Inorganica Chimica Acta, *180* (1991) 133–138

Applications of polymer films and Nujol mulls to spectroscopic studies at low temperatures: electronic spectra of chromate, dichromate, chlorochromate, manganate and permanganate ions at 12–77 K

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(Received May 21, 1990; revised November 15, 1990)

Abstract

Electronic absorption spectra have been obtained for chromate, dichromate, chlorochromate, manganate and permanganate ions in argon and dinitrogen gas matrices, poly(vinyl alcohol) films and Nujol mulls at *c.* 12 and 77 K. All the ions showed well resolved vibrational progressions. There was a good correspondence for the data for caesium chromate between frozen gas matrices, polymer films and Nujol mulls and that previously obtained using single crystals, doped crystals and thin films. The relative ease, speed and inexpensiveness of procedures using polymer films and particularly mulls, which are described for the first time, makes them ideal for low temperature studies especially where gas matrix, organic glass and doped crystal studies are not feasible, e.g. potassium chlorochromate which is not volatile and which disproportionates in solution.

Introduction

The ideal conditions for observing vibrational structure on electronic absorption bands are: (i) in the gas phase at low pressures and (ii) at low temperatures, preferably well below ambient. Unfortunately very few metal compounds and complexes, especially ionic compounds and complexes, are sufficiently volatile to give gas phase electronic spectra and many decompose on attempted volatilisation.

A situation which closely mimics the isolation of molecules in the gas phase is the matrix isolation technique [1]. In this technique substrate molecules are isolated from each other by a large excess of inert host matrix molecules at low temperatures. The preferred host matrix materials are the noble gases, N_2 and CH_4 operating at 10–20 K. The matrix isolation technique, however, still requires that the substrate molecules should be volatile and this requirement excludes the majority of inorganic compounds and complexes.

An alternative approach to gas matrices is to disperse the substrate molecules in other media, e.g. organic glasses, paraffin wax, polymer films, alkali halide discs, crystalline films and doped crystals. Cooling such media affords band sharpening and the possibility of resolving vibrational progressions.

All of the alternative media have drawbacks. For example, inorganic salts do not always dissolve in the solvents used to make organic glasses, alkali halide discs are often very scattering in the ultraviolet (UV) region and growing doped crystals is an art.

In this paper we describe, for the first time, the use of Nujol mulls at 12–77 K to obtain vibrational data for inorganic ionic compounds. We present a comparative study for Cs_2CrO_4 in Nujol mulls, poly(vinyl alcohol) (PVA) films and gas matrices with respect to doped crystals and thin crystalline films [2–6] in order to demonstrate the validity of the alternative media approach. We also describe applications of the Nujol mull technique to compounds which do not sublime, e.g. $KMnO_4$, K_2MnO_4, $K_2Cr_2O_7$ and $KCrO_3Cl$. The use of Nujol mulls at cryogenic temperatures to trap and characterise unstable species using infrared (IR) spectroscopy has been described elsewhere [7].

Experimental

Low temperatures were achieved using a simple glass cryostat (77 K; Applied Photophysics Model

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#700 [8]) or a cryostat cooled by a closed-cycle liquid helium refrigerator (*c.* 12 K; Air Products and Chemicals Inc Model Displex CSCS-202).

Gases for matrices were obtained from B.O.C. Special Gases Ltd. (Ar, N_2; 99.9999% pure).

Samples were obtained commercially (B.D.H. Chemicals Limited, AnalaR grade) with the exceptions of K_2MnO_4 and $KCrO_3Cl$, which were provided by Professor C. Barra and Dr W. Levason, respectively.

Gas matrices containing Cs_2CrO_4 and K_2CrO_4 were obtained by vapourising the metal chromates (Cs_2CrO_4 at *c.* 150 °C and K_2CrO_4 at *c.* 250 °C) and co-condensing the vapour with large excesses of Ar and N_2, fed into the cryostat via a high precision needle valve, and condensed onto cooled CaF_2 and quartz sample windows.

