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Spectroscopy of chromium(VI) species

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CONTENTS

A. INTRODUCTION

This review is concerned with recent developments in the spectroscopy of the chromium(VI) ion covering the literature published mostly in the last decade. Chromium compounds in various oxidation states have been reviewed in a number of books [1–4] and monographs [5–7]. However, the growing industrial importance of chromium(VI) compounds and ecological problems connected with environmental pollution prompted the author to devote this work entirely to the highest oxidation state of this metal.

The chromium–oxygen species described here form discrete units which remain unchanged during various chemical reactions. Contrary to the tetrahedral oxyanion where the CrO_4^{2-} group is clearly established, the CrO^{4+} and CrO_2^{2+} species are often only formal as in CrO_2Cl_2 where strong covalent bonds exist between the metal ion and chlorine [8]. However, since a suggestion of Symmons and coworkers [9] that the position of the longest wave charge-transfer (CT) band in oxyanions can be correlated with the ionic radius of the metal ion, there were further successful attempts to describe similar dependencies valid for MO_2^{2+} [10] and MO_3 [11]

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chromophores. These experimental relationships strengthened the position of various M–O entities as independent units.

B. MONOCHROMATES, CrO_4^{2-}

The investigation of the electronic structure of the chromate ion is still an extensive field of both theoretical and experimental endeavour. The effect of symmetry reduction via halide substitution, incorporation of the ion into various host lattices, single crystal low temperature, and solvent effect studies are still a vast field of exploration. Binding energies of the core electrons have been determined by various theoretical methods [15a] supported by excellent experimental techniques such as X-ray photoelectron spectroscopy [12–14] and soft X-ray valence band spectroscopy [15]. The outer-sphere phenomena were studied mainly by MCD as well as by electronic and infrared spectroscopic techniques [17]. The orbital energies have been recently calculated by Miller et al. [16]. These studies as well as previous ones [17] established that the $1t_1$ (highest occupied MO level) possesses pure oxygen character and the virtual $2e$ and $2t_2$ orbitals are of mostly chromium character with $2e < 7t_2$. The schematic energy diagram for orbitals of chromate, mono-substituted chromate and chromyl chloride in the ground states is shown in Fig. 1.

The primary point of interest in the eighties was the observation of the theoretically predicted lowest triplet states in absorption and emission [18–21]. The observation of these states seems to be the main experimental success in the last years since they confirmed the earlier advanced calculations.

The $1t_2 \rightarrow 2e$ excitation $(t_1 5e^1)$ yields $^{1,3}T_2$ and $^{1,3}T_1$ states. The ordering of these

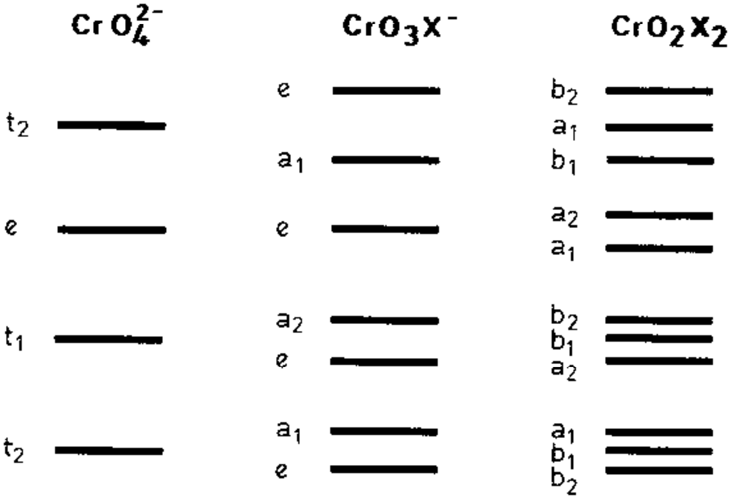


Fig. 1. Schematic energy level diagram for the higher filled and lower unfilled orbitals in the ground states of CrO_4^{2-}, CrO_3Cl^- and CrO_2X_2, (X = F and Cl) [16].

states was established to be ${}^1T_2 > {}^1T_1 > {}^3T_2 \gg {}^3T_1$; thus, for example, the dipole forbidden transition to the ${}^1T_1$ state lies lower than the dipole allowed ${}^1T_2$ state. The phosphorescence observed at low temperature indicated that a triplet state lies below the lowest excited singlet state, just as expected, and has lower symmetry than T_d. The triplet states were found in the low-temperature single crystal studies KBr/CrO_4 [18], K_2SO_4/CrO_4^{2-} [21], B_2O_3/CrO_4^{2-} [22] and in the aqueous frozen solution of oxyanionic Cr(VI) species [136]. The emission of the triplet state ${}^3T_1 \rightarrow {}^1A_1$ in the range (15 000–12 000) cm^{-1} appears to be structured whereas the higher energy transition ${}^1T_1 \rightarrow {}^1A_1$ (14 000–19 000 cm^{-1}) is structureless [21,22]. The long-wave bands in the absorption spectra in the ranges 14 000–19 000 cm^{-1} and 18 000–22 500 cm^{-1} were assigned to ${}^1A_1 \rightarrow {}^3T_1$ and ${}^1A_1 \rightarrow {}^3T_1$, respectively [22]. Belyi et al. [22] observed splitting of the ${}^3T_1$ state of about 100 cm^{-1} which has been confirmed by Raman spectra. The authors also found complexes of the type $M^+{-}CrO_4^{2-}{-}M^+$ (M = Rb, Tl) in borate glasses doped with the respective chromate. The spectral characteristics exhibit symmetry lowering $T_d \rightarrow C_{2v}$ in the chromate ion [22,23].

As shown from infrared and Raman studies, the CrO_4^{2-} ion in solution, has tetrahedral T_d symmetry with four basic modes of vibration: $\nu_1(A_1) = 847$ cm^{-1}, $\nu_2(E) = 348$ cm^{-1}, $\nu_3(T_2) = 884$ cm^{-1} and $\nu_4(T_2) = 368$ cm^{-1} [24]. However, solid state effects, e.g. charge compensation and cation influences, cause various deformations, resulting in splitting of vibrational bands [25–27].

The high-temperature characterization of the chromate ion was studied recently using a combination of matrix isolation and vibrational spectroscopy [28–31]. Ogden and coworkers [29] observed and applied the ${}^{16}O{-}{}^{18}O$ isotope effect to establish the molecular geometry of the M_2XO_4 species. The isotope fine structure of the $B_2(D_{2d})$ component together with the assignment is presented in Table 1. These high-resolution spectra confirm the D_{2d} geometry of the K_2CrO_4 molecule. Moreover, from metal isotope frequency shift, the OCrO bond angle was estimated to be $96 \pm 5°$. A detailed analysis of M_2XO_4 gaseous molecules, i.e. the investigation of cation influence on the interaction force constants of the X–O bonds, allowed the authors [30] to estimate the OCrO angles as 106° for sodium and potassium and 107° for thallium chromate, which are close to values reported elsewhere [30]. From the matrix-isolated infrared studies the CrO_4^{2-} and generally XO_4^{2-} (X = Cr, Mo, W) anions are rigid units with four equivalent X–O bonds and a geometry almost independent of the coordinated metal atom.

The Raman and resonance Raman effect in the CrO_4^{2-} ion was studied recently by Homborg [32] and Campani et al. [33,34]. The rigorous resonance of the $\nu_1(A_1)$ fundamental mode with the lowest allowed ${}^1A_1 \rightarrow {}^1T_2$ transition was reported for the first time [33]. Good agreement between experimental and calculated excitation profiles confirms the Franck–Condon scattering mechanism which is contributing to the totally symmetric modes in the CrO_4^{2-} ion. The authors observed vibrational fine structure in the RRE profiles although the electronic band at ca. 26 000 cm^{-1} in the water solution was structureless. They related this fact to the magnitude of

TABLE 1

Infrared band (cm^{-1}) assignment and isotope fine structure on $B_2\nu(Cr–O)$ mode in K_2CrO_4 (D_{2d} symmetry) [29]

Ar	N_2	Free ion	Assignment
893.4^a	894.9		B_2
		890	$T_2[\nu(X–O)]$
874.8^a	878.1		E
439.3	420.0		B_2
		378	E $T_2[\delta(X–O)]$
247.5			$\nu(K–O)$ (?)

^{a}Centre of complex absorption.

	^{50}Cr	^{52}Cr	^{53}Cr	^{54}Cr
Obs.	901.2	894.9	891.9	889.0
Calc.	901.2	894.9	891.9	889.0

ν calculated assuming $F_{B_2}=F_r+F_{rs}-2F_{rd}=4.87$ mdyn A^{-1} and $2\theta=96°16'$.

the FC overlap resulting in the displacement $\Delta=0.459$ Å and the excited state bond elongation being 0.115 Å.

