using eqns. (3) and (4) the probability of the transition could be expressed as

$$\begin{aligned} D_{ik \to jl} \sim & \langle \psi_i^0(q) | M | \psi_j^0(q) \rangle \langle \chi_{ik} | \chi_{jl} \rangle + \langle \psi_i^0(q) | M | \psi_x(q) \rangle \langle \chi_{ik} | c_{xj} | \chi_{jl} \rangle \\ & + \langle \psi_x^0(q) | M | \psi_j^0(q) \rangle \langle \chi_{ik} | c_{xi} | \chi_{jl} \rangle \end{aligned} \tag{5}$$

The coefficients c_{il} are rather small compared with the other terms of eqn. (5) so the first term becomes the most important factor determining intensity. When the first term is non-zero, the transition is allowed. The expression $\langle \chi_{ik} | \chi_{jl} \rangle = S$ is known as a Franck—Condon integral. If the excited electronic state has an equilibrium geometry identical to that of the ground state and the potential surfaces are identical, the force constants for various vibrations do not change upon excitation; all vibronic states have nearly the same energy and the low temperature spectrum consists of a single electronic line, O—O.

When vibrational functions are no longer identical, transitions are allowed from a single state vibrational level to more than one excited level. The resulting band contains many vibronic transitions which are responsible for its structure and shape. If no progressions are observed all bands correspond to $\Delta\nu = 0$ (potential surfaces are not displaced with respect to each other, Fig. 1(b)). $\Delta\nu$ represents the difference between the vibrational quantum numbers of the initial and final states.

The appearance of progressions in one or several frequencies means that the surfaces are displaced along the corresponding normal coordinates (Fig. 1(c) and (d)). The intensity distribution in the progression depends upon the extent of the displacement of the potential surfaces. The intensity I_n of the n-th member of a vibrational progression in the totally symmetric mode, is given by the Poisson distribution

$$I_n = I_0 \cdot S^n / n! \tag{6}$$

where S represents the Franck—Condon factor usually obtained experimentally from the ratio I_1/I_n. These S values allow us to obtain the value of the distortion parameter Q_0, which takes place under excitation, from the relation

$$S = E_\alpha / \hbar\omega_\alpha = \tfrac{1}{2} k_\alpha (Q_0)^2 / (\hbar\omega_\alpha)^{-1} \tag{7}$$

where E_α is the energy associated with Q_0 (distortion from equilibrium), ω_α is the frequency and k_α is the proper force constant [324].

In considering the vibronic problem the important arguments are symmetry

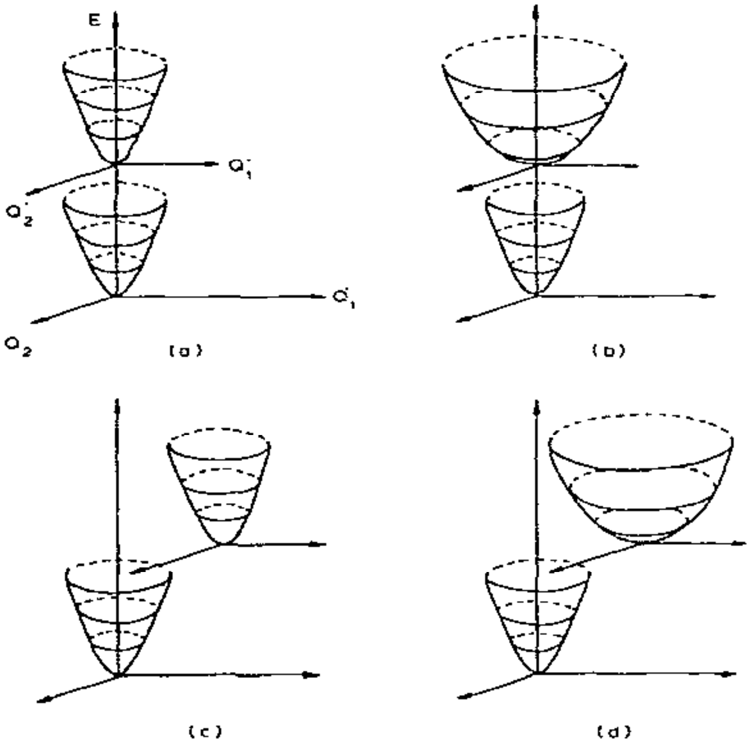

Fig. 1. Potential surfaces of the initial (V_{I}) and final (V_{F}) electronic states [11].

rules and intensity mechanism. Assuming that the first term in eqn. (5) is non-zero (allowed electronic transition) $\psi_i \rightarrow \psi_j$ can have non-vanishing intensity only if $\langle \chi_{ik} | \chi_{jk} \rangle$ is totally symmetric.

If the first term of eqn. (5) is zero, as for example for a $d \rightarrow d$ transition in O_h symmetry, the transition is said to be forbidden. However, in a centrosymmetric complex $d \rightarrow d$ transitions may be magnetic dipole and electric quadrupole allowed. The second and third terms of eqn. (5) also lead to non-zero transition moments. The selection rule for electric dipole forbidden (the first term of eqn. (5) is zero) but vibronically allowed (the second and third terms are non-zero) transitions puts a restriction that $\Gamma[\psi_i] \times \Gamma[M] \times \Gamma[\psi_j]$ must have an irreducible representation in common with $\Gamma[\psi_\nu] \times \Gamma[\psi_{\nu'}]$ and ψ_ν and $\psi_{\nu'}$ must differ in the first order by a single quantum of a non-totally symmetric vibration. This means that O—O bands are strongly forbidden and only non-totally symmetric vibrations can bring intensity to this symmetry forbidden transition. There are vibronic bands corresponding to the transition $O \rightarrow O' + \nu_u$ (vibronic origin) where ν_u' is a non-totally symmetric vibration. The absence of an O—O band together with the weak intensity of the spectrum are characteristic of symmetry forbidden transitions. An important difference between the band envelope of an electronically allowed and a vibrationally allowed transition lies in their temperature dependence (see below).

There are some predictions of vibrationally induced intensities but theoretically it is still a difficult task, especially if several active vibrations are present.

C. INTERACTION WITH ENVIRONMENT

Vibronic spectra are best resolved in crystals at cryogenic temperatures. The use of a single crystal has some advantages. Firstly, a fixed orientation of the molecule in the lattice provides the possibility of anisotropy, and by using polarized light one may obtain detailed information on the vibronic mechanism. Secondly, incorporating a molecule into a crystal of lower symmetry produces a splitting of the states and thus may permit proper assignment of the transitions. The lattice vibrations are very often coupled to "internal" molecular modes providing valuable information about the intermolecular forces acting in the solid state. Theoretical details of the spectra of impurity ions in a host crystal have attracted much attention [1,14,15]. External perturbations reduce the symmetry of the vibrational modes, change vibrational components and in consequence lead to broad absorption bands even at very low temperatures.

Isotropy of environment does not favour resolution of the structure and there are only a few examples of resolved vibronic structure found in solution. For example the spectra of chromium(VI) oxy and chloroxy compounds in organic solvents provide quite good resolution of vibrational structure. The general problems of solute—solvent interactions, band shape and intensity have been studied by many authors [18—20]. It is known that the absorption and the luminescence spectra depend strongly upon the nature of the solvent. In general, under the influence of polar solvent molecules the band shifts without changing its shape. However, in the case of solvents capable of forming hydrogen bonds the band structure depends strongly on the nature of the solvent. This is particularly pronounced for actinyl compounds [16].

D. THE TEMPERATURE EFFECT

An increase in sharpness of the spectra observed upon cooling the sample is due to a decrease in the Boltzmann population of the excited states. Thus the picture obtained at cryogenic temperatures is easier to interpret and more informative. The effect of temperature on band intensities depends upon the kind of transition involved [1,10]. It has been well established that the intensity of an electronically allowed transition is independent of temperature while the intensity of a vibrationally allowed transition is temperature dependent. For the former case the selection rule $\Delta n_i = 0$ gives transitions with the O—O band most prominent upon cooling. The total oscillator strength is temperature independent.

In the case of vibrationally allowed bands the vibrational selection rules are different. In the case where ground and excited potential surfaces are identical and harmonic $\Delta n = \pm 1$ and thus, for example, O—O bands (vibronic origin) are forbidden. The oscillator strength of vibronically induced transitions depends upon temperature according to [15,17]

$$f \simeq \coth h\nu_u'/2kT \tag{8}$$

where ν_u' is a non-totally symmetric vibration taking part in the transition

$$O + \nu_u \rightarrow O' + (n \pm 1)\nu_u'$$

The width of the band, which is a crude measure of the change in potential surfaces which occurs during transition, varies upon cooling in a similar fashion to the intensity (eqn. (8)). Equation (8) which has been derived under the assumption that harmonic vibrations are the same for both states gives reasonably good agreement with experiment. In general, when potential surfaces are not parallel, the calculation of vibrational structure is much more complex.

E. EXPERIMENTAL SURVEY

(i) d^0 Configuration

The optical absorption and MCD spectra of chromate, CrO_4^{2-}, ions have been thoroughly studied [22—36]; the low-temperature spectra appear to have a well structured band at 365 nm. MO calculations show that the transition occurs from a non-bonding t_1^6 to an antibonding $t_1^5\,e$ orbital. As a consequence, the size of the complex changes upon excitation and transition with totally symmetric frequencies $\nu_1(A_1)$ O—1, O—2, O—3, ... are permitted. This fine structure is spaced by 720—730 cm^{-1} [26], 750 cm^{-1} [36], 780—800 cm^{-1} [25,27,28,30,33,34] which is smaller than the ground state value of 847 cm^{-1} [27]. The vibronic spectra reveal that the effect of lowering the symmetry upon vibrational fine structure in different hosts is rather weak. The low symmetry appears as a small splitting of each band into three bands (reflecting a splitting of the $^3T_2$ excited state under the lower symmetry) and/or slight variation of the ν_1 frequency upon changing the matrices. However, the host lattice effect can be seen more prominently in the IR and Raman spectra [30]. Dependence of the resolution of the fine structure on alkali metal radius in alkali metal chromates has been observed by Johnson and McGlynn [26].

The reason for the difference in colour of Ag_2CrO_4 in comparison to other yellow chromates has been discussed by Jørgensen [38] and very recently by Robbins and Day [36]. The main conclusion of the latter workers is that the first intense band in Ag_2CrO_4 at ca. 22 000 cm^{-1} is $^1A_1\,(t_1^6\,e^0) \rightarrow {}^1T_2(t_1^5e^1)$, a charge transfer transition which is shifted to the red in comparison to other CrO_4^{2-} salts.

As the four oxygen atoms around each chromium atom form a distorted tetrahedron, considerable similarity between the spectra of chromates and dichromates has been observed. The electronic structure of the $Cr_2O_7^{2-}$ ion has been calculated by several authors [39,40].

Incorporation of the $Cr_2O_7^{2-}$ ion in the cubic potassium halide matrix [41] resolves the fine structure of the electronic $^1A_2 \rightarrow {}^1T_2(t_1^5e^1)$ transition with a spacing of 780 cm^{-1} corresponding to the $\nu_1(A_1)$ totally symmetric Cr—O stretching frequency. Further splitting of the spectral components has also been noted. This phenomenon has been explained by the contraction of the lattice and lowering of symmetry from T_d to C_{3v}. The optical spectra of aqueous dichromate salts and those dissolved in organic aprotic solvents appear to be different in nature [42]. While the spectrum of the $Cr_2O_7^{2-}$ ion in water exhibits only traces of vibrational structure, the organic solvent spectra show very prominent structure with the average distance between the vibrational components equalling 760 cm^{-1}. This value corresponds to the symmetric stretching vibration (ν_1) of the CrO_3 chromophoric group *. The role of aprotic solvents is restricted mainly to cation solvation and preservation of the electronic vibrational nature of the anion.