Poly(vinyl alcohol) (PVA, B.D.H. Chemicals Ltd.) films containing the metal salts were prepared by dissolving samples of PVA (*c.* 1.25 g) in H_2O (50 ml) at 65 °C with vigorous stirring. After cooling the resulting solution to 25 °C and degassing it with N_2, aliquots of the PVA solution (10 ml) were taken and in them varying amounts of solute (0.1–50 mg) were dissolved. Aliquots (5 ml) of the resulting solutions were pipetted into flat glass petridishes (crystallising dishes) which were maintained horizontally so as to produce films of even thickness. The dishes were left in the dark with a stream of dry N_2 passing over them until they had dried. Once the films had dried they were removed from the petri-dishes, cut to size using a Pyrex disc (25 mm diameter) as a template for the spectroscopic windows, and mounted between two spectroscopic windows (25 mm diameter) in the appropriate cryostat.

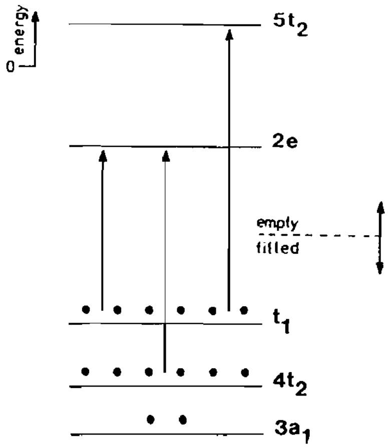
Nujol mulls containing metal salts were prepared by grinding known weights of samples (*c.* 1 mg) in an agate pestle and mortar (at least 1 min) adding two drops of Nujol, and grinding further (5 min). The resulting mull was placed between two spectroscopic windows which were inserted into the window holder. It was found to be essential that the cryostat was not pumped for too long before applying the cooling otherwise there was a tendency for the Nujol to be pumped from between the plates.

Electronic spectra were recorded using a Perkin-Elmer Lambda 7 spectrometer connected into a Perkin-Elmer 3600 data station.

Results

Comparative study of the electronic spectra of Cs_2CrO_4 in a variety of low temperature media at 12–77 K

The UV–Vis absorption spectrum of Cs_2CrO_4 in aqueous solution showed four bands in the region above 200 nm at 254 (shoulder, $\epsilon = 3000$), 272 (3700), 371 (4800) and 420 (300) nm in agreement with previous work [9, 10]. These bands have been assigned to the allowed singlet transitions ($t_1 \rightarrow 5t_2$, $4t_2 \rightarrow 2e$, $t_1 \rightarrow 2e_1$, respectively) and to the forbidden triplet transition ($t_1 \rightarrow 2e$) as defined in the schematic molecular orbital diagram shown in Scheme 1 [11].



Scheme 1.

The UV–Vis spectrum of Cs_2CrO_4 as a PVA film (15 mg of Cs_2CrO_4 in 250 mg of PVA) at 12 K is shown in Fig. 1. Vibrational fine structure is clearly visible on the bands centred at *c.* 260 and 360 nm. Figures 2 and 3 show expansions of these two regions together with second derivative spectra which were used to calculate the vibrational progressions. Both caesium and potassium salts of the CrO_4^- anion were used in this investigation but higher resolution vibrational progressions were observed for the caesium salt as had been noted previously by Johnson and McGlynn in their work on crystalline films [3].

The band positions within the vibrational progressions for Cs_2CrO_4 are given in Table 1 together with the average intervals. Both bands show an average interval of 825 cm^{-1}. This fine structure has been assigned by a number of authors to the A_1 totally symmetric Cr–O stretching mode of the various excited states [11]. In the ground state this mode appears at 847 cm^{-1} [12]. The reduction in the vibrational frequency for the excited state has been correlated with the fact that these states involve promotion of a non-bonding π-electron into an antibonding molecular orbital.