The most striking difference between the isoelectronic MnO_4^- and CrO_4^{2-} ions is the observed difference in the O–O resonance intensity. This was explained by the magnitude of the Franck–Condon parabola displacement: 0.368 Å amu$^{1/2}$ and 0.404 Å amu$^{1/2}$ for MnO_4^- and CrO_4^{2-}, respectively. There are therefore larger changes in geometry upon excitation for the chromate than for the permanganate ion. The O–O transition lies at 26 138 cm^{-1} and can be compared with earlier data obtained from the analysis of the electronic absorption spectra of Cs_2CrO_4 (25 860 cm^{-1}) [35], K_2CrO_4/KCl (25 440 cm^{-1}) [36], CrO_4^{2-}/KBr (25 770 cm^{-1}) [37], CrO_4^{2-} in $Cu(bpy)_2CrO_4$ (DMF soln.) (25 190 cm^{-1}) [38] and CrO_4^{2-} in water [34].

C. MONO-SUBSTITUTED CHROMATES(VI), CrO_3L^{n-}

This is an important class of chromium(VI) compounds because substituted chromates participate in oxidation processes of organic compounds. For example, esters and thioesters $[CrO_3(OR)]^-$ are known intermediates in the interaction of Cr(VI) with biologically important substances [137]. Moreover, some structural problems concerning bond covalency and orbital order in oxymetallates were solved through extensive investigations of the symmetry reduction effect of halide substitution [16,39].

Among mono-substituted chromates, halogeno-substituted CrO_3X^- (X = F, Cl, Br, I) are among the most thoroughly studied [11,39–54]. They are relatively easily obtained from aqueous solutions.

The substitution of one oxide ligand in the tetrahedral CrO_4^{2} entity provides a symmetry-lowering effect ($T_d \rightarrow C_{3v}$) observed both in the infrared and electronic spectra. This effect causes a respective splitting of the degenerate vibrations. The correlation data for the chromate and other tetrahedral ions can be presented as follows.

	T_d	C_{3v}	C_{2v}
ν_1	A_1	A_1	A_1
ν_2	E	E	A_1+A_2
ν_3	T_2	A_1+E	$A_1+B_1+B_2$
ν_4	T_2	A_1+E	$A_1+B_1+B_2$

(1)

Table 2 presents the vibrational frequencies found for halogenochromate ion. Bands ν_1 and ν_4 were found to be slightly solvent-dependent.

Substituted chromates display four main absorption bands in the visible and ultraviolet regions in solution, frozen solution and monocrystals. These bands can be related to trigonally split $t_1 \rightarrow a_2+e$ transitions. Theoretical calculations show that $a_2 > e$ (Fig. 1). The highest filled a_2 orbital retains oxygen character whereas the highest filled e orbital also exhibits some halogen contribution. The lowest unfilled e has chromium $3d$ character [16]. From one electron $t_1 \rightarrow e^*$ excitation in the T_d symmetry, $^1T_1$ and $^1T_2$ are derived. In C_{3v} symmetry they are trigonally split, giving rise to $^1E^a$ and $^1A_2(T_1)$ and $^1E^b$ and $^1A_1$ (T_2) [39]. In the spectrum of halogenochromates, all the singlet transitions at 22 000 cm^{-1} ($^1A_1 \rightarrow {}^1E^a$), 28 000 cm^{-1} ($^1A_1 \rightarrow {}^1A_1$ and $^1A_1 \rightarrow {}^1E^b$) and 36 000 cm^{-1} ($^1A_1 \rightarrow {}^1E^c$) have been observed [39,45]. ($^1E^c$ is derived from the second $^1T_2(a_1 \rightarrow e^*)$ excitation [39].

Triplet states are also expected in the spectra of halogenochromates. In 1985, Miller et al. [16] were able to find phosphorescent triplet states in $KCrO_3X$. They

TABLE 2

Vibrational frequencies of halogeno-substituted chromates

CrO_3F^- (ref. 41)	CrO_3Cl^- (ref. 50)	CrO_3Cl^- (ref. 41)	CrO_3Br^- (ref. 42)	Assgn.	Desc.
955	953	954	948	$\nu_4(E)$	$\nu_{as}(CrO_3)$
911	904	907	906	$\nu_1(A_1)$	$\nu_s(CrO_3)$
637	440	438	395	$\nu_2(A_1)$	$\nu_s(CrX)$
370	363	365	364	$\nu_5(E)$	$\delta_{as}(OCrO)$
338	294	295	242	$\nu_3(A_1)$	$\delta_s(OCrO)$
261	205	209	200	$\nu_6(E)$	$\delta_s(XCrO)$

observed electronic bands both in absorption and emission exhibiting fine structure with the origin of absorption in $KCrO_3Cl$ at 547.6 nm, 700 cm^{-1} to higher energy of the onset of emission. Triplet states in these compounds were also detected with the ODMR technique.

The anions of the CrO_3X^- type exhibit vibrational fine structure in absorption and emission spectra [55]. The observed structure in absorption spectra (and most probably in emission) is attributed to the totally symmetric ν_1 (A_1) Cr–O vibration coupled with electronic transitions. The best resolved spectra were found in single crystal studies and at low temperature [39,40]. However, aprotic solvent data enhanced with computer techniques (spectra resolution into Gaussian bands) also appeared to give reasonable results [53] (Fig. 2). Generally, there are several important factors determining resolution of the vibronic structure: temperature, property of solvent, substituted ligand X in CrO_3X, cation M in $MCrO_3X$ salt and technical advances [55].

(i) *Halogen atom effect*

This effect was studied for 15 alkali metal and alkyl ammonium halochromates [47]. The change of a halogen atom in the CrO_3X^- entity (X = F, Cl, Br) causes a systematic disturbance in the vibronic structure which has been observed both in the nujol mull and the solution spectra: F > Cl > Br. The resolution parameter *R* was found to correlate with Pauling's electronegativity as well as ionic radii [47]. Generally, the magnitude of the vibrational spacings, $\Delta\nu$, in the electronic spectra of

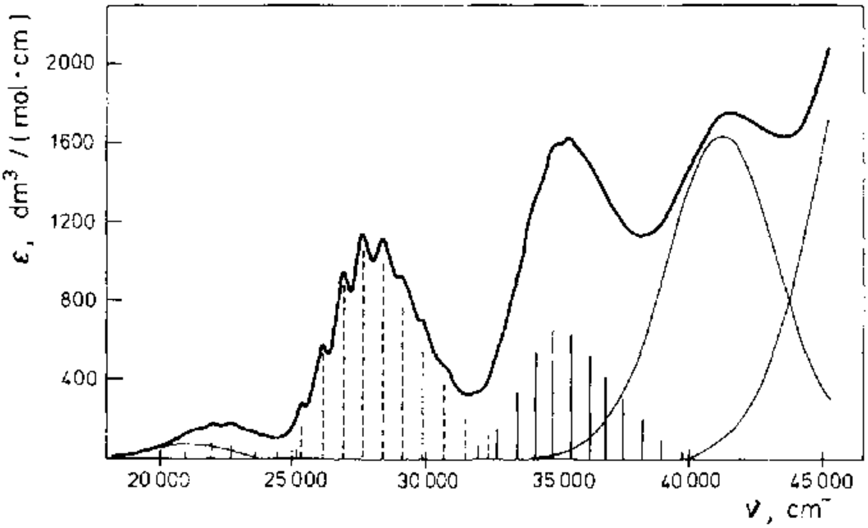


Fig. 2 Computer analysis of the electronic absorption spectrum of $KCrO_3Cl$ in acetonitrile solution [53].

halogenochromates correlate simply with the halogen atom electronegativity χ on the Pauling's scale [46].

(ii) *Cation effect*

A collection of similar salts with the same anion but different cations in the sequence NH_4^+, Li^+, Rb^+, and Cs^+ shows an increase of resolution of the structure in the 365 nm band [47]. Evidently the radius and/or polarizing power of the cation are important in determining such vibronic structure.

(iii) *Solvent and temperature effects*

The solvent perturbing effect was studied for $KCrO_3Cl$ dissolved in water, formamide, methanol and several aprotic solvents [45]. Solvents such as water and formamide, which form hydrogen bonds, interact with $KCrO_3Cl$, seriously disturbing the structure; methanol reduces the Cr(VI) ion.

Aprotic solvent contribution to band structure resolution can be determined indirectly via the magnitude of the error (σ) defined as the difference between the theoretically predicted FC parameters and that obtained from the spectra [52]. The smaller the value for σ, the smaller is the solvent effect on the spectra. Solvents with increasing interaction with the chlorochromate anion can be put in order: DMSO > DMF > AN > A where the symbols represent dimethylsulphoxide, dimethylformamide, acetonitrile and acetone, respectively.