The spectra of the $Cr_2O_7^{2-}$ ion in aprotic solvents resemble those of the low-temperature crystal spectra, whereas the polar solvents such as H_2O or formamide seriously disturb the vibrational fine structure. Some interesting results have been obtained from reflectance spectra of the dichromate salts of alkali metals. As the ionic radius of the cation increases, the vibronic structure is better resolved. In the cesium salt the contribution of the ionic $Cs^+ \cdots O^-$ bond is higher than that in the sodium salt and therefore the energy levels of the $Cr_2O_7^{2-}$ are less influenced by the cation [42,43].

The structure of the monosubstituted chromate CrO_3L^- ions, where L is a univalent ligand (halogen, CN^-, etc) or a neutral molecule, has been the subject of several spectroscopic investigations [43—57] (Fig. 3). In general, the structures of the electronic bands agree well with those of the parent CrO_4^{2-} ion and it has been established from polarized absorption spectral data of CrO_3L^- (L = F, Cl, Br, IO_3) single crystals at liquid helium temperature, that replacement of one of the oxide ligands has almost no effect upon the tetrahedral t_1 orbital in CrO_4^{2-} [43,44]. The great similarity between these ions has also been observed by analyzing IR and Raman spectra, as well as by crystal structure analysis [53,54,58—63]. Assignment of the electronic bands has been confirmed by solution MCD spectra [44].

A remarkable feature of the spectra of the CrO_3L^- ions is the well-defined vibrational progression of ca. 750 cm^{-1} (Fig. 2, Table 1). This dominant progression has been identified as the $\nu_1(A_1)$ totally symmetric vibration and the substructure, which sometimes appears in the low temperature spectra, was found to be a result of the excitation of a single quantum of ν_3, the non-totally symmetric vibration.

High resolution spectra of pure single crystals of $KCrO_3Cl$ measured at 4 K show extremely weak and sharp lines on the red edge (500—540 nm) of the

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* The vibrational analysis of $Cr_2O_7^{2-}$ in organic aprotic solvent shows that the lengthening of the Cr—O bond upon excitation is 10.2 pm (0.102 Å) [37].

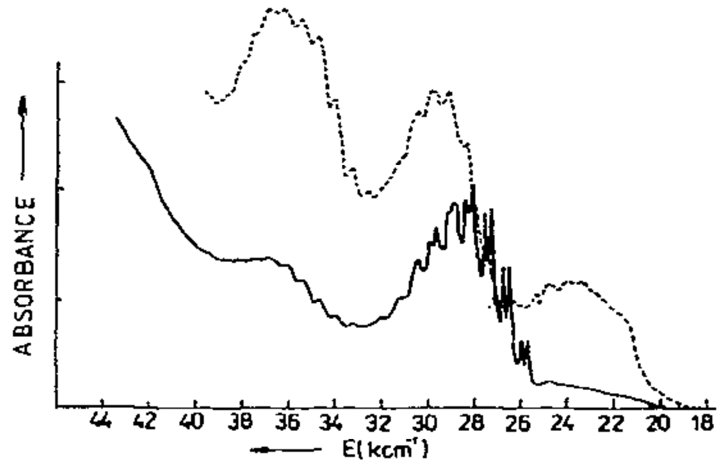


Fig. 2. Electronic absorption spectra of a CrO_3F^- doped crystal of $LiClO_4 \cdot 3\ H_2O$ at 5 K with the electric vector ∥ to the *c* axis, ——— and ⊥ to the *c* axis, - - - - - - [43].

lowest energy band [43]. The richness of the vibrational structure in this absorption region, as well as the polarization behavior, indicates the presence of at least two electronic states with the transitions showing a strong coupling to the lattice vibrations. It has been suggested that these features can be explained by assuming the presence of two spin triplet states together with singlet states. The sharp lines are built upon the spin singlets $^1E^a$, $^1A_2$ whereas the spin triplets may only contribute to the diffuse nature of the background.

Solvent effects upon the vibronic spectra have been studied using organic Lewis base salts obtained in organic solvent solution as well as on the alkali metal and alkylammonium salts previously isolated in the solid state [46,56, 57]. The absence of changes in the energy of the electronic transition (neglecting a bathochromic shift at lower temperature) confirms the conclusion previously derived from the solid state investigation, that substitution of the oxygen atom by the chlorine atom does not affect most long-wave transitions in the spectrum. However, the effect of hydrogen bond formation results in a specific interaction between the CrO_3L^- anion and a given solvent. This is manifested by the appearance of new bands, a shift in the main bands, change in absorption coefficients and disturbance or disappearance of the vibrational fine structure [46].

Influence of the ligand L upon CrO_3L^- ion spectra appear to be rather small, although observable. It has been established that a shift in the ν_{00} band depends primarily upon the ligand donor-acceptor properties as measured in σ_1, Taft's inductive substituent constants, obtained from NMR studies [56]. The change in the Franck—Condon shift of the band at ca. 27 000 cm^{-1} in CrO_3F^-, CrO_3Cl^- and CrO_3Br^- has been found to vary $Br^- \sim Cl^- < F^-$. This trend is probably due to the weakening of the excited state Cr—O bond in fluorochromates compared to other halochromates [56].

The vibrational intervals and resolution as well as position of the electronic

TABLE 1

Vibronic structure at 57 K in the $\perp_c$ and $\parallel_c$ electronic spectra of CrO_3F^- doped into $LiClO_4 \cdot 3\ H_2O$ crystals [43]

Polarized ⊥ to c		Polarized ∥ to c	
$\bar{\upsilon}$(cm^{-1})	Assignment	$\bar{\upsilon}$(cm^{-1})	Assignment
System I	${}^1E^a \leftarrow {}^1A_1$	System II	${}^1A_1 - {}^1A_1$
		(sh?) ~ 25 400	ν^d_{0-0}(?)
System II	${}^1E^b \leftarrow {}^1A_1$	25 660	$\nu^d_{0-0} + \nu^d_3$
~ 27 500	ν^b_{0-0}(?)	25 926	$\nu^d_{0-0} + 2\nu^d_3$
~ 28 300	$\nu^b_{0-0} + \nu^b_1$	26 205	$\nu^d_{0-0} + \nu^d_1$
29 090	$\nu^b_{0-0} + 2\nu^b_1$	26 469	$\nu^d_{0-0} + \nu^d_1 + \nu^d_3$
29 797	$\nu^b_{0-0} + 3\nu^b_1$	26 731	$\nu^d_{0-0} + \nu^d_1 + 2\nu^d_3$
30 404	$\nu^b_{0-0} + 4\nu^b_1$	27 012	$\nu^d_{0-0} + 2\nu^d_1$
(sh) ~ 31 250	$\nu^b_{0-0} + 5\nu^b_1$	27 270	$\nu^d_{0-0} + 2\nu^d_1 + \nu^d_3$
(sh) ~ 32 000	$\nu^b_{0-0} + 6\nu^b_1$	27 541	$\nu^d_{0-0} + 2\nu^d_1 + 2\nu^d_3$
System III	${}^1E^c \leftarrow {}^1A_1$	27 820	$\nu^d_{0-0} + 3\nu^d_1$
		28 082	$\nu^d_{0-0} + 3\nu^d_1 + \nu^d_3$
32 562	ν^c_{0-0}(?)	28 329	$\nu^d_{0-0} + 3\nu^d_1 + 2\nu^d_3$
33 267	$\nu^c_{0-0} + \nu^c_1$	(sh) ~ 28 650	$\nu^d_{0-0} + 4\nu^d_1$
33 980	$\nu^c_{0-0} + 2\nu^c_1$	28 881	$\nu^d_{0-0} + 4\nu^d_1 + \nu^d_3$
34 690	$\nu^c_{0-0} + 3\nu^c_1$	(sh) ~ 29 095	$\nu^d_{0-0} + 4\nu^d_1 + 2\nu^d_3$
35 450	$\nu^c_{0-0} + 4\nu^c_1$	(sh) ~ 29 455	$\nu^d_{0-0} + 5\nu^d_1$
36 190	$\nu^c_{0-0} + 5\nu^c_1$	29 665	$\nu^d_{0-0} + 5\nu^d_1 + \nu^d_3$
36 900	$\nu^c_{0-0} + 6\nu^c_1$	29 904	$\nu^d_{0-0} + 5\nu^d_1 + 2\nu^d_3$
37 900	$\nu^c_{0-0} + 7\nu^c_1$	(sh) ~ 30 193	$\nu^d_{0-0} + 6\nu^d_1$
(sh) ~ 38 200	$\nu^c_{0-0} + 8\nu^c_1$	30 423	$\nu^d_{0-0} + 6\nu^d_1 + \nu^d_3$
(sh) ~ 38 800	$\nu^c_{0-0} + 9\nu^c_1$	(sh) ~ 30 675	$\nu^d_{0-0} + 6\nu^d_1 + 2\nu^d_3$
Average values			
	$\nu^b_1 \simeq 750$ cm^{-1}	31 201	$\nu^d_{0-0} + 7\nu^d_1 + \nu^d_3$
	$\nu^c_1 \simeq 710$ cm^{-1}	(sh) ~ 31 495	$\nu^d_{0-0} + 7\nu^d_1 + 2\nu^d_3$
	$\nu^d_1 \simeq 805$ cm^{-1}	~ 31 980	$\nu^d_{0-0} + 8\nu^d_1 + \nu^d_3$
	$\nu^d_3 \simeq 265$ cm^{-1}	(sh) ~ 32 790	$\nu^d_{0-0} + 9\nu^d_1 + \nu^d_3$

bands $\bar{\upsilon}_1$, $\bar{\upsilon}_2$, $\bar{\upsilon}_3$, $\bar{\upsilon}_4$ depend upon the nature of the halogen atom introduced into the CrO_4^{2-} skeleton [45,48,55]. Linear correlation between $\Delta\nu$, the structure resolution parameter R_x, and energies of the CT bands on one hand and

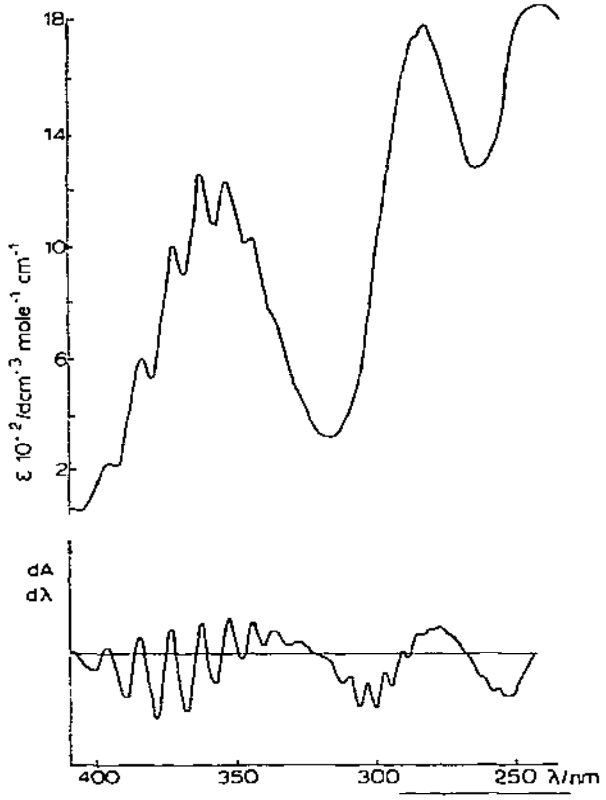


Fig. 3. Room temperature electronic spectra (and first derivative) of $KCrO_3Cl$ in acetonitrile [46].