The reduction in the A_1 symmetric vibrational frequency in the excited state was much more in PVA films than in Nujol mulls where a vibrational progression of 720 ± 30 cm^{-1} was observed (Table 2). Interestingly, the Nujol mull result agreed well with the previous work of Johnson and McGlynn

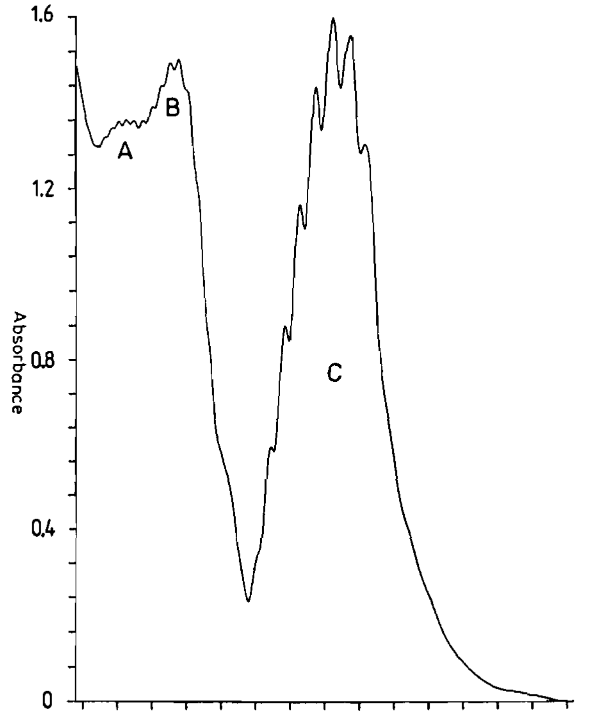


Fig. 1. The absorption spectrum of Cs_2CrO_4 in a PVA film (15 mg in 250 mg PVA) at *c*. 12 K showing the three principal absorption bands (A, B and C) with vibrational progressions.

[3] who used thin crystalline films deposited on optically flat surfaces ($\bar{\nu}=730$ cm^{-1}). This value was slightly lower than the results for doped crystals ($\bar{\nu}=750$–800 cm^{-}) [2, 4–6]. The thin crystalline films were deposited by controlled evaporation of aqueous solutions spread over plates.

Co-condensation of Cs_2CrO_4 with excess Ar and N_2 at *c*. 12 K afforded good optically transparent matrices but superior resolution in the vibrational progressions was achieved using N_2 matrices (Table 2).

Electronic spectra of $KMnO_4$ and K_2MnO_4 in PVA films and Nujol mulls at 12–77 K

Attempts to obtain UV–Vis spectra for MnO_4^- and MnO_4^{2-} ions in Ar and N_2 matrices were unsuccessful because the salts would not sublime. Even resorting to a heavier cation gave no improvement, cf. the lower subliming temperature of Cs_2CrO_4 compared to K_2CrO_4. This illustrates the need for some other means of obtaining vibrational data.

PVA films and Nujol mulls both afforded good quality UV–Vis spectra with resolved vibrational progressions. Similar values for the excited state vibrational symmetric stretching vibrations were ob-

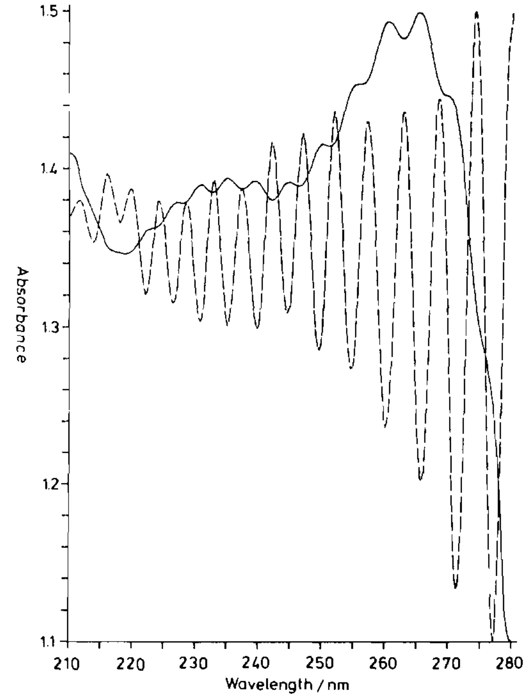


Fig. 2. An expansion of bands A and B for Cs_2CrO_4 in a PVA film at *c*. 12 K: absorption spectrum (——) and second derivative spectrum (– – –).