At lower temperature, the spectra become sharper according to the decreased Boltzmann population of the higher levels.

Franck–Condon analysis of the vibronic spectra has received renewed interest since the appearance of both new experimental techniques and computer-analysis. In the case of $KCrO_3Cl$, analysis was performed using the simple Poisson formulae but later on expanded with some additional features (vide infra). The relative intensities of each progression member of the vibronic band can be approximately expressed

$$I_n = I_0 \frac{S^n}{n!}$$

where I_n and I_0 are the intensities of the nth and the first member of the progression, respectively. The relationship between S, defined as a Franck–Condon factor and usually obtained from the ratio I_n/I_0, and the distortion parameter Q_0 is given by

$$S = \frac{E}{h\omega_\alpha} = \frac{1}{2} k_\alpha (Q_0)^2 (h\omega_\alpha)^{-1} \tag{2}$$

where E is the energy associated with Q_0, ω_x the frequency ($2\pi c v$) and k_x the force constant.

Unfortunately, this method neglected the differences between the ν_1 frequencies occurring in the ground and excited states. By introducing the real frequencies in the ground and excited states of the CrO_3Cl^- ion, further development of the FC analysis became possible [52]. As previously shown by Yersin et al. [56], the neglect of this frequency change can cause an error of as much as 70%! In the case of the chlorochromate ion, this error was about 10% [52].

In order to calculate the excited state geometry, the energies $E_{v'v''}$ and the relative intensities $I_{m,0}$ and $I_{0,0}$ are taken from the spectra.

$$\frac{I_{(\mathrm{abs})m,0}}{I_{(\mathrm{abs})0,0}} = \tau_m = \frac{E_{m,0}}{E_{0,0}}\left(\frac{R_{m,0}}{R_{0,0}}\right)^2 \tag{3}$$

$$R_{0,0} = \left[\frac{2\delta}{(1+\delta^2)^{1/2}}\right]\exp\left(-\frac{1}{2}\rho^2\right) \tag{4}$$

$$R_{n+1,0} = \frac{-2\delta D R_{n,0} - (2n)^{1/2}(\delta^2-1)R_{n-1,0}}{(\delta^2+1)[2(n+1)]^{1/2}} \tag{5}$$

where $\delta = (\nu'/\nu'')^{1/2}$, $D = c(m\nu'')^{1/2}\Delta S$, $\rho = D/(1+\delta^2)^{1/2}$, and $c = 0.1722$.

Computer trial and error method varied the parameter ΔS until the theoretical intensities matched best the experimental values. A measure of fit, σ, can be defined by the equation

$$\sigma = \sum_{m=1}^{M} \frac{[(\tau_{\mathrm{m,calc}} - \tau_{\mathrm{m,obs}})/\tau_{\mathrm{m,obs}}]^2}{M} \tag{6}$$

where M is the number of the relative intensities τ_m.

The values of the parameter c are erroneously given in ref. 52 which was based on ref. 56. When one introduces a correct value of $c = 0.1722$, the value for ΔS is 13.4 pm [53]. The computer resolution of the bands together with the Franck–Condon analysis of the spectrum of potassium chlorochromate dissolved in acetonitrile has been reported recently by Bartecki et al. [53]. The contours of the spectra were differentiated and resolved into component bands and progressions similar to a previously reported analysis of $KMnO_4$ [57]. The displacement of the potential surface ΔS for the CrO_3Cl^- anion upon excitation was found to be 13.2 pm. This may be compared with previously reported data for the MnO_4^- anion, $\Delta S = 10.5$ pm [57]. Generally, as the value of ΔS increases, the length of the progression and the M–O distance increases upon excitation.

D. CrO_2X_2, $CrOX_4$, $CrOX_5^-$ and CrX_6

Among disubstituted chromates, CrO_2Cl_2 has been the most thoroughly studied and a separate section chapter (see Sect. E) is devoted to this halo-oxide. Other chromyl halides and oxyhalides investigated recently were CrO_2F_2, CrO_2Br_2, and mixed CrO_2ClBr, together with $CrOF_4$, and anionic $CrOF_5^-$. We also intend to mention the preparation and spectroscopic data for highly unstable chromium hexafluoride. First we describe shortly some oxochromium(VI) compounds which do not contain halogen.

Gillespie and Kapoor [58], studying the conductivity, cryoscopy and spectra of chromate and dichromate ions in 100% sulphuric acid and dilute oleum, found evidence for the presence of $CrO_2(HSO_4)_2$ in these systems. However, in our opinion, the longest wave band at 780 nm lies too far to the red to be assigned to a CrO_2 entity. Its intensity (ε about 400) indicates that it can be connected with electron transfer, most probably from the HSO_4^- part of the molecule.

CrO_2Cl_2, CrO_3, K_2CrO_4 and $K_2Cr_2O_7$ solvolyse to $CrO_2(SO_3Cl)_2$ in chlorosulphuric acid [59,60]. Various steps for the solvolytic reaction have been proposed [60], with the following fitting very well with the experimental conductivity and spectroscopic data

$$K_2CrO_4 + 6\ HSO_3Cl \rightarrow CrO_2(SO_3Cl)_2 + 2\ K^+ + 2\ SO_3Cl^- + 2\ H_2SO_4 + 2\ HCl \quad (7)$$

Twelve hitherto unknown alkoxy-bridged chromyl alkoxides of the type $[CrO_2(OR)_2]$ and $[CrO_2Cl(OR)]$ ($R = CH_2CCl_3$, CH_2CF_3, CH_2CH_2Cl) have recently been synthesized and spectroscopically and cryoscopically characterized [61]. The mass spectra have also been reported. These compounds appeared to react with oxygen and nitrogen donor ligands, forming the adducts of 1:1 and 1:2 stoichiometry [61].

The molecular structure of chromyl fluoride, CrO_2F_2, has recently been reinvestigated by French et al. [62]. This structure, similar to the structure of chromyl chloride (vide infra) appears to be 'abnormal' from the point of view of the valence-shell electron-pair repulsion theory (VSEPR), which predicts that the amount of space occupied by part of a molecule increases with increasing bond multiplicity [62]. The FCrF bond angle was found to be 111.9(9)° whereas the value for the OCrO angle (double bonds) = 107.8(8)°. The results of Beattie et al. [63] obtained from isotopic shifts are in agreement with these values.

Preparation and matrix isolation studies on chromyl bromide and chromyl chloride bromide have recently been described by Hope et al. [64]. Chromyl chloride and liquid HBr were condensed in a 77 K trap to give CrO_2Br_2, a compound stable below 200 K. The IR spectrum was recorded in 12 K matrices. Vibrational fundamentals (in cm^{-1}) for chromyl halides were included in Table 3. The high resolution splitting of the Cr–O stretching modes shows evidence for chromium isotope fine structure. This structure was used to estimate the OCrO angle in CrO_2Br_2 [64] according to the formulae

$$\lambda A_1(\mathrm{Cr{=}O}) = (F_R + F_{RR})\left(\frac{1}{M_O} + \frac{2\cos^2\theta}{M_{Cr}}\right) \quad (8)$$

$$\lambda B_1(\mathrm{Cr{=}O}) = (F_R + F_{RR})\left(\frac{1}{M_O} + \frac{2\sin^2\theta}{M_{Cr}}\right)$$

TABLE 3

Vibrational fundamentals (cm^{-1}) for chromyl halides CrO_2X_2 (X = F, Cl, Br) collected by Ogden and coworkers [64]

CrO_2F_2		CrO_2Cl_2			CrO_2Br_2	Mode
Gas	N_2Matrix	Gas	Liquid	Ar Matrix	Ar Matrix	
1016	1013.9	1002.0	994	997.8	995.4	$B_1\nu(Cr{=}O)$
1006	1006.7	991.0	984	983.6	982.6	$A_1\nu(Cr{=}O)$
789	784.8	502.7	497	501.3	403.5	$B_2\nu(Cr{-}X)$
727	721.7	470.0	465	467.9	399.0	$A_1\nu(Cr{-}X)$
364		355.8	357	355.9	(305?)	$A_1\delta(CrO_2)$
304			263	257.0		B_2
274			216	212.0		B_1
259			230			$A_2\tau$
208			144	139.2		$A_1\delta(CrX_2)$

where $\lambda = 4\pi^2\nu^2$, F_R and F_{RR} are the principal stretching and the stretching–stretching interaction force constants (Cr=O), M_{Cr} and M_O the atomic masses of chromium and oxygen. A_1 and B_1 are frequencies of different isotopic species observed at 995.4 cm^{-1} and 982.6 cm^{-1} and 2θ is the OCrO angle in the CrO_2Br_2 monomer of C_{2v} symmetry. The calculated angle was 107°.