Pauling's halogen atom electronegativity χ, on the other, have been observed. There is a linear relationship between χ and the effective nuclear charge Z_{eff}. The Z_{eff} of the halogen atom appears to be the most important parameter influencing the electronic and vibrational structures of halochromates.

The extraordinary nature of the CrO_2Cl_2 molecular spectrum leads to satisfactory interpretation not only of the nature of the electronic states, but also of the activities of the vibrations coupled therewith. Chromyl chloride is a pseudotetrahedral molecule [289] which possesses well resolved vibrational and rotational fine structure both in the vapor and the solid state. The structure of the gaseous absorption spectrum was first characterized by de Kronig et al. [64] and then by other authors [65,66]. Recently, fluorescence of gaseous and solid chromyl chloride has been observed by McDonald [67] and Dixon and Webster [68]. The reduction of symmetry $T_d \to C_{2v}$ produces excited states A_1, A_2, B_1 and B_2, equivalent to the $t_1 \to 2e$ or $t_2 \to 2e$ transitions in the parent T_d molecule. The absorption, excitation and fluorescence spectra are characterized by long progressions of the ν_4 mode assigned to $CrCl_2$ bending, which has a value 140 cm^{-1} in the ground electronic state [69] and 136 cm^{-1} in the excited state [64—68]. The vibrational structure of the fluorescence spectrum is particularly rich since all remaining totally symmetric vibrations ν_1'', ν_2'', ν_3'' are active in addition to ν_4''. However, Dixon and Webster [68] show no evidence for activity for any non-totally symmetric vibrations proposed by Dunn and co-workers [70,71].

The complex structure of the spectrum arises also from a superposition of the rotational structure of each band with vibrational structure of the ν_4 sequences. Very recently Blazy and Levy [96] were able to observe the detailed rotational structure in the fluorescence excitation spectrum of CrO_2Cl_2. The rotational constants were calculated to be: $A'' = 0.1073 \pm 0.0002$ cm^{-1}; $A' = 0.0910 \pm 0.0003$ cm^{-1}; $B'' = 0.0620 \pm 0.0004$ cm^{-1}; $B' = 0.0659 \pm 0.0003$ cm^{-1}; $C'' = 0.0521 \pm 0.0010$ cm^{-1}; $C' = 0.0524 \pm 0.0010$ cm^{-1}. Further complications in the spectrum of chromyl chloride are due to the relative distribution of chlorine isotopes: $CrO_2Cl^{35}Cl^{35}$, $CrO_2Cl^{35}Cl^{37}$, $CrO_2Cl^{37}Cl^{37}$ in the ratio 9 : 6 : 1. This reflects a broadening of the bands for the higher quanta observed. The change in charge density distribution is reflected in the vibrational structure which allows for identification of the proper electronic transition in each absorption region. For example, the similarity of vibrational structure in two different electronic states where the major excitation involves the ν_4 bending mode, is to be attributed to the influence of the nature of the $7a^*$ orbital [72]. A partial reassignment of the upper state vibrational structure has recently been proposed [73]. Analysis of the CrO_2Cl_2 emission spectra in rare gas matrices leads to the general conclusion that the geometry of the upper state of CrO_2Cl_2 differs substantially from the ground state.

Studies on solutions of CrO_2Cl_2 in various organic and inorganic solvents show that the CrO_2Cl_2 molecule possesses a strong oxidizing ability and is very sensitive to solvolysis [74,75]. The spectra of liquid CrO_2Cl_2 and its solution in $CHCl_3$ and CCl_4 do not exhibit any vibronic activity [70] although Bartecki [74] was able to find traces of structure. On the basis of the spectra of CrO_2Cl_2 dissolved in acetone, the suggestion has been made that CrO_2Cl_2 in these solvents forms a complex compound of the type $CrO_2Cl_2 \cdot S$, where S is the aprotic solvent [76].

The vibronic spectra of MoO_4^{2-} have been studied in potassium halide crystals at 300, 77 and 4.2 K [28]. The authors found that at 77 and 4 K the $^1A_1 \rightarrow {}^1T_2(t_1 \rightarrow 2e)$ band at 43500 cm^{-1} possesses a well resolved vibrational structure with a spacing of 840 cm^{-1}. This progression has been attributed to the $\nu_1(A_1)$ totally symmetric vibration which is reduced by 10% in comparison to the ground state value [22].

Although the electronic spectrum of the MnO_4^- ion has been extensively investigated both theoretically and experimentally [32,34,77—89] some details are still controversial. The spectrum appears to have five main absorption regions with energy depending upon the site symmetry of host crystals containing the MnO_4^- ions [90]. Two low-lying absorption regions, both being $\pi \rightarrow \pi^*$ transitions at 18 000—23 000 cm^{-1} and 24 500—30 000 cm^{-1}, with a pronounced vibrational structure have been assigned to $^1A_1 \rightarrow {}^1T_2(t_1 \rightarrow 2e)$ and $^1A_1 \rightarrow {}^1T_2(3t_2 \rightarrow 2e)$ transitions [32,83—86]. The former band possesses a very rich pattern of structure with the dominant progression in the totally symmetric breathing mode a_1 (770 cm^{-1}). There are also two different vibrations $\nu_2 = 334$ cm^{-1}, $\nu_3 = 272$ cm^{-1} as well as lattice vibrations; all are coupled in a very complex way [79]. Johnson and McGlynn [84] gave an alternative interpretation of the feature previously described as ν_2 and Jain et al. [88] questioned the appearance of ν_1, the symmetric stretching frequency, in this absorption region. The nature of the 230 nm band has also been the subject of considerable debate [79,84,88]. The assignments of the so called "Teltow band" in the 600—700 nm region to the $^1A_1(t_1{}^6) \rightarrow {}^1T_1(t_1{}^52e^1)$ transition has been confirmed by the application of uniaxial pressure to single crystals of $LiClO_4 \cdot 3\ H_2O$ and of $LiClO_4 \cdot 3\ H_2O/LiMnO_4 \cdot 3\ H_2O$ [87], as well as by an MCD study at 4.2 K [91]. An external pressure lowering the site group symmetry from T_d to C_s splits the $^1T_1$ state into $^1A' + 2A''$ oppositely polarized in the plane σ_h. This splitting in the mixed lithium salt appears to be less than 10 cm^{-1} in disagreement with the value cited by Johnson et al. (540 cm^{-1}) [86] but similar to that of Butowiez for potassium chromate (6 cm^{-1}) [92].

Whereas the optical absorption spectra of the tetrahedral MnO_4^- anion have been the subject of many investigations, studies on its halo derivatives are scarce. Very recently the electronic and MCD spectra of gaseous MnO_3Cl and MnO_3F have been carefully examined [93,94] and earlier, Aymonino et al. [95] studied IR and electronic spectra of MO_3X-type compounds. Generally, in MnO_3F and MnO_3Cl the absorption spectra appear to be very similar to the MnO_4^- spectra. The low lying band, $\bar{\nu}_1$, for these compounds falls in the following order [95]: $\bar{\nu}_1(MnO_4^-) > \bar{\nu}_1(MnO_3F) \approx \bar{\nu}_1(MnO_3Cl)$. In the visible and near IR absorption region MnO_3Cl possesses two main structured bands centred at ca. 550 nm and ca. 750 nm which originate in the trigonally split $^1A_1 \rightarrow {}^1T_2$ and $^1A_1 \rightarrow {}^1T_1$ transitions of the parent MnO_4^- band, respectively [94]. The dominant feature appears to be the ν_1 Mn—O(a_1) totally symmetric vibration with 786 and 760 cm^{-1} quanta in two different electronic origins at 18860 and 18940 cm^{-1}, respectively together with the ν_2 Mn—X (e) with a sequence of 230 cm^{-1} superimposed thereon. The ν_3 O—Mn—O bending mode has also been observed [93]. The trigonal splitting $\Delta E = E(E_1) - E(A_1)$ is 80 cm^{-1}. The assignment of the O—O electronic band has been provided by MCD. As previously observed with the CrO_3X complexes, reduction in the symmetry only weakly perturbs the $^1T_2$ parent state. The complex MCD spectrum has been explained as an interaction of the degenerate ^1E state with an intramolecular vibration mode (J—T coupling).

The lowest energy region (750 nm) concerned with the $^1A_1 \rightarrow {}^1E$ transition is very structured. The shape of the vibronic bands shows evidence for the presence of rotational fine structure in the spectrum. Such structure has also been observed in the MCD spectrum which appears to be the first example of the identification of this feature in the MCD spectrum of a gaseous molecule.

Vibronic spectra of pertechnetates and perrhenates have been studied recently [81,92]. The low temperature polarized absorption spectra show two band systems with a pronounced regular progression in ν_1, the totally symmetric vibration. The ${}^1A_1 \rightarrow {}^1T_1$ "Teltow band" (see permanganate ion) has not been found. This has been explained as a consequence of an increase in the energy separation between the oxygen ligand orbitals and metal *nd* orbitals in the sequence MnO_4^-, TcO_4^-, ReO_4^-. An indication of the presence of a spin forbidden $S = O \rightarrow 1$ transition on the red side of the ${}^1A_1 \rightarrow {}^1T_2$ band has also been made. The electronic vapor phase spectra of ReO_3Cl and TcO_3Cl molecules have been studied recently by Guest et al. [98]. The spectra exhibit vibrational structure with an irregular spacing of 800—900 cm^{-1}. The authors interpreted the spectra in terms of a dynamic Jahn—Teller effect operating in the systems.

The electronic spectra of osmium and ruthenium tetroxides have been measured by Wells et al. [102]. The structure which appeared in the spectra was found to be irregular and the resolution sensitive to temperature.

The vibronic spectra of the nitridoosmate(VIII) ion, OsO_3N^-, have been measured in solution as thin films and doped crystals at 5 K [99,100]. The polarized crystal spectra show four absorption regions composed of superimposed ${}^1A_1 \rightarrow {}^1A_1$ and ${}^1A_1 \rightarrow {}^1E$ transitions in C_{3v} symmetry which are comparable to the ${}^1A_1 \rightarrow {}^1T_2$ transitions in the parent OsO_4 molecule [101,102]. The second and the fourth systems of OsO_3N^- correlate well with the ${}^1A_1 \rightarrow {}^1T_2$ bands of the OsO_4 molecule whereas, according to the data of Miskowski et al

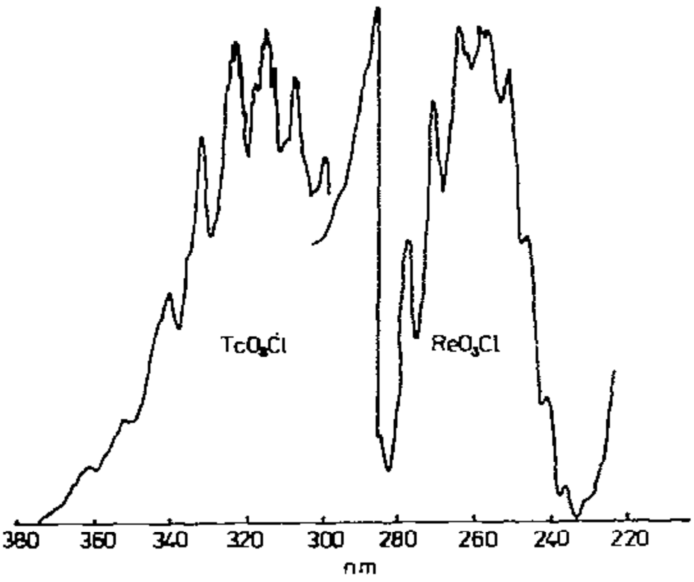


Fig. 4. The low resolution vapour phase spectra of ReO_3Cl and TcO_3Cl [98].