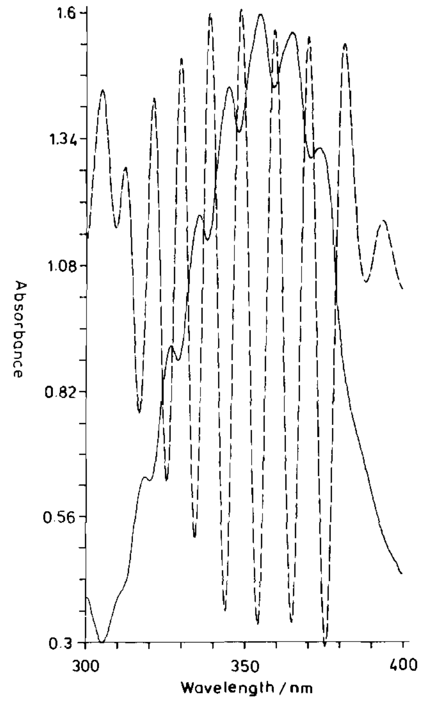


Fig. 3. An expansion of band C for Cs_2CrO_4 in a PVA film at *c*. 12 K: absorption spectrum (——) and second derivative spectrum (– – –).

TABLE 1. The vibrational structure observed in the absorption spectrum of Cs_2CrO_4 as 15 mg PVA film at *c.* 12 K

Assignment[a]	Band position (nm)	Band position (cm^{-1})	Interval (cm^{-1})
$^1A_1 \rightarrow {}^1T_2$	266.0	37590	
$(4t_2 \rightarrow 2_e)$	260.0	38460	870
	254.6	39280	820
	249.5	40080	800
	244.5	40900	820
	239.7	41720	820
	235.0	42550	830
	230.8	43330	780
	226.4	44170	840
	222.0	45050	880
	218.0	45870	820
	214.0	46720	860
Average = 830 ± 30 cm^{-1}			
$^1A_1 \rightarrow {}^1T_2$	388.0	25770	
$(t_1 \rightarrow 2_e)$	376.4	26570	800
	365.0	27400	830
	354.1	28240	840
	343.9	29080	840
	334.1	29930	850
	325.5	30720	790
	317.0	31550	830
	309.0	32360	810
Average = 825 ± 20 cm^{-1}			

[a] From ref. 11.

TABLE 2. Comparison of the electronic spectral band positions and vibrational structure observed in the absorption spectra of Cs_2CrO_4 in a variety of low temperature media at *c.* 12–77 K

Medium	Temperature (K)	λ_{max} (nm)	Vibrational splitting (cm^{-1})
N_2 matrix	12	360.5	720 ± 15
Ar matrix	12	359	815 ± 30
PVA film	77	354	820 ± 40
PVA film	12	354	825 ± 20
Nujol mull	77	378	725 ± 50
Nujol mull	12	379	720 ± 30
Crystalline film[a]	77	366	720 ± 20
Doped crystals[b]	20	358	790 ± 10

[a] Data from ref. 3. [b] Data from ref. 2; CrO_4^{2-} doped into K_2SO_4.

TABLE 3. The vibrational structure observed in the absorption spectra of a range of $(MO_4)^{n-}$ ions (M = Cr, n = 1; M = Mn, n = 1 or 2) as both PVA films and Nujol mulls at *c.* 12 and 77 K