A new compound, CrO_2ClBr, formed from the mixture of CrO_2Cl_2 and CrO_2Br_2 has been obtained and spectrally characterized [64]. The bands observed were assigned to the following vibrations: 996, 985.5 cm^{-1}, ν(Cr=O); 483 cm^{-1}, ν(Cr–Cl); and 412.5 cm^{-1}, ν(Cr–Br).

By fluorination of CrO_3 in an autoclave, $CrOF_4$ was obtained, a little known species in comparison with its analogue $MoOF_4$ and WOF_4 [65]. It is a strong fluorinating and oxidizing agent comparable with $CrOF_3$ [66] and CrF_5 [67]. The compound has been satisfactorily characterized by IR and UV/Vis spectra. Infrared spectra of the matrix isolated $CrOF_4$ (C_{4v} monomer) show the characteristic absorptions at 1027.7 cm^{-1}, 746.3, and 741.6 cm^{-1} assigned to the A_1(Cr=O) and E(Cr–F) vibrations, respectively. Electronic spectra exhibit prominent charge transfer bands at 22 000 cm^{-1} and 27 000 cm^{-1} assigned to oxygen–chromium and fluorine–chromium transitions, respectively. Vibrational fine structure appearing at 27 000 cm^{-1} and containing a single progression in 615 + 70 cm^{-1} has been attributed to the totally symmetric A_1(Cr–F) mode identified in the ground state at 686 cm^{-1}. It is known that well-resolved fine structure appears in the spectra of various chromium oxo and chromium oxo-substituted species in the 27 000 cm^{-1} region [35,39]. The latter structure is connected with the chromium–oxygen vibrations coupled to the electronic transition. The presence of a band with roughly the same energy connected with the F–Cr transition is striking and perhaps an accidental feature. Together with $CrOF_4$, a $Cs(CrOF_5)$ compound has been obtained and characterized by IR [65].

The preparation of higher chromium fluorides involves critical conditions. The static fluorination of CrO_3 in a Monel autoclave yields chromium hexafluoride, CrF_6 [68]. The IR and electronic spectra of unstable CrF_6 together with those of the fluorides CrF_5 and CrF_4 were measured [68]. The data for the lower fluorides indicate fluorine-bridged polymeric structures. Intense IR bands at 763.2 cm^{-1} show that CrF_6 is octahedral. The electronic spectra of chromium hexafluoride exhibit prominent CT bands at ca. 38 450 cm^{-1} ($t_{2u} \rightarrow t_{2g}$), 26 700 cm^{-1} ($t_{1g} \rightarrow t_{2g}$) and a shoulder at 31 250 cm^{-1} ($t_{1u} \rightarrow t_{2g}$). The assignment is in agreement with both MoF_6 and WF_6 analogs and with theoretically predicted CT bands in the MX_6 molecule. A partially resolved progression of ca. 530 cm^{-1} on the 26 700 cm^{-1} band has also been recorded and assigned to the A_{1g} (F–Cr) stretch (720 cm^{-1} in the ground state).

E. SPECTROSCOPY AND REACTIVITY OF CHROMYL CHLORIDE, CrO_2Cl_2

The molecular structure of chromyl chloride, CrO_2Cl_2, as well as its oxidation properties have been the subject of many investigations in the 1970s and 1980s [8,16,69–90]. The importance of electrophilic reactions in the biological systems prompted some authors to investigate the electronic structure of chromyl chloride as a model oxidant for cytochrome P-450 activity [70–72].

The reinvestigated electron diffraction measurement by Marsden et al. [8] is consistent with C_{2v} symmetry for this molecule and in excellent agreement with the previous data of Palmer [73]. Marsden et al. [8] found that the OCrO angle (a double bond) is smaller than the ClOCl angle (a single bond). This is in contradiction of the prediction of the VSEPR theory.

Varetti and Müller have analyzed the IR spectrum of chromyl chloride in an argon matrix at 20 K [74]. They observed frequencies attributed to different isotopic species of the molecule. Using these data in connection with the gas-phase IR and molecular structure frequencies, the authors determined the symmetry force constants. The infrared data for the matrix isolated spectra together with data published elsewhere for vapour and liquid spectra have been collected in Table 3.

Many experimental data for CrO_2Cl_2 absorption, emission and photoelectron spectra have been reported and compared with theoretical prediction (see, for example, refs. 75,77,78,80). Generally, there is reasonable agreement between theoretical and experimental data [82]. The relative order of the energy levels for CrO_2Cl_2 recently calculated by Miller et al. [16] has been presented in Fig. 1. The order of the levels, although slightly different as different methods of calculation were used [70,75,76], follows the general trend: highest filled orbitals derived from $t_1 \rightarrow 2e(T_d)$ in parent CrO_4^{2-} are the nearly degenerate a_2, b_1, b_2 (t_1) orbitals mostly localized on oxygen and chlorine atoms and only slightly on chromium atoms. A Mullican population analysis indicates that they are non-bonding [75]. The lowest energy orbital order calculated recently with the X_α-scattered wave method was found to be $b_2 > b_1 > a_2$ with b_2 as the highest occupied orbital possessing oxygen character and with increasing halogen character of b_1 and a_2 [16]. As they are nearly degenerate, various methods differ in their order. The lowest unfilled virtual orbital, $7a^*$, has mainly chromium character. It appears to be strongly antibonding and weakly Cr–O bonding [75]. These theoretical predictions are related both to the photoelectron (Fig. 3) and electronic absorption spectra of the molecule [76].

The most detailed study on the electronic spectra of chromyl chloride was reported for the compound in the gas phase (Fig. 4) [76]. Five areas of absorption were found in the 15 000–50 000 cm^{-1} region (vide infra). However, various studies were focused on the lowest energy region between 500 and 650 nm (15 000–20 000 cm^{-1}). In this region there are at least three electronic transitions: 589, 576 and 540 nm,

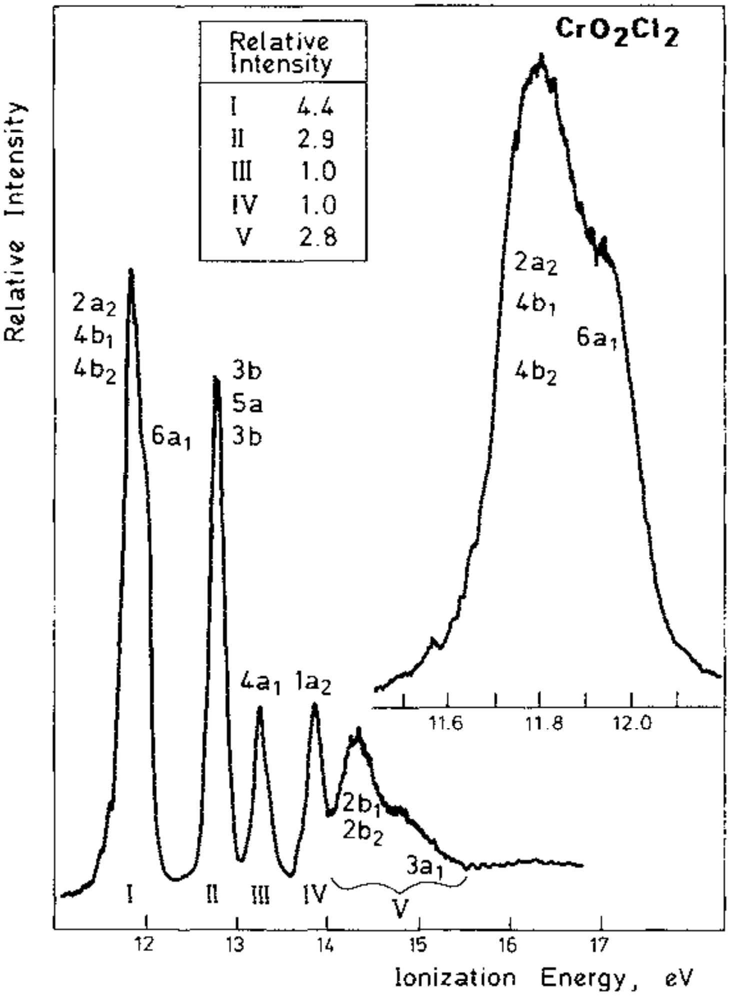


Fig. 3 Photoelectron spectrum of vapour-phase CrO_2Cl_2 [75].