[100], the first and the third systems are triplet—singlet components of these transitions. No evidence for states derived from the T_1 parent state has been observed. All bands show distinct vibrational progressions in a frequency of 820—900 cm^{-1}. This represents a totally symmetric ν_2(Os—N) vibration reduced by 10—17% in frequency in comparison to the ground state value [103]. Besides the dominant ν_2 mode a subprogresssion in a frequency of 230 cm^{-1} has been found. This frequency has been identified as the ν_3 δ(O—Os—O) and ν_4(O—Os—N) modes. A characteristic feature of the spectra is the lack of the ν_1, totally symmetric Os—O stretching vibration. The absence of the ν_1 progression indicates that Os—O bonding is little affected by the electronic transition. The nitrido ligand appears to dominate the π bonding in the ion.

(ii) d^1 Configuration

There is only one paper devoted to information on vibronic structures of the vanadyl d^1 ion [104]. This phenomenon has been observed for single crystals of vanadyl acetylacetonate at 70 K. The sharp structure which appears in the visible region (ca. 14 000 cm^{-1} and 25 000 cm^{-1}) has been ascribed to the ν_1 totally symmetric vibrational mode of ca. 700 cm^{-1}.

There are a few systematic studies of the vibronic spectra of the chromate-(V) anion [105—108]. Simo et al. [108] investigated the low temperature polarized absorption spectrum of CrO_4^{3-} doped in single crystals of Ca_2PO_4Cl. Of the four absorption systems, those at 28 000 and 11 000 cm^{-1} appear to have strongly polarized sharp lines associated with electronic-vibrational excitations. The bands have been assigned on the basis of D_{2d} symmetry [107,108]. In the lowest energy near IR band (ca. 10 000 cm^{-1}), the vibrational origins have been found at 9912 and 10 204 cm^{-1}, ⊥ and ∥ to the z molecular axis, respectively. The progression spacings are ca. 450 cm^{-1} ($\parallel z$) and 406 cm^{-1} ($\perp z$). The former has been interpreted to result from a combination of the $T_2(\nu_4)$ mode (410 cm^{-1} in the ground state) and a lattice vibration, whereas the latter is the pure $\nu_4(T_2)$ vibration. A small reduction of frequency shows that in the excited state the Franck—Condon parabola does not expand significantly.

The vibrational structure of the visible absorption band (28 000 cm^{-1}) comprises two progressions in ca. 760 cm^{-1} and ca. 760—806 cm^{-1} parallel and perpendicular to z respectively [109,110]. Analysis of the spectrum shows that the lines correspond to excitation in the $T_2(\nu_3)$ fundamental vibration, though in our opinion the $\nu_1(T_2)$ stretching vibration, usually observed in vibronic spectra, is more probable.

At liquid helium temperature the polarized single crystal electronic spectrum of $[(C_6H_5)_4As]CrOCl_4$ shows two low-lying structured bands at 13 000 and 18 000 cm^{-1} [111]. The lower one, considered to be the $^2B_2 \rightarrow {}^2E$ d—d transition, appears to possess two electronic origins at 12 900 and 13 500 cm^{-1} and $(E_1 + \nu)$ and $(E_2 + 2\nu)$ coupled vibronic transitions where ν is the totally symmetric Cr—O stretching mode. The absorption band at ca. 18 000 cm^{-1} which has been assigned to the $9e \rightarrow 16a_1$, Cr—O (π) → Cr—O(σ^*), electronic transition, possesses vibronic structure similar to the B_1 Cr—Cl stretching mode of ca. 300 cm^{-1}.

The spectrum of the $MoCl_6^-$ ion incorporated into cubic crystals of Cs_2ZrCl_6 shows one single *d*—*d* band $^2T_{2g} \rightarrow {}^2E_g$ at 24 100 cm^{-1}, richly structured at 4 K [127]. Above 136 K the vibrational fine structure disappears. Three progressions are observed in the spectrum: $\nu_7 + n\nu_1$, $\nu_4 + n\nu_1$ and $5\nu_7 + n\nu_1$, where $\nu_1(a_{1g})$, $\nu_4(t_{1u})$ and $\nu_7(t_{1u})$ are normal modes of vibration for the $MoCl_6^-$ ion. From the spectrum the energies of vibration of the $\Gamma_8(^2E_g)$ excited state have been determined. The MCD spectra, however, show that the assignment of this 24 000 cm^{-1} band to a *d*—*d* transition is incorrect [128].

The vibronic spectra of the MnO_2Cl_2 molecule have been interpreted via correlation with the parent MnO_4^{2-} ion [112—118] and CrO_2Cl_2 molecule [66]. Since there are no data concerning the ground state frequencies of MnO_2Cl_2, vibrational assignments of the bands have been made using frequencies for the CrO_2Cl_2 molecule [69,119,120]. As the vibronic pattern is rather complicated further study of this system should be continued. The bands show progressions in the totally symmetric ν_1 mode spaced at ca. 912 and 755 cm^{-1}, ν_2 mode ca. 464 cm^{-1} and ν_3 362 cm^{-1} as well as "hot band" fine structure separated by 20—60 cm^{-1}. The variations in the magnitude of ν_2 are interpreted with respect to the possible existence of interactive states from newly overlapping excitations.

Spectroscopic studies of the technetate and rhenate ions are described in only one paper [121]. In contrast to the MnO_4^{2-} ion [112,122], the splitting of the bands as well as the vibrational fine structure of the *d*—*d* transition indicate strong Jahn—Teller distortion in the first excited $^2T_2$ state. The dominant feature of the 15 000 cm^{-1} ligand field band is the progression in 330 cm^{-1} quanta. The authors assign this to the $\nu_2(E)$ normal mode of vibration in the TcO_4^{2-} tetrahedron. This represents the only evidence for this vibration since thermal instability of these compounds does not allow any Raman measurements.

The ReF_6 molecule is octahedral in the gas phase but tetragonally distorted in the crystal. The 5000 cm^{-1} absorption region, theoretically assigned to a *d*—*d* crystal field transition, has been thoroughly investigated by several authors [123—125]. Because of a large spin—orbit coupling constant (ζ = 3050 cm^{-1}) as well as reduction of the symmetry in the solid state, interpretation of the spectrum is interesting. The vapour and high resolution crystal measurements at 1.5 K show some characteristic features of the vibronic band system which allow one to conclude that the origin of the band is a magnetic dipole transition. On the other hand, strong single quanta of ν_4 and ν_6 bending vibrations introduce a relatively strong electric dipole component due to vibronic coupling with higher electronic states of odd parity. While comparing the site splitting of ν_6'' with ν_6' vibrations, it has been observed that the ground state potential is more distorted than the excited state. The latter is quite harmonic, especially in the pure crystal, and is assigned to vibronic coupling and two-particle transitions [125]. Regular progressions of ca. 300 cm^{-1} attributed to ν_5 or to a component of ν_5 in the lower D_{4h} symmetry of the solid state have been found. These progressions appear to be evidence of Jahn—Teller distortion in the electronic ground state suggested earlier in several papers [124]. The quantitative parameters, distortion and unperturbed vibrational frequency, indicate a "mild" coupling effect. The intensity distribution in the ν_1, 715 cm^{-1}, totally symmetric progression indicates a minimal Franck—Condon shift. Two-particle transitions are responsible for the great part of the total vibronic intensity in the host—guest crystals.

(iii) d^2 Configuration

The absorption spectrum of the V(III) ion in the corundum lattice has been studied by McClure [126]. The sharp structure observed at 77 K has been attributed to vibrational intervals characteristic of the corundum lattice. The distortion from C_3 symmetry in the excited state appears to be quite large as the Franck—Condon maximum occurs in the 8th or 9th member of the progression; this provides an order of magnitude of displacement of 0.3—0.4 Å. The temperature effect shows that at low temperature the vibronic contribution to the band strength is rather small but increases at higher temperatures.

The spectrum of the $MoCl_6^{2-}$ ion incorporated into a Cs_2ZrCl_6 host crystal has recently been recorded by Collingwood et al. [128]. The temperature dependence of the MCD spectrum infers the presence of a weakly allowed electronic transition lying under the vibronic fine structure. This structure is consistent with a small Jahn—Teller effect involving both the $\nu_2(e_g)$ and $\nu_5(t_{2g})$ vibrational modes [128].

The absorption and emission spectra of MnO_4^{3-} have been carefully examined in solution, at room and liquid helium temperatures, as well as in different host lattices by many authors [129—133]. Ligand field calculations, polarization measurements as well as vibrational fine structure of the spectra permitted assignment of the observed bands to ligand field, 8000—24 000 cm^{-1}, and charge transfer, >24 000 cm^{-1}, transitions [133]. The similarity in spectra between the solution and the solid state indicates the presence of the MnO_4^{3-} ion in the system [130]. Doped in Li_3PO_4, MnO_4^{3-} possesses a regular tetrahedral configuration [131] whereas its symmetry is lowered to D_{2d} in spodiosite, $Ca_2(PO_4)Cl$, crystals [130,131,133]. The presence of ν_1, 750 cm^{-1}, totally symmetric ν_4-bending as well as several lattice, PO_4^{3-}, modes in the visible and near IR regions of the spectra has been found. The sharp structured emission spectra indicate the absence of a Stokes shift. From analysis of the vibrational structure the bond bending force constants are reduced by 28% in the MnO_4^{3-} ion.

Series of tetrahalonitrido complexes of osmium(VI), $OsNX_4^-$, as well as $OsNX_4(OH)_2^-$ have been investigated by Cowman et al. [134]. The electronic spectra at low temperature are rich with several progressions of ca. 800 cm^{-1}, a_1(Os=N), and 390 cm^{-1} a_1(Os—Cl) spacing. Using the Poisson formula the authors estimated the Os=N bond lengthening to be approximately 0.09 Å and 0.17 Å in the ^3E and $^3B_2$ excited states, respectively.

(iv) d^3 Configuration

One of the most extensively studied ions with a d^3 configuration is Cr(III). It is examined in various host lattices of different symmetries and in rigid solutions [135—211]. The importance of Cr(III) in the development of lasers accounts for such wide interest.