Compound	Medium	Temperature (K)	Vibrational splitting (cm^{-1})
K_2CrO_4	PVA	77	810 ± 40
K_2CrO_4	Nujol	77	720 ± 40
K_2CrO_4	PVA	12	820 ± 30
K_2CrO_4	Nujol	12	720 ± 30
Cs_2CrO_4	PVA	77	820 ± 40
Cs_2CrO_4	Nujol	77	725 ± 50
Cs_2CrO_4	PVA	12	825 ± 20
Cs_2CrO_4	Nujol	12	720 ± 30
$KMnO_4$	PVA	77	820 ± 20
$KMnO_4$	Nujol	77	730 ± 25
$KMnO_4$	PVA	12	830 ± 10
$KMnO_4$	Nujol	12	725 ± 10
K_2MnO_4	Nujol	77	730 ± 40[a] 370 ± 40[b]
K_2MnO_4	Nujol	12	740 ± 30[a] 370 ± 30[b]

[a] Observed on the first charge transfer band of the $^2T_2$ excited state between 15 000–20 000 cm^{-1}. [b] Observed on the ligand field band of the $^2T_2$ excited state below 15 000 cm^{-1}.

served for the MnO_4^- ion as for the CrO_4^{2-} ion, including the high (PVA)/low (Nujol) trends (Table 3). The Nujol mull technique afforded satisfactory spectra for K_2MnO_4, which was not amenable to the casting PVA films because it decomposed in H_2O.

The data for the PVA films and Nujol mulls agreed reasonably well with previously reported data from doped crystal studies [13–18]. Data from PVA films always gave higher values for vibrational progressions. Resonance Raman studies on the same molecules in crystalline media [19–21] yielded values for the totally symmetric mode close to those of the PVA films rather than those obtained with crystalline samples.

Electronic spectra of $K_2Cr_2O_7$ and $KCrO_3Cl$ in PVA films and Nujol mulls at 12–77 K

Neither $K_2Cr_2O_7$ nor $KCrO_3Cl$ was volatile and thus did not afford UV–Vis spectra via the gas matrix isolation technique. Indeed the latter compounds decomposed to yield CrO_2Cl_2 on attempted volatilisation while in aqueous solution it is readily hydrolysed to give $CrO_3(OH)^-$ [22]. Studies using alternative low temperature media were, therefore, essential for investigating whether $Cr_2O_7^{2-}$ and CrO_3Cl^- ions give rise to vibrational progressions in their electronic absorption bands.

Potassium dichromate was studied in PVA films and Nujol mulls while $KCrO_3Cl$ was only studied in a Nujol mull because of the hydrolysis problem. In both cases well-resolved spectra were obtained and the frequencies of the metal–oxygen vibrations in the vibrational progressions were similar to those already observed for the series of MO_4^{n-} ions (Table 4). The vibrational frequencies obtained from Nujol

TABLE 4. The vibrational structure observed in the absorption spectra of $K_2Cr_2O_7$ and $KCrO_3Cl$ as PVA films and Nujol mulls at *c.* 12 and 77 K

Compound	Medium	Temperature (K)	Vibrational splitting (cm^{-1})
$K_2Cr_2O_7$	PVA	77	$830+30$
$K_2Cr_2O_7$	Nujol	77	750 ± 35
$K_2Cr_2O_7$	PVA	12	820 ± 20
$K_2Cr_2O_7$	Nujol	12	760 ± 20
$KCrO_3Cl$	Nujol	77	750 ± 40
$KCrO_3Cl$	Nujol	12	760 ± 30

mull spectra were slightly lower than comparable studies using crystals [23–25] while those from PVA studies were closer to ground state values [26, 27].

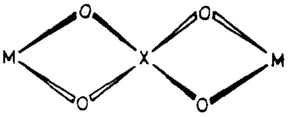
Discussion

The use of polymer films for studying absorption spectra of inorganic compounds and complexes is not new but this is the *first* report of work with Nujol mulls. The transition metal MO_4^{n-} ions were selected for the comparative study because their spectra have been extensively investigated in early attempts to determine the general rules governing the ordering of energy levels in a simple tetrahedral species [9, 11] and also because a number of theoretical calculations have been performed [10, 28–31]. In fact investigations of MO_4^{n-} ions have been so prolific that such ions have come to be regarded as test-bed molecules for new theoretical modelling techniques [32, 33].