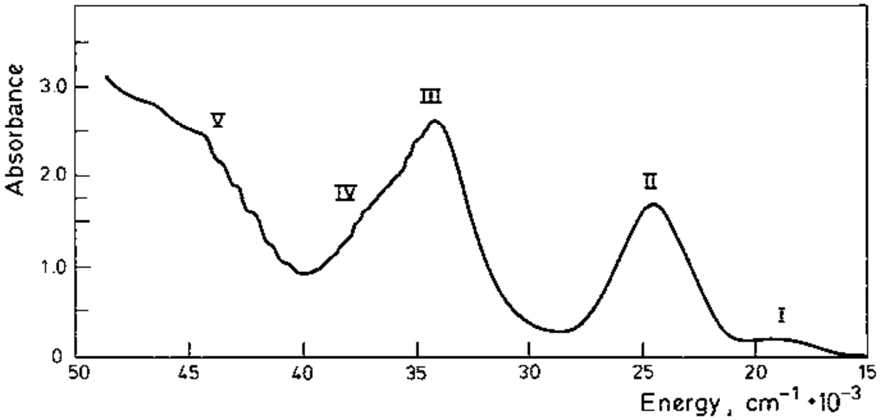


Fig. 4 Gas-phase electronic spectrum of CrO_2Cl_2 [76].

which can be related to $t_1 \rightarrow 2e$ (T_d), i.e. a_2, b_1, $b_2 \rightarrow 7a_1{}^*$ (C_{2v}). From the rotational analysis [77], the lowest excited singlet state has been found to be $^1B_2$. The lowest excited triplet state, $^3B_2$, lies only 0.03 eV below the lowest excited singlet state [79,80,88]. The overlapping electronic transition together with the vibrational and rotational structure, the great amount of 'hot' bands and finally isotope effects are responsible for the extremely complicated pattern of the lowest energy region of the chromyl chloride absorption. The solid state spectrum consists of $CrO_2{}^{35}Cl^{35}Cl$, $CrO_2{}^{35}Cl^{37}Cl$, and $CrO_2{}^{37}Cl^{37}Cl$ appearing in the ratio 9:6:1, respectively. Ignoring oxygen isotopes and including naturally occurring chromium isotopes, there are 12 molecular species (four chromium and two chlorine isotopes). The isotope effect usually causes band broadening.

Blazy and Levy [77] studied the rotational fine structure in the spectra of chromyl chloride and took into account all the 12 chromyl chloride species. The main feature of the longest wave region of the electronic spectra is the long progression in 141 cm^{-1}; it is attributed to the ClCrCl bending mode (ν_4) containing one quantum of 217 cm^{-1} vibration together with ν_1 (Cr–O stretching), ν_2 (Cr–Cl stretching) and ν_3 (Cr–O scissoring) modes. A long progression in the ν_4 mode, which is dominant in absorption and emission spectra, has almost the same frequency in both states. This phenomenon is usually attributed to the molecule which shows a different geometry in both states. In the case of CrO_2Cl_2, ν_4 shows almost no anharmonicity. The 217 cm^{-1} mode assigned previously to the ν_7 rocking vibrations of the CrO_2 fragment was reinterpreted by Bondybey [80] as the ν_2 (Cr–Cl) stretching mode. The latter interpretation implies a dramatic lowering of the stretching energy in the excited state (466 $cm^{-1} \rightarrow 217$ cm^{-1}). Concerning the antibonding character of the first unoccupied orbital and the appearance of this mode in the emission spectra, this interpretation seems reasonable.

A detailed analysis of the rotational structure of the excited electronic state of

CrO_2Cl_2 and the analysis of possible geometries in the ground and excited states was presented by Blazy and Levy [77]. There are four parameters determining the geometry of a molecule with C_{2v} symmetry: two bond lengths (Cr–O and Cr–Cl) and two bond angles (OCrO and ClCrCl). By measuring the rotational constants and fixing the Cr–O bond length, the authors obtained all four parameters in agreement with the antibonding character of the lowest unoccupied orbital. The ClCrCl bond angle decreases in the excited state by about 14° (the FC analysis showed a decrease of about 12° [81]).

A mass spectral analysis was reported recently by Owen et al. [87]. Samples were unradiated and radiated with a CO_2 laser. In the former case, CrO_2Cl was a primary product of decomposition. In the irradiated sample, strong traces of molecular chlorine were found. This analysis suggests an extremely low threshold for dissociation in CrO_2Cl_2.

At room temperature, the colour of liquid and gaseous chromyl chloride is very deep red [78,91]. This colour is retained when the compound is diluted with CCl_4 or other neutral solvents and results from absorption of vibrationally 'hot' bands appearing in the region of ca. 640 nm [78]. The solutions of chromyl chloride up to ca. 1.25 M obey the Lambert–Beer law and thus no solute–solvent interaction has been observed in the system [91].

Upon cooling down to 193 K, the absorption shifts hipsochromically (640→580 nm) and the colour changes to orange-red [78]. Further cooling to 77 K changes the colour to orange. The important difference between vapour, solution and the solid state is the presence of the band system at 410–420 nm in vapour and solution. The crystal spectrum does not show any significant absorption in this region. Jasinski et al. [76] observed five main absorption regions (Fig. 4): 15 000–20 000 cm^{-1} (Band I), 20 000–28 000 cm^{-1} (Band II), 28 000–40 000 cm^{-1} (Bands III and IV) and ca. 45 000 cm^{-1} (Band V). They are derived from the following transitions in T_d symmetry: $t_1 \rightarrow 2e$ (Band I), the $t_1 \rightarrow 2e$ with some overlapping of the $6t_2 \rightarrow 2e$ transition (Band II), $6t_2 \rightarrow 2e$ transition (Band III) and $5t_2 \rightarrow 2e$ transitions (Bands IV and V). The great disturbance of the structure in Band II (25 000 cm^{-1}) can be explained by strong overlapping of the states derived from different electronic transitions [76]. The totally symmetric stretching vibration at 667 cm^{-1} (Cr–O) was observed in Bands IV and V.

Chromyl chloride spectra in neutral organic solvents have been studied by Bartecki [91], and in aprotic solvents by Bartecki et al. [48,90] and Cieślak-Golonka and Golonka [83]. The band position at 418 nm (ca. 24 000 cm^{-1}) in CrO_2Cl_2 solution spectra in neutral solvents is in good agreement with that labelled as Band II in the vapour spectra [76]. However, the spectrum of CrO_2Cl_2 in aprotic solvents, e.g. acetonitrile, differs dramatically from that of the liquid, neutral solution and vapour [48,83,90,91]. The spectral range 300–600 nm exhibits two significant bands at ca. 360 and 420 nm. The higher frequency band shows well-pronounced vibrational fine structure which was recently the subject of computer analysis [90]. This structure at ca. 760 cm^{-1} and intensity (ε) of 1200 (DMF), 1400 (AN) and 730 (A) [48] can be compared with the respective values for the CrO_3Cl^- ion: ca. 750 cm^{-1} and intensity of 1300, 1200 and 1100 in DMF, AN and A, respectively [45]. Moreover, CrO_3L^{n-}-type species are well known to participate in oxidation processes with various organic compounds [49], thus this case can also be understood to be CrO_3Cl^- formation as the pre-reduction step of the chromium(VI) ion. (Chromyl chloride is one of the most popular oxidants [69,84,85].) Infrared data on CrO_2Cl_2 dissolved in aprotic solvents are also rather closer to CrO_3 or CrO_3X than to CrO_2Cl_2 in neutral solvent [45,48]. Another possibility is the formation of CrO_2Cl_2S (where S represents solvent molecule) [83] with a C_{3v} environment around the chromium atom. The most recent proposition suggests the presence of the CrO_2^{2+} chromophore in the chromyl chloride–aprotic solvent system [90].

Chromyl chloride is one of the most popular oxidizing agents towards almost all types of organic compound [69]. Applying various theoretical methods, Rappe and Goddard [89] suggested that the second oxygen atom of the CrO_2Cl_2 molecule plays a special role in the oxidation of hydrocarbons by chromyl chloride. The authors called it 'the spectator oxo group' and explained its role by comparison with the electronic structure of mono- and di-oxochromium species.

Although the investigation of this fascinating chromyl chloride molecule has solved many problems, some enigmas are still left, e.g. the order of the singlet and triplet states, full resolution of excited state geometry, molecule–molecule interaction in the solid state and the complete explanation of the CrO_2Cl_2–aprotic solvent system.

F. $CrO_4^{2-}/Cr_2O_7^{2-}$ IONIC EQUILIBRIA

During the last decade, there has been renewed interest in chromate–dichromate equilibria [50,92,93]. The existence of H_2CrO_4, $HCrO_4^-$, $HCr_2O_7^-$ species together with CrO_4^{2-} and $Cr_2O_7^{2-}$ was postulated for a long time and assumed at present in equilibrium studies of the Cr(VI) ion [92,94,136]. These equilibria between protons and ionic forms of chromium were expressed as

$$CrO_4^{2-} + H^+ \rightleftarrows HCrO_4^- \tag{9}$$

$$2\ HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O \tag{10}$$

and hence

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftarrows Cr_2O_7^{2-} + H_2O \tag{11}$$

with pH-dependent concentration of the various forms according to the proper equilibrium constants. The chromate/dichromate equilibria were investigated using various physicochemical methods, e.g. cryoscopy and conductivity. For example, Tandon et al. [92] calculated the percentage of each chromium form at a given pH.