The octahedral $t_{2g}{}^3$ strong configuration of Cr^{3+} (d^3) gives rise to one quartet and three doublet states. The transitions between ground $^4A_{2g}$ and excited ^2E_g, $^2T_{1g}$ and $^2T_{2g}$ states show considerable vibronic structure. In very rare cases the chromium(III) ion is surrounded by a perfect octahedron of ligand ions as for example in K_2NaGaF_6, and MgO host lattices [135—138]. However, in the latter case the Zeeman effect and magnetically induced circular emission (MCE) show a small orthorhombic perturbation [139]. Intensity calculations of the well structured $^4A_{2g} \to {}^4T_{2g}$ band indicate that only about 1/3 of the total intensity may be ascribed to a magnetic dipole transition and the rest to the electric dipole mechanism involving a non totally symmetric vibration [136]. The spectrum of Cr(III) in a cubic MgO lattice exhibits a single sharp line in the fluorescence spectrum at 14319 cm^{-1}. The temperature dependence of the width and position of the lines has been discussed based on the results obtained from emission, MCE and chronospectroscopic techniques [135,139]. The chronospectroscopic results show that the distinct lines which appear in the fluorescence spectra are the origins of the $^4T_{2g}$ rhombic emission. The emission from the cubic as well as tetragonal sites has also been reported by other authors [140—142]. The $^4A_{2g} \to {}^4T_{2g}$ transition in $Cr(NH_3)_6{}^{3+}$ and $Cr(H_2O)_6{}^{3+}$ ions is in most cases not resolved but the vibrational fine structure of the $^4A_{2g} \to {}^2E_g$ transition is seen well both in absorption and in emission [137—149]. The source of intensity of the ground state to excited state transitions has been thoroughly discussed by Flint and co-worker [145, 148]. The observed relatively high intensity of the t_{2u} and t_{1u} NH_3 and OH_2 rocking vibrational modes observed in the electronic spectra has been explained by the motion of the electron density in the lone pair orbital during these vibrations [148]. Vibronic band shape calculations of the $^2E_g \to {}^4A_{2g}$ phosphorescence in $3d^3$ compounds has been provided by Kupka [150] using Cr(III) octahedral complexes as an example. By considering the $K(H_2O)_6$ (Al/Cr)$(H_2O)_6(SO_4)_2$ diluted crystal it has been found that the $Cr(H_2O)_6{}^{3+}$ may be treated as an isolated ion with approximately O_h environment [143]. From the absorption and MCD spectra it follows that the intensity of the $^4A_{2g} \to {}^4T_{2g}$ and $^4A_{2g} \to a^4T_{1g}$ transitions in the $Cr(H_2O)_6{}^{3+}$ ion, similar to the previously studied $Ni(H_2O)_6{}^{2+}$ [151] and $Co(H_2O)_6{}^{2+}$ ions [152,153], are derived from a vibrational mode of t_{1u} symmetry. The values of the mean active vibrational frequency and the dipole strength at different temperatures of these transitions have been calculated using the hyperbolic cotangent formulae given by Ballhausen [10]. Recently Schwartz [138] has reported the absorption and MCD spectra of Cr^{3+}: Cs_2NaYCl_6 in a wide temperature range. The difficulties in assigning the $^4A_{2g} \to {}^2T_{2g}$ transition have been discussed. The effect of a large variation in ζ, i.e. the spin-orbit coupling constant obtained from the particular term has been ascribed to varying degrees of covalency of each term.

The vibrational fine structure of the $Cr(CN)_6^{3-}$ ion has been the subject of several spectroscopic investigations [1,154—161]. Flint and Palacio [154] studied the electronic spectra of this ion in various lattices to obtain a criterion of differentiation of internal and lattice vibrations. Porter and Schläfer were the first to report the luminescence spectrum of the $Cr(NCS)_6^{3-}$ ion [162]. The luminescence and the absorption spectrum has also been measured by other authors [163,164,212].

The first excited state ^2E, studied extensively in the case of ruby [165—167], is split by the action of spin—orbit coupling and the trigonal field. The emission, absorption and luminescence excitations of the nearest-neighbour Cr^{3+} pairs in spinel $MgAl_2O_4$ have been studied very recently [168,169]. The 686 nm line which is found to be independent of the chromium concentration has been assigned to chromium pairs [169]. The luminescence excitation experiments give a distinction between pair and single ion lines. Pair spectra of Cr^{3+}, V^{2+} and Mn^{2+} have also been studied by other authors [170—174]. The vibronic spectra of low symmetry chromium(III) spin forbidden transitions have recently been used to prove the importance of covalency in the interelectronic repulsion parameters [176] criticised by Ferguson and Wood [177,178]. The R lines of emerald $Be_3Al_2(SiO_3)_6$ are of interest because of their sharpness [178]. The width of the lines, 1.5 cm^{-1}, allows one to determine the ground state splitting as 1.78 ± 0.06 cm^{-1}.

Some details of the $^2E \rightarrow {}^4A_2$ luminescence and $^4A_2 \rightarrow {}^2E$, $^2T_1$ absorption spectra of the $Cr(en)_3^{3+}$ ion as well as M—N stretching vibrations of ethylenediamine complexes have been reported by Flint and Matthews [180]. Low temperature single crystal spectra of $Cr(en)_3^{3+}$ in 2 $Cr(en)_3Cl_3 \cdot 6\ H_2O$ and $Cr(en)_3Cl_3 \cdot 3.5\ H_2O$ have been measured by McCarthy and Vala [179] and Flint and Matthews [180]. The interference effect between spin-forbidden and spin-allowed bands has been observed in the spectra. According to these authors [179], the satellite bands, found around the doublet at 14 883 cm^{-1}, R_1, and 14 902 cm^{-1}, R_2, are due to several different sites in the crystal arising from different hydrogen bond stabilized-spatial conformations of three ethylenediamine ligands. They also observed one phonon relaxation process. A decrease in the intensity in the emission of the R_1, R_2 lines upon cooling has been interpreted as a result of a vibronic intensity gaining mechanism in which a single ground electronic state phonon couples with one of the excited quartet levels [179]. Studies on the vibronic spectra of $Cr(en)_3^{3+}$ complexes suggest also that the vibration of 280—320 cm^{-1}, assigned from vibrational spectra to the N—M—N bending mode, has at least as much M—N stretching character as that of the 450—600 cm^{-1} band which is ascribed to the totally symmetric M—N stretching mode [180].

There are some papers dealing with the tetragonal CrN_5X^{n+} type complexes (N = nitrogen ligand, X = halogen ion, OH^-, H_2O) [181—186]. In the $Cr(NH_3)_5OH^{2+}$ ion a large splitting of the second spin-allowed band is observed in the solution and diffuse reflectance spectrum [186]. The tetragonal splitting of the ^2E_g state in $Cr(NH_3)_5H_2O^{3+}$ is equal to 20 ± 10 cm^{-1} which is inconsistent with the value reported by Flint and Matthews [185]. The electronic structure of the basic rhodo and acidic dinuclear cations $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ and $[(NH_3)_5CrOHCr(NH_3)_5]^{5+}$, respectively, have been the subject of several investigations [187,190,192,196]. Low temperature polarized spectra of the former show that the near UV 36 200 cm^{-1} absorption band is characteristic of the CrOCr grouping, and that the transition takes place through a symmetric double excitation allowed through 870 cm^{-1} quanta, a vibrational exchange-induced electric dipole mechanism [195]. The polarized electronic spectrum of the $[(NH_3)_5CrOHCr(NH_3)_5]^{5+}$ ion has been studied very recently by Engel and Güdel [196] with respect to the intensity gaining mechanisms in pair excitations. Some of the most prominent bands in the Cr(III) pair spectra of Al_2O_3 [197], $LaAlO_3$ [172] and $ZnGa_2O_4$ [198] have been found to be due to an exchange-induced electric dipole mechanism. The tetragonal complexes *trans*-$[Cr(en)_2F_2]X$ as well as $Cr(IDA)_2^-$, $Cr(MIDA)_2^-$ and $Cr(PDC)_2^-$ where IDA = iminodiacetate, MIDA = methyliminoacetate and PDC = pyridine-2,6-dicarboxylate, have been studied by Hoggard and Schmidtke [199—201] and Flint and Matthews [202]. The vibronic analyses indicate the presence of origins involving the skeletal vibrations of the CrO_4N_2 chromophore in the spectra.

Among those Mn(IV) compounds whose spectra show the presence of fine structure, the most extensively studied has been the MnF_6^{2-} ion. A large number of vibronic components have been observed in absorption, emission, magnetic circularly polarized emission and magnetic circular dichroism spectra of the MnF_6^{2-} and Mn^{4+} ions in pure and diluted crystals [213—220]. Comparison of MnF_6^{2-} spectra in various environments with those of the Cr^{3+} ion shows that in the former case an "isolated" hexafluoro ion possessing a site symmetry dependent upon the host lattice is present [213,217,220]. Interpretation of the vibrational structure has been completed by considering vibronic coupling, spin-orbit interaction and the Jahn—Teller effect. Special attention has been paid to the intense $^2E_g \rightleftharpoons {}^4A_{2g}$ magnetic dipole allowed transition. The intensity has been studied using several techniques. The major source of intensity of the $\nu_2(E)$ progression observed in the spectra appears to be the Jahn—Teller effect induced in the $^4T_{1g}$ state. Resonance between ν_3 of the MnF_6^{2-} ion and ν_3 of the $CsGeF_6$ host crystals has been recorded for the first time [220].

The $^4A_{2g} \rightleftharpoons {}^2E_g$ transition in the spectra of trigonally distorted MnF_6^{2-} octahedra in Cs_2TiF_6 single crystals has been reported recently by Manson et al. [221]. The trigonal field appears to act on octahedral vibrations, the electronic states involving $^4A_{2g}$ and ^4E_g being almost undisturbed.

It is of interest that the spectrum of $MnCl_6^{2-}$ in a K_2SnCl_6 lattice appears not to be structured. The optical features are due rather to Mn(III), as the Mn(IV) in this host is thermally unstable and is reduced to Mn(II) via Mn(III).

Several papers appeared recently in which attempts were made to interpret the spectra of rhenium(IV) incorporated into single crystals of different hosts

[222—230]. The first observation of resolved sharp lines was made by Dorain and Wheeler [222] who proposed an energy level diagram. Interest has been concentrated upon transitions within the $t_{2g}{}^3$ configuration. Reinvestigation of the low energy optical spectra as well as of MCD measurements led to a correct assignment of the d—d transitions [226]. The lack of Franck—Condon progressions within the d—d transition energy range has been explained as being due to an unchanged radial wavefunction at the transition from the ground to excited states [225]. The calculated densities of states based on the O'Leary and Wheeler model [231] are in good accord with the optical spectra of the Re^{4+} ion in K_2PtCl_6 single crystals [225].

The first low temperature studies of optical spectra of single crystal Cs_2ReF_6 as well as the $ReF_6{}^{2-}$ ion doped in a cubic Cs_2GeF_6 lattice have recently been reported by Lo Menzo et al. [229]. For $t_{2g}{}^n \rightarrow t_{2g}{}^n$ type transitions, $\Gamma_8({}^4A_{2g}) \rightarrow \Gamma_7({}^2T_{2g}), \Gamma_8({}^2T_{2g})$, the magnetic dipole and vibronically induced electric dipole mechanisms have been proposed.

Luminescence as well as magnetic circularly polarized emission spectra are also reported for Re^{4+} doped into the cubic hosts Cs_2ZrBr_6 [224,227], Cs_2ZrCl_6 and Cs_2HfCl_6 [223,228] and A_2SnCl_6, A = K, Rb, Cs [227,230]. Comparison of the vibrational energies in the ground ${}^4A_{2g}$ and excited ${}^2T_{2g}$ levels shows very small differences [230]. On the other hand MCD and MCPE spectra gave a pattern implying different phonon coupling in both electronic states [228]. From studies of concentration dependence as well as excitation spectra and theoretical considerations, it was possible to attribute an interesting feature of the lowest energy transition at 740—770 nm to rhenium dimer formation, e.g. $Re_2Cl_9{}^{1-}$, $Re_2Cl_9{}^{2-}$ which, in consequence, may perturb the lattice structure [228].

The vibronic spectra of IrF_6 ($5d^3$) have been measured in the vapour phase as well as at liquid helium temperatures [232]. It has been found that an electric dipole component introduced via vibronic coupling with odd parity electronic states is responsible for the intensity observed.