The resolution achieved for the vibrational progressions of Cs_2CrO_4 in PVA films and Nujol mulls was superior to that for Ar matrices and at least as good as that for N_2 matrices. It was observed that the resolution was higher for 12 K than at 77 K. The quality of the data obtained from PVA and Nujol mull experiments was also as good as that previously reported for unpolarised doped crystal experiments. An advantage of doped crystal studies is that by aligning a single crystal detailed polarisation measurements can be carried out. In situations where single or doped crystal cannot be grown techniques using polymer films and Nujol mulls have the potential to produce good quality UV–Vis data quickly.

A closer examination of the data for CrO_4^{2-} ions in Table 2 reveals no immediate systematic trends (see below). For example, N_2 and Ar matrices which should afford discrete isolated species gave almost identical values of λ_{max} while their values for the vibrational splitting were very different, cf. in doped crystals λ_{max} is definitely dependent on the doping crystal (KCl/CrO_4^{2-} at 335 nm, KBr/CrO_4^{2-} at 355 nm and KI/CrO_4^{2-} at 365 nm) but there is little change in the vibrational splitting (800 cm^{-1}) [4]. It might appear that a PVA film resembles an Ar matrix and a doped crystal while a Nujol mull resembles a N_2 matrix. It was expected that the data for Nujol mulls would be very similar to those for crystalline films, since crystalline/microcrystalline particles are involved,and this expectation was fulfilled.

Infrared studies of MO_4^{n-} ions in doped crystals of D_{2h} symmetry showed that the dopant species underwent a reduction from the 'ideal' T_d to C_s in the host crystal lattice as a result of the site symmetry [34]. Gas matrix isolation studies of vapour phase K_2MO_4 (M = Cr, Mo, W) co-condensed with either Ar or N_2 have established that the salts are isolated as discrete molecules adopting D_{2d} geometry (Scheme 2) in the matrix with bands for K_2CrO_4 at 893.4 and 874.8 cm^{-1} (Ar matrix [35]; compared to 890 cm^{-1} for the 'free ion' [36]). No such doublet splitting indicating D_{2d} geometry was detected in the best resolved UV–Vis spectra of any of the ions in this work.



Scheme 2.

The most likely contributions to the discrepancy between the values of the symmetric stretching vibration progressions obtained from polymer film studies compared to those from crystalline sampling studies, including Nujol mulls, are: (i) in crystalline systems (doped crystals and Nujol mulls) the MO_4^{n-} ions will experience greater cooperative effects by virtue of the crystal lattice; (ii) the MO_4^{n-} ion local symmetry would appear to be probably higher for a polymer film sample ('free ions') than for solid crystalline phases [11]; (iii) ions are likely to be in more spacious isolation sites in polymer films than in crystalline systems, i.e. the tight 'cage' of the lattice has a more pronounced solvent effect. Consistent with this latter factor is the fact that a N_2 matrix will have smaller sites and thus tighter packing than the sites in an Ar matrix. Further work with other matrices, e.g. Kr, Xe, O_2, CH_4, CF_4 and SF_6 will be undertaken in order to attempt to clarify this matter.

Conclusions

Polymer films and various mulls (Nujol, chlorocarbon, fluorocarbon, poly(propylene oxide)) would seem to have considerable potential as media for obtaining highly resolved spectra as well as affording the means to trap and characterise unstable species [7, 37] in situations where gas matrices and organic glasses are inappropriate.

The relative ease and inexpensiveness of experiments using polymer films and various mulls at 77 K, especially when used in conjunction with a simple glass cryostat, makes them ideal for demonstrations and teaching experiments in addition to their applications in primary research. A particularly important potential application for polymer film and mull spectroscopic studies is in relation to chemical reactions and their mechanistic pathways in natural and man-made polymers and membranes [38].

Acknowledgements

We thank the S.E.R.C. for a studentship (to A.K.C.) and support (to A.J.R.) and the Universidad Tecnica Federico Santa Maria for support (to M.A.O.). We also thank Professor C. Barra and Dr W. Levason for the gifts of compounds and The British Council for a travel grant (to A.J.R.) and sabbatical study support (to M.A.O.) under the Link Scheme.

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