Recently, Michel et al. [50,93] carefully examined the Raman spectra of chromate, dichromate and chlorochromate species and found that the protonated form of chromate $HCrO_4^-$ does not exist in aqueous solutions of Cr(VI) compounds. Moreover, further studies show that the hydrochromate ion, as well as H_2CrO_4 and $HCr_2O_7^-$, do not need to be considered in these solutions. From the spectroscopic point of view, the hypothetical $HCrO_4^-$ ion belonging to C_{3v} symmetry should exhibit six fundamental vibration modes, as observed in other CrO_3X-type compounds [51]. However, the authors do not observe vibrations which could be related to the $HCrO_4^-$ ion. According to the equilibrium (10), an increase of the hydrochromate concentration should be significant with dilution. The Raman spectra of the diluted solutions did not confirm the existence of any protonated form of the Cr(VI) oxoanions. Instead, the authors proposed a simple equilibrium (11) existing in the pH range between 1 and 11.

Examining Raman lines under dilution, the authors showed that at pH = 11, the Cr(VI) ion was 100% present in the form of the CrO_4^{2-} ion whereas at pH = 1.2, it was 100% as the $Cr_2O_7^{2-}$ ion. At a pH of about 6, where the existence of hydrochromate was previously postulated, the Raman spectra exhibit lines characteristic of chromate and dichromate ions. In very acidic solutions, the spectra show the presence of polychromates

$$3\ Cr_2O_7^{2-} + 2\ H^+ \rightleftarrows 2\ Cr_3O_{10}^{2-} + H_2O \tag{12}$$

$$4\ Cr_3O_{10}^{2-} + 2\ H^+ \rightleftarrows 3\ Cr_4O_{13}^{2-} + H_2O \tag{13}$$

The equilibrium constant of reaction (11) was found to be $\log \beta_{22} = 13.77 + 0{,}02$ (at 20°C and $KNO_3 = 0.8$ M). The distribution diagram obtained on the basis of β_{22} has been presented in Fig. 5.

Finally, it should be stressed that, if these results are confirmed by other methods, it would simplify significantly the important field of chromium(VI) equilibria.

G. DICHROMATES AND POLYCHROMATES

Crystallographic studies show that the $Cr_2O_7^{2-}$ ion consists of two slightly distorted tetrahedra sharing one corner. Moreover, there are two crystallographically distinct dichromate ions in the cell; they differ by 5° in the CrO_3 angle and 3.6° in the Cr–O–Cr bridge [95]. For a long time, a great similarity has been observed in the spectral characteristics of the dichromate ion and mono-substituted chromates, which suggests a similar electronic structure [39]. Thus, the O_3CrO^- chromophore in the dichromate ion with roughly C_{3v} symmetry explains this striking resemblance.

Recently it was stated that triplet excitation is localized on one half of the anion, which enhances the importance of the O_3CrO^- chromophore [96,97]. The emissive spin triplet states have recently been found in the low-temperature spectra of potassium dichromate [96–101]. The emission, absorption, excitation and optically de-

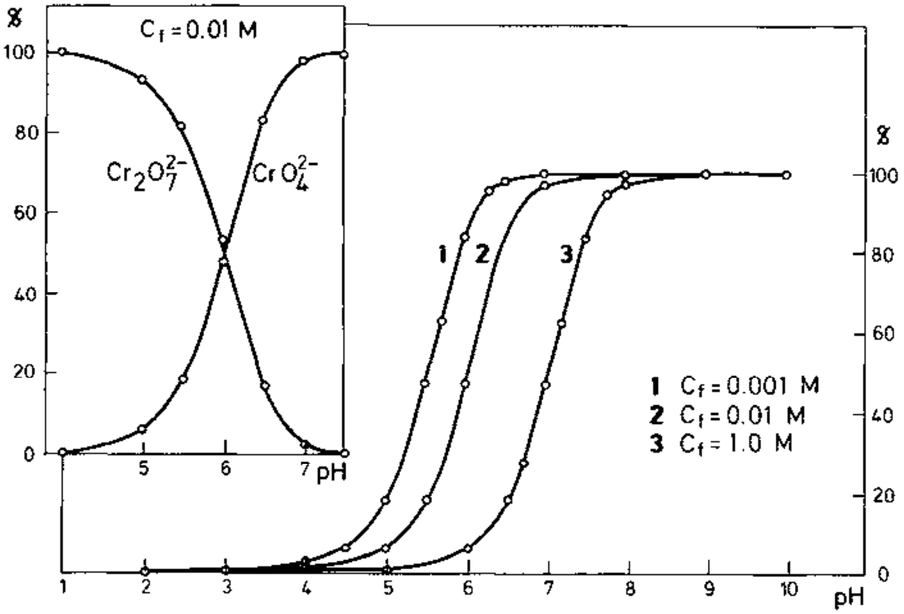


Fig. 5 Distribution curves for the Cr(VI) species versus pH [50].

tected electron magnetic resonance spectra (ODMR) were recorded, indicating the presence of triplet states. Similarly to mono-substituted chromates, the interpretation employed the energy level structure of the tetrahedral CrO_4^{2-} ion. However, as established crystallographically, in the unit cell there are two non-equivalent $Cr_2O_7^{2-}$ ions, labelled by van der Poel et al. [96] as site A and B, which have emitting triplets at 563.5 and 547.4 nm, respectively. The authors also found the lowest excited singlet states in sites A and B at 550.3 and 535 nm, respectively. Six zero-field ODMR transitions were detected and grouped into two triplets of sites A and B [54].

These studies confirmed the data of van der Poel et al. [96] that the emission was a phosphorescence resulting from two triplets. Miller and Tinti [54] and van der Poel et al. [96] also studied the kinetics of the emissive triplet state. Van der Waals and van der Poel also suggested that triplet excitation is trapped only on one half of the $Cr_2O_7^{2-}$ ion [101]. Hence the triplet state originates from the O_3CrO^- chromophore exactly as previously observed in the electronic spectra derived from transitions between singlets [39,102]. Thus the assignment of the electronic transitions in CrO_3Cl^- is also valid for the dichromate ion. Three lowest energy singlet transitions observable in the spectrum of the dichromate ion: 430 nm (22 800 cm^{-1}), 365 nm (27 400 cm^{-1}) and 273 nm (36 600 cm^{-1}) can be described as ${}^1A_1 \rightarrow {}^1E^a$, ${}^1A_1 \rightarrow {}^1A_1 + {}^1E^b$ and ${}^1A_1 \rightarrow {}^1E^c$, respectively [39]. Together with the singlet absorption region, there is long wave absorption in the 17 500–13 300 cm^{-1} region in the spectra of liquid and frozen solutions [48].

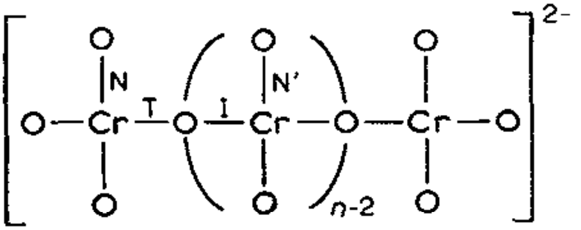
Similar to the spectra of the chromates and mono-substituted chromates, the electronic spectra of the $Cr_2O_7^{2-}$ ion in aprotic solvents show very distinct vibrational structure in the second band system (360 nm) with a mean value of $750\ cm^{-1}$ and a maximum of 9 progression members [48,102].

In highly acidic solutions. trichromate and tetrachromate units are formed (eqns. (12) and (13)). Contrary to various molybdenum and tungsten polyanions, the known chromium analogs are only trichromates and tetrachromates. Crystal data were recently collected on a number of polychromates of organic and inorganic cations [103]. Similar to the dichromate anion, they consist of tetrahedra sharing an oxygen atom.