(v) d^4 Configuration

The electronic spectrum of the $Mo_2Cl_8{}^{4-}$ ion has been measured and interpreted by several authors [234—236]. The structured system at 19 000 cm^{-1} with electronic origin at 17 897 cm^{-1} has been ascribed to a δ—δ^* one-electron transition. The resonance Raman spectrum of $Cs_4(Mo_2Cl_8)$ has been studied by Clark and Franks [234]. The authors found that upon excitation within the contour of the δ—δ^* 514.5 nm band the resonance Raman effect has been observed. The difference in spectral behaviour between $Mo_2Cl_8{}^{4-}$, $Mo_2(SO_4)_4 \cdot 2\ H_2O$ and $Mo_2(O_2CR)_4$ where R = H, CH_3, CD_3 and CF_3 [237—241] was found to be related to the different bond distances of these complexes [242]. The band system in the visible range of the spectra displays the 350 cm^{-1} vibrational spacing attributed to the ν_1(Mo—Mo) a_{1g} mode. This dominant progression was observed on each of several vibronic origins in the spectrum of $Mo_2(O_2CCH_3)_4$ [241]. The intensity I_n of the *n*th member of the a_{1g} vibrational progression is used to determine the Franck—Condon *S* factor. Displacement of the excited state geometry, Q_0^{MoMo} was found to be equal to 0.1 Å. The photoreactivity of the $Mo_2(SO_4)_4^{4-}$ ion in aqueous sulfuric acid has been reported by Erwin et al. [243]. The reaction product $Mo_2(SO_4)_2^{3-}$ exhibits a previously unknown near IR band at 1405 cm^{-1} which is structured even in the room temperature spectra.

Although the spectra of Mn(III) compounds have been the subject of several papers there is only one report dealing with its vibronic structure [244]. Detailed study of the spectra of Mn^{4+} in a K_2SnCl_6 crystal showed that the structured 24 000—27 000 cm^{-1} band is characteristic of the manganese(III) ion.

The spectra of octahalodirhenate(III) anions of the type $Re_2X_8^{2-}$ have attracted much interest since this binuclear complex with a strong metal—metal bond possesses well resolved vibrational fine structure in the electronic and resonance Raman spectra [233,245—250,351] (Fig. 5, Table II). Three prominent bands at 14 180, 30 870 and 39 215 cm^{-1} have been observed in the polarized absorption spectrum of the $Re_2Cl_8^{2-}$ ion. Similar to related systems, e.g. $Mo_2Cl_8^{4-}$, and contrary to Cotton's assignments [251], the δ—δ^* transitions have been assigned to the low energy region [235,245]. Detailed analysis of the ca. 680 nm electronic band shows that two progressions due to $a_{1g}(\nu_2)$ Re—Re stretching and $a_{1g}(\nu_3)$ Re—Re—Cl bending are present in the spectra. The polarized crystal spectral measurements of $Re_2Cl_6[P(C_2H_5)_3]_2$ have been provided by Cotton et al. [252,253].

A characteristic feature of Ru^{4+}, Os^{4+} and Ir^{4+} ions is the resemblance of the electronic spectra of their MX_6^{2-} complexes. A low temperature single

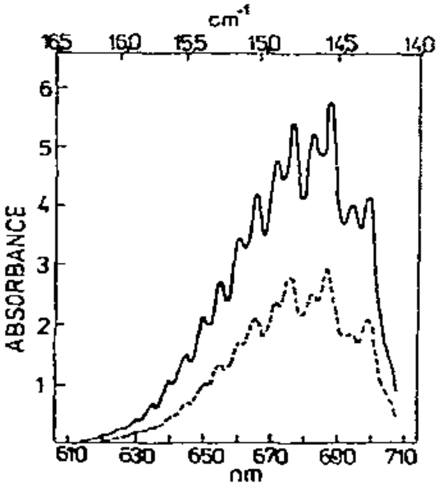


Fig. 5. Parallel ——— and perpendicular - - - - - polarized absorption spectra of $Re_2Cl_8^{2-}$ ion [233].

TABLE 2

Vibrational structure of the 14 183 cm^{-1} band in $Re_2Cl_8^{2-}$ at 5 K [233].

nm	cm^{-1}	$\Delta\bar{\nu}$(a) (cm^{-1})	$\Delta\bar{\nu}$(b) (cm^{-1})	Assignment
705.06(10)	14.183(2)	0	0	Origin
699.41	14.298		115	$a_{1g}(\nu_3)$
694.12	14.407	224		$a_{1g}(\nu_2)$
687.65	14.542		245	$\nu_3 + \nu_2$
682.41	14.654	247		$2\nu_2$
676.24	14.788		245	$\nu_3 + 2\nu_3$
671.00	14.903	249		$3\nu_2$
665.06	15.036		249	$\nu_3 + 3\nu_2$
660.00	15.152	248		$4\nu_2$
654.35	15.282		246	$\nu_3 + 4\nu_2$
649.29	15.401	250		$5\nu_2$
644.12	15.525		243	$\nu_3 + 5\nu_2$
639.00	15.649	248		$6\nu_2$
634.29	15.766		240	$\nu_3 + 6\nu_2$

crystal study of the ruthenium(IV) ion doped into K_2PtCl_6 and Cs_2ZnCl_6 has been carried out by Patterson and Dorain [254] and in Cs_2ZrCl_6 and Cs_2SnBr_6 by Collingwood et al. [255]. The latter paper also contains a very detailed interpretation of a magnetic circular dichroism study of this ion. The MCD spectrum reveals the charge-transfer character of the transition in the absorption region greater than 16 000 cm^{-1}. Comparison of the vibrational fine structure of Ru(IV) with that found for Os(IV) shows less resolution of the former [254]; however the $RuCl_6^{2-}$ spectra are not resolved as well as those of $RuBr_6^{2-}$ [255]. The detailed analysis of the RuX_6^{2-} spectra allows for partial reinterpretation of the OsX_6^{2-} spectra. The high resolution absorption and MCD spectra of the RuX_6^{2-} ions have been interpreted in terms of electron transfer from $t_{1g}(\pi)$, $t_{1u}(\pi + \sigma)$ and $t_{2u}(\pi)$ ligand orbitals to the $t_{2g}(4d)$ metal orbitals. An intensity mechanism has been suggested for the E_g and T_{1g} excited states via borrowing of t_{1u} vibrations (ν_3, ν_4 and ν_7) and for T_{2g} via ν_6 vibration.

Dorain et al. were the first to study the "cold" spectra of the osmium(IV) ion [256]. However, their assignment of the visible and UV spectral ranges has been criticized by several authors [257—260]. Upon reinvestigation of all features of the ca. 16 000 cm^{-1} spectral region, the conclusion has been drawn that this should be interpreted as a ligand to metal charge-transfer transition, in contradiction to the earlier interpretation. High resolution low temperature optical and MCD spectra of the $Os^{4+}(5d^4)$ ion have been reported for single crystal [112,191,256—261] as well as for KBr pellets [262]. The results of a phonon density calculation of a K_2PtCl_6 single crystal doped with Os^{4+} ion showed that all lattice vibrations must be used in a detailed assignment of the spectra [225].

The spectra of hexahaloosmates(IV) OsX_6^{2-} at liquid helium temperature were characterized by a series of very narrow absorption bands and a close correspondence between chloro, bromo and iodo complexes and hexahaloiridates was found. The resemblance of the osmate $5d^4$ and iridate $5d^5$ spectra ruled out a ligand field interpretation of the ca. 16 000 cm^{-1} absorption.

The absorption and MCD spectra of *trans*-mixed $OsCl_4Br_2^{2-}$, $OsBr_4Cl_2^{2-}$, $OsBr_4I_2^{2-}$, $OsI_4Cl_2^{2-}$ and $IrCl_4Br_2^{2-}$ ions have been measured by Piepho et al. [262]. The presence of a vibrational mode $\nu_1(a_{1g})$ with the energy ca. 300 cm^{-1}, characteristic of a pure totally symmetric vibration of the $OsCl_6^{2-}$ ion (ground state 343 cm^{-1}) has been given as evidence of some mixing of the t_{1u} and t_{2u} orbitals via tetragonal distortion.

Sharp line luminescence and absorption spectra of the $OsBr_6^{2-}$ ion in the visible and near IR region have been observed by Nims et al. [261]. Detailed vibrational analysis shows the presence of the $\nu_2(e_g)$ mode which may be evidence of a weak dynamic Jahn—Teller coupling in the $\Gamma_4(^3T_{1g})$ electronic state.

(vi) d^5 Configuration

A general theoretical treatment of the $3d^5$ configuration has been completed recently by Vala et al. [263]. In the manganese(II) ion low intensity *d—d* transitions are difficult to study because the features corresponding to the single ion are often obscured by exchange interactions between neighbour ions [264—266]. Ferguson et al. [264] observed single ion transitions in the cubic hosts $KMgF_3$ and $KZnF_3$ and found many and various vibrations of both *g* and *u* origins. Schwartz et al. [267,268] reported the electronic and MCD spectra of the Mn(II) ion diluted in cubic sites in CdF_2. The results show that the intensity in the spectrum of the MnF_8^{6-} moiety is gained via a single vibration in ca. 155 cm^{-1} (t_{1u}).

The tetrahedral Mn^{2+} ion has been studied by Tacon et al. [270] and Vala et al. [269]. The former investigators found that two quanta of $\nu_1(a_1)$ symmetry vibrations (277 cm^{-1}) are superimposed on the origin at 394.7 nm of the tetrachloromanganate $MnCl_4^{2-}$. The splitting of side band components (ca. 2.1 cm^{-1}) has been attributed to a chlorine isotope effect in the spectrum. The calculated relative intensities of the split bands are in excellent agreement with experiment.

Single crystal absorption, emission and excitation spectra of tris(octamethylpyrophosphoramide)manganese(II), $Mn(OMPA)_3^{2+}$ have been studied by Hempel et al. [271]. The rich fine structure observed in the spectra has been ascribed partly to spin-orbit and partly to vibronic interactions. The structure of the 32 000 cm^{-1} band is characterized by a vibrational interval of ca. 300 cm^{-1}.

The intensity mechanism in the spectra of linear-chain antiferromagnetically ordered, $AMnX_3$ (A = alkali metal, X = halogen) compounds has been studied by Cole et al. [272,273] and Srivastava and Mehra [274]. Abnormally large intensities are due to cooperative magnon-induced and vibronic electric dipole mechanisms. Although there are similarities in the band positions of

$RbMnBr_3$ and $CsMnBr_3$ the temperature dependence of the intensities is different.

While the vibronic spectra of $Mn^{2+}(d^5)$ have been studied thoroughly, the spectra of the isoelectronic Fe^{3+} ion are not well known. Hexaurea complexes $[Fe(urea)_6](ClO_4)_3$ display vibrational structure in ca. 300 cm^{-1} quanta [275]. The absorption spectra of FeX_4^- ion (X = Cl, Br) in the form of polymeric films have been investigated by Rivoal and Briat [276]. Moment analysis, confirmed by MCD data, indicates that "non-cubic" M—X stretching modes play an important role in the band broadening mechanism. The active modes appear at 170 cm^{-1}, symmetric breathing mode; 95 cm^{-1}, bending $\nu_4(t_2)$; and 285 cm^{-1}, stretching $\nu_3(t_2)$ [276]. Electronic spectra of ferricenium complexes, $[Fe(C_5H_5)_2]X$ where X = PF_6, BF_4 reveal interesting examples of vibronic activity. The 300 cm^{-1} vibrational progression present in the spectrum has been assigned to the ν_4 totally symmetric ring—metal—ring stretch [277—280]. Exchange interactions between neighboring ferricenium ions cause some splitting of all the progression bands. A comparison of the ν_4 stretch in the ferrocene and ferricenium spectra shows a close similarity in the ring—metal bond in these complexes.