An interesting comparison of Cr–O bond lengths for all types of Cr(VI) anions, i.e. chromates, dichromates and polychromates, was reported by Gard and coworkers [103] who found that:

(1) terminal bridging bond lengths (T-type) and inner tetrahedral bridging bond lengths (I-type) increase smoothly with growing polymerization of the chromates,

(2) non-bridging bond lengths (N-type) show a smooth decrease in Cr–O bond distance



(14)

A new series of polyoxoanions (heteropolyanions) of the type $(XCr_nO_{3n+4})^{3-}$ (X = P, As) has been obtained and crystallographically characterized by Averbuch-Pouchot and Durif [104]. The infrared and Raman spectra of compounds of this type, i.e. $HPCr_2O_{10}^{2-}$, $PCr_3O_{13}^{3-}$ and $PCr_4O_{16}^{3-}$ were recently studied by Baran and Cabello [105] and interpreted in terms of terminal CrO_3 and PO groups as well as P–O–Cr bridge vibrations. The vibrations of CrO_3 lie in the range similar to that found for the dichromate ion. The positions of the P–O–Cr bridge vibrations observed for $K_2HPCr_2O_{10}$ at $630\ cm^{-1}$ (ν_{as}) and 485, $460\ cm^{-1}$ (ν_s) are bathochromically shifted in comparison with the known Cr–O–Cr [106] and Ag–O–Cr bridge vibrations [27].

II. THE CHROMATE ION AS A LIGAND

The chromate ion belongs to a class of inorganic oxyanions whose coordination ability has been determined using available crystallographic data for various chromates [107–110] and their spectroscopic properties [27,111–116]. Since the CrO_4^{2-} anion was found to interact strongly with genetic material [137], this ability could be an important factor in understanding chromate ion toxicity.

Until now, X-ray crystallographic studies gave the most reliable information concerning the role of the chromate ion, or any oxyanion, as a potential ligand [107]. The CrO_4^{2-} ion possesses three most important factors determining the coordination ability of any anion: proper size, rigid geometry and electron donor properties, which are, however, relatively weak in comparison with traditional ligands such as water [107].

The investigation of weak-field oxyanions as ligands leads to the fundamental question of how close must the central metal and oxygen atoms of the anion be to define a coordination bond. Crystallographic studies show that, for the first row of transition metals, the M–O distance lies in the range 1.9–2.2 Å for a strong covalent bond and between 2.7 and 3 Å for the weak ones [107]. The second important factor is the degree of deformation of the oxyanion upon coordination. Generally, from X-ray studies, there are no dramatic changes in the shape of the anions: the X–O elongation is ca. 0.1 Å and O–X–O angles are changed by up to 10° (X denotes the central atom in the anion).

The free chromate ion forms a nearly regular tetrahedron with a Cr–O bond length of 1.646 Å. Table 4 shows M–O and O–Cr distances as well as OCrO angles for chromate and dichromate complexes. These results indicate that, in the chromate complexes, a rather strong covalent M–O bond (1.9–2.4 Å) is formed. However, the elongation of the bridging X–O. . .M distance as well as deviations of the OCrO angles are not significant. Thus the coordination roughly retains chromate internal

TABLE 4

M–O and Cr–O distances (in Å) and OCrO (and CrOCr) angles (degrees) in chromates and dichromates

Compound	M–O	M...O–Cr	OCrO	Ref.
$L_2Fe_2(CrO_4)_3H_2O$	1.97–2.11	1.549–1.686	106.9–110.6	108
$(NH_4)_2Cu(CrO_4)_2(NH_3)_2$	2.022–2.425	1.636–1.686	108.05–110.4	109
$[Cu_3(CrO_4)_3(OH)_2(py)_2]$	1.942–2.459	1.621–1.694		110
$K[Fe(CrO_4)_2]H_2O$	1.97–2.11	1.67	107.71–111.22	120
$(SnMe_3)_3(OH)CrO_4$	2.16, 2.29	1.78–1.70		138
$(SiPh_3)_2CrO_4$		1.51, 1.57		139
$[L_2Fe_2O(CrO_4)_2]4H_2O^a$	1.819	1.615–1.664		121
$[Ag_2CrO_4]$	2.34–2.62	1.63–1.6912		127
$[HgCrO_4]$	2.097–2.121	1.70	107–112	122
$[CuCrO_4]$	1.965–2.4	1.599–1.731	108.9–111.3	123
K_2CrO_4	2.681–3.660	1.637–1.648	108.68–109.99	124
$Cu(en)_2Cr_2O_7$	2.5–2.5	1.597–1.790	127.0(CrOCr)	125
$K_2Cr_2O_7$	3.25–3.82	1.79–1.240	127.6(CrOCr)	126
$(NH_4)_2Cr_2O_7$	2.853–3.493	1.781	121	127
$Ag_2Cr_2O_7$	2.37–2.67	1.67		128

[a] L = organic ligand.

geometry. The data for $Cu(en)_2Cr_2O_7$ (Table 4) suggest that the Cu–O bonds are significantly longer than the respective bonds in the chromate complexes, and indicate the weaker coordination of the $Cr_2O_7^{2-}$ unit. This conclusion was supported by IR data [113] and, indirectly, by electronic spectra [117].

Next to X-ray studies, the important techniques with which to analyze the coordination ability of oxyanions are infrared and Raman spectroscopy. Generally, the coordinated cation affects the XO_4^{n-} anion by altering the stretching modes or distorting its tetrahedral structure. Since slight changes of the symmetry of an anion effectively influence its vibrational spectra, this method can sometimes be a more sensitive structural probe than the diffraction studies (Table 5). The degenerate mode

TABLE 5

Band position (in cm^{-1}) assigned to Cr–O vibration in chromate complexes

Compound	ν_1	ν_3	ν_2	ν_4	Ref.
$[Co(NH_3)_5CrO_4]Cl$	875	915	340	373	112
		875		358	
$[Co(NH_3)_4CrO_4]NO_3$	850	944	350	398	112
		925			
		893			
$[Co(NH_3)_5CrO_4]Br$	870	917			113
		900			
$[Co(en)_2CrO_4]Cl$	830	930			113
		900			
$[Cr(NH_3)_5CrO_4]NO_3$	870	900–915			
		900–905sh	370	460	114
		805–810			
$[Cr(NH_3)_4CrO_4]ClO_4$	890	935–940	370	440–450	114, 115
$[(CH_3)_2SnCrO_4]$	845	975		465	111
		928	305	390	
		880		348	
$[(CH_3)_2SbCrO_4]$	700?	964		420	111
		940		390	
		838		355	
$[L_2F_2(CrO_4)_3]H_2O$[a]	780	945			108
		905			
		840			
$[Ag_2(HMTA)CrO_4]$	825	930		395	27
		900		385	
		865	358	368	
$[Ag_2(4,4\ bpy)CrO_4]$	830	950	360	385	27
		930		378	
		860			

[a] L = organic ligand.

of vibration of the free tetrahedral ion resolves into non-degenerate components in lower symmetries as shown in the scheme in Sect. C. Sometimes, coordination causes small or no splitting of the bands but only shifts in band position. However, the spectra usually become richer with new bands of various intensity.

For C_{3v} and C_{2v} symmetries all the vibrational modes are IR and Raman active. Thus for a monodentate $OCrO_3^{-2}$ we expect ν_3 and ν_4 to split into doublets and ν_1 should be activated in IR. For bidentate $O_2CrO_2^{2-}$, ν_1 should be activated in IR, and ν_2 split into a doublet whereas ν_3 and ν_4 split into triplets. The results included in Table 5 show that ν_3, the totally symmetric Cr–O vibration at ca. 850 cm^{-1}, splits into doublets and triplets, suggesting monodentate or bidentate coordination of the chromate anion, respectively. However, the effect of the splitting is not evident in the ν_2 and ν_4 frequencies. These bands are not always split as expected and sometimes do not appear at all.

Generally, ν_1 and ν_3 frequencies increase upon coordination as the M–O–Cr bond formation causes an increase of the degree of multiple bonding in the remaining CrO_x unit (a decrease of the Cr–O terminal bond length).

In the vibrational spectra, one may expect modes associated with the Cr–O–M bridge (both in monodentate and bidentate) or with the $Cr < \substack{O \\ O} > M$ (bidentate chelate) ring. The position of the bridge vibrations can be elucidated roughly from the well-known transitions of the Cr–O–Cr bridge in the dichromate ion: $\nu_{as} = 770$ cm^{-1} and $\nu_s = 550$ cm^{-1} [106,117,118]. The ν_{as} mode in the $Cr_2O_7^{2-}$ ion is very strong and suggests the presence of considerable multiple bonding in the Cr–O–Cr linkage. On that basis, bands at 818 and 601 cm^{-1} in $[Co(NH_3)_5CrO_4]^+$ were ascribed to the ν_{as} and ν_s vibrations in the Cr–O–Co bridge, respectively [112]. For the bidentate bridging complexes $[Ag(HB)_xCrO_4]$ (HB = heterocyclic base), ν_{as} vibrations were found as strong bands at 790 and 801 cm^{-1} in $[Ag_2(HMTA)CrO_4]$ and $[Ag_2(4,4'bpy)CrO_4]$, respectively [27].

The conclusions concerning chromate coordination in silver chromate complexes with heterocyclic amines are consistent with UV–Vis spectra studies. The Ag–O interaction present in parent Ag_2CrO_4 is also observed in the complexes [27]. On the other hand, heterocyclic ligands evidently destroy weaker Ag–O(Cr_2O_7) bonds. Thus spectroscopic observations [113,117] of the lower coordination tendency of the dichromate anion in comparison with the chromate are in line with the X-ray data (Table 4).

The Cu^{2+}–L–CrO_4 interaction has only recently been studied with the crystal structure [109,110] and spectroscopic properties [38] of copper chromate complexes. From the data presented in Table 4, it is clear that these compounds also form strong covalent Cu–O(CrO_4) bonds. On the other hand, on the basis of IR studies (Fig. 6) the Cu–O–Cr bridge vibrations are in accordance with known Cr–O–Cr [106], Ag–O–Cr [27] and Fe–O–Fe bonding modes [119]. Unexpectedly, all the M–O–M vibrations are found almost in the same region, which seems to be a characteristic feature for the metal–oxide bridges.

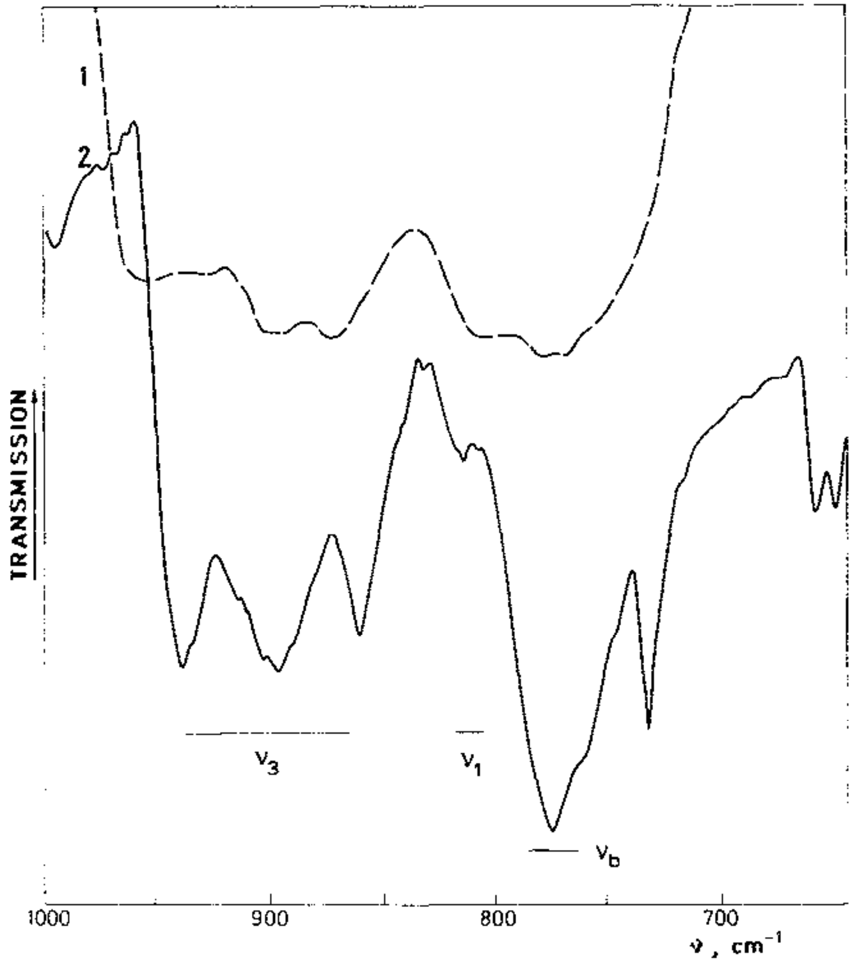


Fig. 6 Infrared spectrum of $CuCrO_4$ (1) and $(Cubpy_2)_2CrO_4Cl_2$ (2).

Some attempts have been made to determine the mode of coordination in the case of bidentate chromate complexes. Infrared studies can only imply coordination or not. A simultaneous distinction between bridging or chelating structures is not obvious [107]. However, the geometry of the CrO_4^{2-} ion significantly prefers the bridging structure; only in $[Co(NH_3)_4CrO_4]NO_3$ has the bidentate chelating coordination of the chromate ion been suggested [112].

In probing the coordination ability of any oxyanion from vibrational analysis, one should remember that the bands can also be split under the influence of the crystal lattice. However, these splittings appear to be rather small. Finally, underlying the sensitivity of the spectroscopic technique in determining the coordination of the anions, only by using multiple methods, e.g. X-ray, IR, Raman, NQR etc., is it possible to obtain the most reliable picture of the behaviour of the oxyanion as a ligand.

I. SPECIFIC CATION–ANION INTERACTIONS IN SILVER CHROMATE COMPLEXES

The importance of cation–anion interactions in Ag_2CrO_4 and other post-transition metal chromates is evident from the insolubility of the compound in polar solvents. Generally, the depth of colour increases with the covalent character of the metal–ligand bonds [129]. Both silver salts as well as other post-transition metal compounds exhibit a variety of colours attributed to covalency of the bonds. Table 4 shows the Ag–O bond distances together with the respective distances in alkali metal salts. The former are shorter, as expected.

The cation–anion interaction in Ag_2CrO_4 and $Ag_2Cr_2O_7$ as well as its complexes with heterocyclic ligands have been studied by resonance Raman (RR), IR and electronic spectra [27,134,135]. In the electronic spectra of single crystal and powdered Ag_2CrO_4, a long-wave absorption band at ca. 450 nm is observed. The nature of this band was the subject of various interpretations.

(a) an inter-ionic charge transfer $M \rightarrow O(CrO_4)$ transition [130,131]

(b) due to the lower symmetry in Ag_2CrO_4 [132]

(c) as a bathochromic shift of the 360 nm CT transition in the tetrahedral chromate ion due to strong Ag–O interaction (the so-called second-order Davydow effect [133]). The 450 nm band has been studied by Clark and Dines [134] using RR experiments. Under resonance conditions, the $\nu_1(a_1)$ band is enhanced without any overtone progression, in contrast to yellow alkali metal chromates. The excitation profiles maximise over 5000 cm^{-1} to the red. No bands attributable to the Ag–O stretching modes have been observed in the vibrational spectra but lower frequency shifts of the Cr–O modes are connected with shortening of the cation–oxygen bond in comparison with alkali metal chromates. The lack of progression in the RR spectra is explained by the presence of the significant Ag–O covalent bond restricting any structural changes in the excited state. Thus strong interactions favour fast vibrational relaxation. Moreover, the authors suggest a semi-conducting character for the 450 nm CT band as observed in other compounds [134].

Some interesting results have been obtained from the study of the influence of the matrix on the 450 nm band in Ag_2CrO_4 [135]:

(1) matrices such as NaBr containing small cations and anions fully exchange silver ion in the compound,

(2) compounds with big organic and inorganic cations, e.g. $(CH_3)_4N^+$, Cs^+, partly exchange silver ion. One can observe both 'Ag_2CrO_4' (450 nm) and 'K_2CrO_4' (360 nm) bands in the spectra, and

(3) matrices with big anions (Li_2CO_3, Ag_2SO_4) retain the spectral characteristics of Ag_2CrO_4.

The results of the electronic spectra studies on silver chromate and dichromate complexes $Ag_2(HB)_xCrO_4$ (HB = heterocyclic base: 2,2′-bpy, 1,10-phen, 4,4′-bpy and HMTA) show that, on the basis of the spectra, the complexes can be divided into two groups:

(1) red $Ag_2(HB)_xCrO_4$-type complexes (HB = 2,2′-bpy, 1,10-phen) with a strong, broad 500 nm band, and

(2) yellow $Ag_2(HMTA)CrO_4$ and $Ag_2(4,4'\text{-bpy})_3CrO_4$ with the 360 nm band.

A colour dependence upon the number of ligand molecules (nitrogen atoms N) attached to silver ion has been found for silver dichromate complexes with heterocyclic ligands: M:N = 1 or 2 for red coloured and 3 for yellow coloured [117].

A comparison of the influence of ligand attack in Ag_2CrO_4 and $Ag_2Cr_2O_7$ shows that the former is more resistant towards ligand attack than the latter. Ag_2CrO_4 in its red complexes retains, to a great extent, its spectral characteristics [27]. For example, the RR effects in the spectra of $Ag_2(HB)_2CrO_4$ measured at three different lines (514.5, 488.0, and 457.9 nm) display only two strong lines at 812.0 and 778.0 cm^{-1}, exactly as in Ag_2CrO_4 itself. This means that the electronic band around 500 nm results only from transition in the chromate ion [135].

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