The solution, mull and single-crystal spectra of osmium(III) tris(acetylacetonate) show considerable vibrational structure in the near IR (5000—10 000 cm^{-1}) region. Two electronic origins at 4020 and 6500 cm^{-1} together with vibrational progressions in 300 cm^{-1} and 1400 cm^{-1} have been observed [281].

High resolution absorption and MCD spectra of Ir(IV) have been studied in solution [282] and in crystalline $SnCl_6^{2-}$ [283], $SnBr_6^{2-}$ [284], Cs_2ZrCl_6 [285—290], Cs_2GeF_6 [191] (Fig. 6) and in Cs_2ZrBr_6 [280]. MCD measurements favoured a reassignment of several transitions previously reported by Douglas [286]. The assignment of the structured 22 900 cm^{-1} band in the $IrCl_6^{2-}$ spectrum

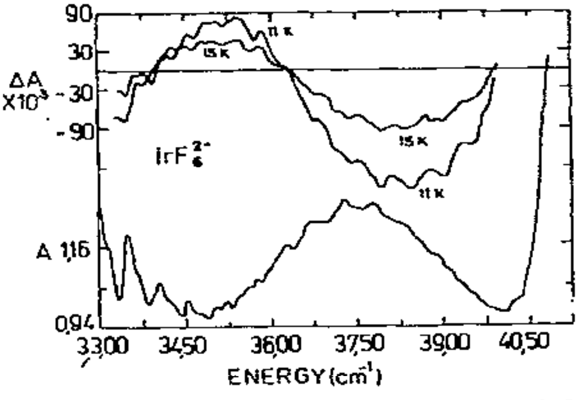


Fig. 6. The absorption spectrum at 9 K and MCD spectrum at 11 and 15 K for the high-energy interconfigurational region of Cs_2GeF_6 : Ir^{4+} [191].

has been the subject of considerable attention and controversy [285,287—289]. In one interpretation it is assigned to the fully allowed charge-transfer transition $E''_g(^2T_{2g}) \rightarrow E''_u(^2T_{2u}) + U_u(^2T_{2u})$; this interpretation has been supported by MCD and Zeeman effect measurements as well as the observed Jahn—Teller and Ham effects. Alternatively this band is explained as a parity forbidden electronic transition activated by an ungerade vibration $E''U'_{g'}(t_{1u})$ [281]. The splitting of the $a_{1g}(\nu_1)$ progression, 316 cm^{-1}, has also been explained in a different way by Massuda and Dorain [288]. These authors attributed the low frequency fine structure to the coupling between the electronic excited state and a threefold degenerate vibrational lattice Γ_{4u} mode. According to Tacon et al. [270] the structure may be due to an isotope effect arising from the different abundance of chlorine isotopes present in the molecules: $Ir^{35}Cl_n{}^{37}Cl_{6-n}$ (n = 0—6). The position and intensity of the lines are in good agreement with those obtained experimentally. However, Dorain [291] indicated some significant differences between predicted and observed features of the spectra if based solely on the isotope effect. Other explanations of the splitting in the a_{1g} progression have been suggested by Yeakel et al. [287].

The vibrational fine structure of the near IR transition (5000—6000 cm^{-1}) in $Cs_2ZrCl_6 : Ir^{4+}$ spectra has been reported by Keiderling et al. [290]. They found $\gamma_u + n\nu_1(a_{1g})$, $\gamma_u = t_{1u}, t_{2u}$ vibrations corresponding to the $E_g{}^2T_{2g} \rightarrow \nu_g{}^2T_{2g}$ electronic transition, with a short progression of the totally symmetric $\nu_1(a_{1g})$ frequency.

(vii) d^6 *Configuration*

The vibrational structure of the 18 960 cm^{-1} electronic absorption band ($^1A_1 \rightarrow {}^1T_{1g}$) in $Coen_3{}^{3+}$ has been studied by Dingle and Ballhausen [292]. In addition to the (O, O) pure electronic lines there are three false origins at 185 cm^{-1}, 345 cm^{-1} and 400 cm^{-1} to higher energy of the 18 960 cm^{-1} band. The characteristic feature of the transition is the 255 ± 5 cm^{-1} totally symmetric progression. The Franck—Condon maximum occurs at the eleventh quantum which signifies a large expansion of the excited state.

Other Co(III) complexes which exhibit vibrational structure are $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5F]^{2+}$, $[Co(NH_3)_5Cl]^{2+}$ as well as *trans*-$[Co(NH_3)_4Cl_2]^+$ and *trans*-$[Co(NH_3)_4Br_2]^+$, recently studied by Fukuda and Urushiyama [97,293]. Low temperature measurements showed that this structure consists of progressions in the totally symmetric CoN stretching vibrations.

The luminescence and absorption spectra of the hexahaloplatinum(IV) ions have been widely studied [294—296]. The former spectra revealed valuable information about changes in the Pt-ligand internuclear distances in both excited and ground states. Using the method of Henderson et al. [345], Patterson et al. [296] were able to find that both for pure $PtF_6{}^{2-}$ ion and mixed $CsPtF_6$—Cs_2GeF_6 and Cs_2PtF_6—Cs_2SiF_6 systems, the value of Δ, the difference in bond length between the initial and final state, is 0.20 Å, (for Rb_2PtF_6 this value is equal to 0.23 Å). Discussion of the change of the ν_1

energy, as well as the effect of cation have been given. Emission and absorption spectra of other d^6 transition metal complexes, Ru(II), Rh(III), Os(II), and Ir(III) which also display vibrational fine structure have been known [297, 298], but this structure has not yet been fully studied.

(viii) d^7 Configuration

Under the influence of an octahedral field the ground state ^4F splits into the $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}$ states. The octahedral $Co(H_2O)_6^{2+}$ system has been studied thoroughly by detailed absorption, CD and MCD measurements [299—304]. All the absorption regions appear to have complex vibronic structure with molecular and lattice vibrations. It has been shown that the intensity of the principal transitions $E'(^4aT_{1g}) \rightarrow {}^4A_{2g}, {}^4bT_{1g}, {}^4T_{2g}$ is generated by two cobalt oxygen skeletal vibrations of t_{1u} symmetry. The near IR region at 8065 cm^{-1}[$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$] in the spectra of Co^{2+} ions doped into ammonium perchlorate revealed a large number of vibrational modes corresponding to the various vibrations of ClO_4^- and NH_3 species [305].

Electronic absorption spectra of pure $CoBr_2$, as well as $CoBr_2$ in $CdBr_2$ solid solutions, have been recently studied by Bailey and co-workers [306,307]. The E' spin-orbit component of the $^4T_{1g}(P)$ state shows a vibrational progression with an interval of about 135 cm^{-1}. In dilute solution this progression consists of subprogressions in a 26 ± 3 cm^{-1} frequency. Unusual vibronic structure of this system has been observed: successive four members in each of the 26 cm^{-1} progressions have increasing intensities until this increase suddenly stops. According to the authors [307], this reflects a point defect resulting from the difference between the masses of Co and Cd.

The spectra of tetragonal and pseudotetragonal $CoCl_2 \cdot 6\,H_2O$, $CoCl_2 \cdot 6\,D_2O$, $CoCl_2 \cdot 2\,H_2O$ and $CoCl_2 \cdot 2\,D_2O$ as well as CoF_4^{2-} and $Mg(CO)F_4^{2-}$ ions have been investigated in detail by Ferguson and Wood [308—310]. Three types of bands are observed in the spectra: water overtones, "normal" crystal-field bands and "anomalous" crystal-field bands. "Normal" CF vibronic bands contain metal—ligand stretching vibrations which perturb the centro-symmetric field at the cobalt ion. The "anomalous" vibronic CF bands are induced by vibrations of coordinated water which provide a non-centro-symmetric field at the metal ion. The same mechanism has been found in the $Ni(BrO_3)_2 \cdot 6\,H_2O$ spectrum. The tetrahedral CoX_4^{2-} ion in a Cs_2ZnCl_4 host lattice possesses, in the 6000 cm^{-1} ($^4A_2 \rightarrow {}^4T_1$) region, a very complicated pattern of structure resulting from the following effects: superposition of spin-orbit coupling, lower symmetry fields and vibronic interactions. The vibrational structure forms progressions in 280 ± 2 cm^{-1} (in the ground state the totally symmetric vibration is 276 cm^{-1}) [304].

High resolution absorption and MCD spectra of spin forbidden ligand field transitions of the $CoBr_5^{3-}$ ion have been studied by Quested et al. [311]. The wealth of structure has been assigned both to internal $CoBr_4^{2-}$ modes as well as to lattice modes. An interesting fact has been observed: for some transitions non-totally symmetric modes are much more intense than totally symmetric. Apart from progressions in appreciably high frequencies, there are two progressions in very low frequencies, 2 cm^{-1} and 7.5 cm^{-1}. Two possible explanations for such modes are librations of the tetrahedral anions, or acoustic modes.

(ix) d^8 Configuration

There are many octahedral Ni^{2+} complexes whose spectra appear to be structured. For example the spectra of the nickel ion in a cubic site of the cubic crystal KNiF_3 in $\text{KMg}_{1-x}\text{NiF}_3$ develop fine structure when cooled to low temperature [312—315]. The vibrational structure in the spectra can be analyzed using three t_{1u} and one t_{2u} phonon modes split under the influence of the spin-orbit interaction. Ferguson et al. [316] also studied the electronic pair transitions in crystals of KZnF_3 and KMgF_3 doped with Mn^{2+} and Ni^{2+} ions. In addition to strong bands recognized as arising from the two simultaneous excitations $^6A_{1g}$(Mn) $^3A_{2g}$(Ni) → $^4E_g{}^{a4}A_{1g}$(Mn) ^1E_g(Ni) and $^6A_{1g}$(Mn) $^3A_{2g}$(Ni) → $^4E_g{}^b$(Mn) ^1E_g(Ni) structured band systems associated with the Mn—Mn pairs have also been observed. Two sharp structured bands at 42 and 38 000 cm^{-1} appear to have totally symmetric vibrational modes. On the basis of the similarity between the structure of a single transition $^3A_{2g} \rightarrow {}^3T_{1g}$ in Ni^{2+} ion, the authors ascribed these vibrations to the totally symmetric Ni^{2+}—F mode quasi-localized on the Ni^{2+}—F_6 octahedron.

Octahedral hydroxonickel complexes have been widely studied both theoretically and experimentally. An important feature of these investigations is the "red" band at ca. 640 nm which is assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ transition [317—325]. Mixing of the $^1\Gamma_3$ and $^3\Gamma_3$ components derived from ^1E and $^3T_{1g}(\text{F})$, respectively, accounts for the unusual shape of this band [324]. Detailed low temperature optical, MCD as well as IR spectral measurements on sixteen $\text{Ni(H}_2\text{O)}_6{}^{2+}$ complexes permitted the assignment of the odd parity origins of these $^3\Gamma_3$ and $^1\Gamma_3$ interacting levels on which a totally symmetric a_{1g} vibrational mode is built [324]. Potential curve analysis of the states shows that the $^3\Gamma_3$ level can have a pronounced effect on the absorption band contour. MCD spectra of $\text{Ni(H}_2\text{O)}_6{}^{2+}$ have been studied by Harding et al. [326], who found that only t_{1u} vibrations of the NiO_6 skeleton make a substantial contribution to the band intensity.

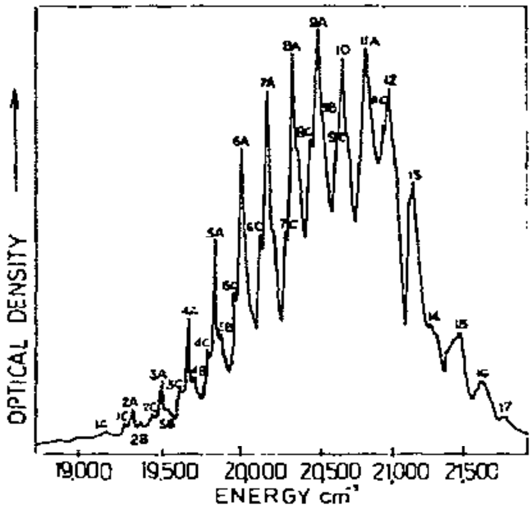
The vibrational fine structure of the octahedral complex ion, hexaaminonickel(II), $\text{Ni(NH}_3)_6{}^{2+}$, has been studied over the 2—300 K temperature range [327,328]. Distinct vibronic progressions displayed on intra- and inter-electronic configurational excitation ($t_{2g}{}^5 e_g{}^3$ and $t_{2g}{}^6 e_g{}^2$) have been observed in the spectra. Each member of these progressions involves excitation of a_{1g}, e_g, t_{1u} and t_{2u} NiN_6 skeletal modes as well as the symmetric N—H stretching mode of NH_3. A linear dependence of the position of the $^3A_{2g} \rightarrow {}^1A_{1g}$ (24 470 cm^{-1}) band on the effective anion radii and the length of unit cell seems to be a good indicator for the extent of interaction between crystalline lattice (anion) and the complex cation.

The spectra of the tetragonal chloronickelate ion, Rb$_2$NiCl$_4$ · 2 H$_2$O have been studied by Shankle and Bates [329]. The resemblance of these spectra to those of CsMg(Ni)Cl$_3$ indicates that the octahedrally coordinated nickel ion is resistant to small variations of local environment. The same conclusion has also been drawn from a study of the absorption and MCD spectra of the Ni^{2+} ion in KMgF$_3$, KZnF$_3$, K$_3$Ni$_2$F$_7$ and K$_2$NiF$_4$ sites [330]. Besides M—L vibrations in the NiCl$_4$(H$_2$O)$_2^{2-}$ ion connected with the 5899 cm^{-1} electronic transition, the O—H stretching modes are also active in the optical spectra. A detailed study shows that the vibrational Hamiltonian of NiCl$_4$(H$_2$O)$_2^{2-}$ ion is more sensitive to a small departure from O_h symmetry than are its electronic and vibronic Hamiltonians [329].

The tetragonally distorted D_{2d} tetrahedral NiX$_4^{2-}$ (X = Cl, Br) ion has been studied by Couch and Smith [331] and Mooney et al. [332]. A full assignment of the electronic transitions together with phonon frequencies has been presented [331]. Fine structure is primarily due to two vibrational progressions in the totally symmetric ν_1 (285 cm^{-1}) and ν_2 (114 cm^{-1}) modes, the latter originating in each ν_1 band. In addition, the bending vibration of $\nu_6(b_2)$ (156 cm^{-1}) and some lattice vibrations have been observed in the spectra.

The well resolved luminescence spectrum of (Et$_4$N)$_2$(Zn : Ni)Cl$_4$ has recently been reported by Koester and Dunn [333]. The dominant progression in 830 cm^{-1} has been assigned to the C—C—N bending mode. However, these results have been criticized by Flint [334] who suggested that the presence of the UO$_2^{2+}$ species incorporated into the system investigated are responsible for the spectra. Vibrational fine structure in the polarized crystal spectra of tris(octamethylpyrophosphoramide) nickel(II) and cobalt(II) complexes, M(OMPA)$_3$Cl$_2$ have been observed by Palmer and Taylor [335]. These trigonal compounds show two distinct vibronic progressions in 250 cm^{-1} and 1200—1230 cm^{-1} quanta. The 250 cm^{-1} vibration is the M—O stretch whereas the 1200—1230 cm^{-1} is the phosphorus—oxygen stretching mode observed in the IR spectra of M(OMPA)$_3$(ClO$_4$)$_2$ compounds.

The isomorphous PtX$_4^{2-}$ and PdX$_4^{2-}$ (X = Cl, Br) complexes possess very rich vibrational structure in the optical and MCD spectra. The high resolution optical spectra of the tetrahalopalladate(II) PdX$_4^{2-}$ ions have been reported for pure [336,337] as well as for mixed crystals [338]. In addition to electronic spectra, MCD measurements have also been reported [339—342]. The transition regions, 19 185—21 836 cm^{-1}, exhibit sharp vibrational features due to progressions in the totally symmetric ν_1, ν_6-asymmetric stretching, ν_7-in plane bending mode, a lattice vibration and a combination mode [337,338] (Fig. 7, Table 3). The vibrational structure is mainly associated with the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition. However, in K$_2$PdBr$_4$, vibrational fine structure has also been detected in the ${}^2A_{1g} \rightarrow {}^1E_{1g}$ transition. In general the spectrum of the PdBr$_4^{2-}$ ion is best resolved among the four homologues, K$_2$PtCl$_4$, K$_2$PtBr$_4$, K$_2$PdCl$_4$ and K$_2$PdBr$_4$ [337]. A Franck—Condon analysis of the d—d $\Gamma_1({}^1A_{2g}) \rightarrow \Gamma_2({}^1A_{1g})$ transition shows a change of 9% in the equilibrium Pd—Br distance of the excited ${}^1A_{2g}$ state in comparison to the ground state. The influence of cation on band posi-



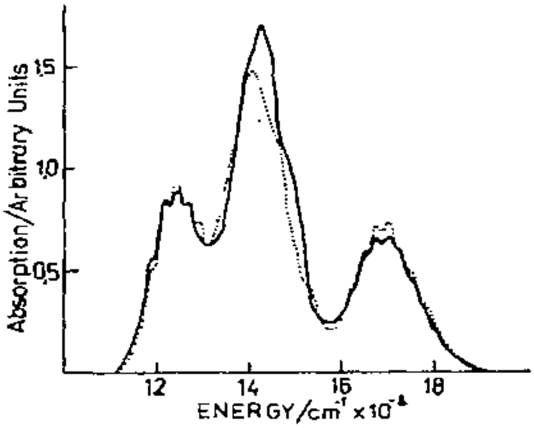


Fig. 7. Microphotometer tracing of the bands for the $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_2(^1A_{2g})$ transition for $PdBr_4{}^{2-}$ in Cs_2ZrBr_6 at 2 K [338].

Fig. 8. The electronic spectrum of $CuCl_4{}^{2-}$ at 77 K [350].

tions and intensity has also been observed [338] (Table 3).

Vibrational structure in the electronic spectra of $PtX_4{}^{2-}$ ions has been well characterized both in solution and in the solid state [342—349]. The rich structure which can be seen both in absorption and in emission has been assigned to progressions in the symmetric modes coupled with the odd vibrational modes of the ions. The Franck—Condon analysis based on the method of Henderson et al. [345] has shown that the Pt—Cl equilibrium distance in the excited state is 0.16 Å greater than in the ground state [344]. There is also a close correlation between transitions in K_2PtCl_4 and K_2PtBr_4. It is interesting that the spectra of the dimeric $Pt_2Br_6{}^{2-}$ ion show no structure [346]. The lack of resolution has been explained to result from overlapping transitions in the dimeric ion in comparison to the monomeric $PtBr_4{}^{2-}$ ion spectra.

(x) d^9 Configuration

There is only one example of resolution of vibrational structure in the spectra of (d^9) Cu^{2+} ions in the literature [350]*. In liquid nitrogen the spectrum of (N-methylphenethylammonium)$_2$$CuCl_4$ exhibits a regular progression in 265 ± 20 cm^{-1} (Fig. 8). Comparison with the Raman spectrum (276 cm^{-1}) suggests that this value is characteristic of an a_{1g} symmetry mode acting in the planar $CuCl_4{}^{2-}$ ion.

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* Recently the authors carried out a more comprehensive study of the system [3].

TABLE 3

Assignment of vibronic peaks for the $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_2(^1A_{2g})$ transition for $PdBr_4^{2-}$ in Cs_2ZrBr_6 at 2 K [338]

Peak no.	Energy (cm^{-1})	Excited state assignment I
1A	19 184.5	$\Gamma_2(^1A_{2g}) + \nu_6$
1C	19 297.0	$+ \nu_1 + \nu_1$
2A	19 350.8	$+ \nu_6 + \nu_1$
2B	19 392.1	$+ \nu_L + 2\nu_1$
2C	19 481.7	$+ \nu_1 + 2\nu_1$
3A	19 530.0	$+ \nu_6 + 2\nu_1$
3B	19 570.9	$+ \nu_L + 3\nu_1$
3C	19 639.0	$+ \nu_1 + 3\nu_1$
4A	19 683.8	$+ \nu_6 + 3\nu_1$
4B	19 717.6	$+ \nu_L + 4\nu_1$
4C	19 804.3	$+ \nu_7 + 4\nu_1$
5A	19 851.1	$+ \nu_6 + 4\nu_1$
5B	19 883.5	$+ \nu_L + 5\nu_1$
5C	19 970.9	$+ \nu_7 + 5\nu_1$
6A	20 016.0	$+ \nu_6 + 5\nu_1$
$6B_1$	20 045.3	$+ \nu_L' + 6\nu_1$
$6B_2$	20 068.3	$+ \nu_L'' + 6\nu_1$
6C	20 139.0	$+ \nu_7 + 6\nu_1$
7A	20 178.0	$+ \nu_6 + 6\nu_1$
7B	20 211.1	$+ \nu_L + 7\nu_1$
7C	20 303.0	$+ \nu_7 + 7\nu_1$
8A	20 344.8	$+ \nu_6 + 7\nu_1$
$8B_1$	20 372.9	$+ \nu_L' + 8\nu_1$
$8B_2$	20 387.5	$+ \nu_L'' + 8\nu_1$
8C	20 472.2	$+ \nu_7 + 8\nu_1$
9A	20 514.2	$+ \nu_6 + 8\nu_1$
9B	20 545.4	$+ \nu_L + 9\nu_1$
9C	20 640.5	$+ \nu_7 + 9\nu_1$
10A	20 678.5	$+ \nu_6 + 9\nu_1$
10B	20 714.4	$+ \nu_L + 10\nu_1$
10C	20 808.9	$+ \nu_7 + 10\nu_1$
11A	20 842.3	$+ \nu_6 + 10\nu_1$
11C	20 966.9	$+ \nu_7 + 11\nu_1$
12	21 006.5	$+ \nu_6 + 11\nu_1$
13A	21 167.9	$+ \nu_6 + 12\nu_1$
13C	21 288.3	$+ \nu_7 + 13\nu_1$
14A	21 328.7	$+ \nu_6 + 13\nu_1$
14C	21 425.2	$+ \nu_7 + 14\nu_1$
15A	21 498.0	$+ \nu_6 + 14\nu_1$
15C	21 618.4	$+ \nu_7 + 15\nu_1$
16	21 665.7	$+ \nu_6 + 15\nu_1$
17	21 836.1	$+ \nu_6 + 16\nu_1$

F. GENERAL REMARKS

The material presented here attests to some very complicated problems concerning the interpretation of vibronic structure. A generally unfavorable factor is the lack of agreement between experimental data and interpretation presented by various authors even for relatively simple ions. However, the information available from well structured vibronic bands makes the description of such systems worthwhile in spite of these difficulties. From the large number of excellent papers, new techniques applied for the measurements and analysis of data, it is clear that the depth of understanding of these difficult problems is greater now than for example ten years ago. If this review will help the reader to realize the progress in this matter and how far we are from a full understanding of vibronic interactions, we consider our task fulfilled.

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