Matrix Isolation and Mass Spectrometric Studies on the Vaporisation of Chromium(III) Chloride. The Characterisation of Molecular $CrCl_4$ and $CrCl_3$†

J. Steven Ogden * **and Robert S. Wyatt**
Department of Chemistry, The University, Southampton SO9 5NH

Mass spectrometric and matrix isolation i.r. studies on the vaporisation of solid chromium(III) chloride over the temperature range 550—800 °C reveal three different molecular chromium halides. At the lowest temperatures, $CrCl_4$ is identified as the most volatile species and its tetrahedral structure confirmed by isotope patterns. At *ca.* 600 °C, a new molecular species, $CrCl_3$, appears and its structure is similarly shown to be planar (D_{3h}). Further heating to *ca.* 780 °C results in the formation of molecular $CrCl_2$. The results are discussed in the light of previous studies on transition metal halide systems.

It has been known for many years[1-4] that heating anhydrous chromium(III) chloride in the presence of chlorine produces a higher chromium chloride in the vapour phase, and several thermodynamic studies based on vapour pressure measurements have been carried out assuming equilibria of the type (1)—(3). However, although a brown solid with a composition

$$2\,CrCl_3(s) \rightleftharpoons 2\,CrCl_2(s) + Cl_2(g) \qquad (1)$$

$$2\,CrCl_3(s,g) + Cl_2(g) \rightleftharpoons 2\,CrCl_4(g) \qquad (2)$$

$$2\,CrCl_3(s,g) \rightleftharpoons CrCl_2(s) + CrCl_4(g) \qquad (3)$$

Cr:Cl approaching 1:4 may be obtained from these high-temperature systems by rapid quenching,[2] it is only relatively recently that firm spectroscopic evidence for molecular $CrCl_4$ has been obtained.[5] Chromium(II) chloride is known to vaporise[6] as a mixture of monomeric $CrCl_2$ and dimeric Cr_2Cl_4, but nothing is known about molecular $CrCl_3$.

As part of our research programme on the stabilities and shapes of transition metal halide molecules, we became interested in the vaporisation of chromium(III) chloride. On the basis of the earlier thermodynamic studies, this system might be expected to produce molecular $CrCl_4$ and $CrCl_2$ under appropriate conditions, and additional species such as $CrCl_3$ or Cr_2Cl_6 could also be present. A combination of mass spectrometry and matrix isolation i.r. spectroscopy was therefore used to study the vaporisation of anhydrous chromium(III) chloride *in vacuo*, and supporting experiments were also carried out on anhydrous chromium(II) chloride. The aim of this research was first to identify any new chromium chloride species which might be present in the vapour, and secondly to establish their shapes using i.r. selection rules together with a detailed study of chromium and chlorine isotope frequency shifts.

Experimental

The samples of anhydrous chromium(III) chloride used in these experiments were obtained by direct reaction between chlorine and chromium using standard procedures,[7] and also from a commercially available source (Fluka >97% pure), whilst anhydrous chromium(II) chloride was obtained by reduction of the trichloride.[7] Both materials were extensively degassed at *ca.* 450 °C *in vacuo* prior to use.

In both the mass spectrometric and matrix isolation studies, samples were vaporised from silica holders heated to *ca.* 550—800 °C by an external furnace. However, in contrast to our previous studies on high-temperature systems, it was found that the matrix i.r. spectra obtained from chromium(III) chloride were dependent on the geometry of the sample holder. In particular 'free' vaporisation from a relatively large diameter silica tube (>6 mm) yielded spectra significantly different from those obtained with the tube 'stopped down' to a diameter of *ca.* 1—2 mm. These two types of experiment, and a possible explanation for this behaviour, are discussed later.

The mass spectrometer used in these studies was a VG SXP 400 quadrupole instrument, modified so that its (analog) output could be fed directly into the a–d converter in a BBC B+ computer. This method of data collection was not only very convenient in terms of cost, speed and sensitivity, but allowed the possibility of spectral averaging, and easy manipulation and storage.

High purity nitrogen and argon (BOC 99.999%) were employed as matrix gases in the i.r. studies, and deposition times were typically *ca.* 30—60 min. During this period, the central caesium iodide window in our cryostat was maintained at *ca.* 12 K, and spectra were subsequently recorded using PE 225 and 983G spectrometers. Matrix deposits were warmed to *ca.* 30 K during diffusion studies.

Results

When anhydrous chromium(III) chloride is heated in a 4-mm diameter silica tube *in vacuo*, its mauve colour darkens considerably, and at a temperature of *ca.* 560 °C chlorine gas is evolved, and a brown sublimate may be observed on the cooler walls of the tube. Further heating to *ca.* 620 °C results in the appearance of a mauve sublimate, and if this temperature is maintained, the remaining residue turns white. On further increasing the temperature to *ca.* 780 °C, this residue also sublimes to give a white deposit, which on analysis, proves to be anhydrous chromium(II) chloride.

The molecular beam mass spectrum (70 eV) obtained at *ca.* 560 °C using a relatively small diameter orifice (*ca.* 2 mm) shows intense signals due to Cl_2^+ (70, 72, 74 a.m.u.) and prominent clusters at 124, 159, and 194 a.m.u. These heavier ion peaks show isotope mass and intensity patterns which correspond to $CrCl_2^+$, $CrCl_3^+$, and $CrCl_4^+$ respectively. When the line of sight to the ionizing region is blocked by a shutter, all the chromium chloride signals disappear, but the peaks due to Cl_2^+ are unaffected. The appearance potentials for $CrCl_2^+$, $CrCl_3^+$, and $CrCl_4^+$ were estimated as *ca.* 15, *ca.* 13, and *ca.* 13 V respectively,

---

† *Non-S.I. units employed:* eV ≈ 1.60×10^{-19} J, a.m.u. ≈ 1.66×10^{-27} kg, dyn = 10^{-5} N, Torr ≈ 133 N m^{-2}.

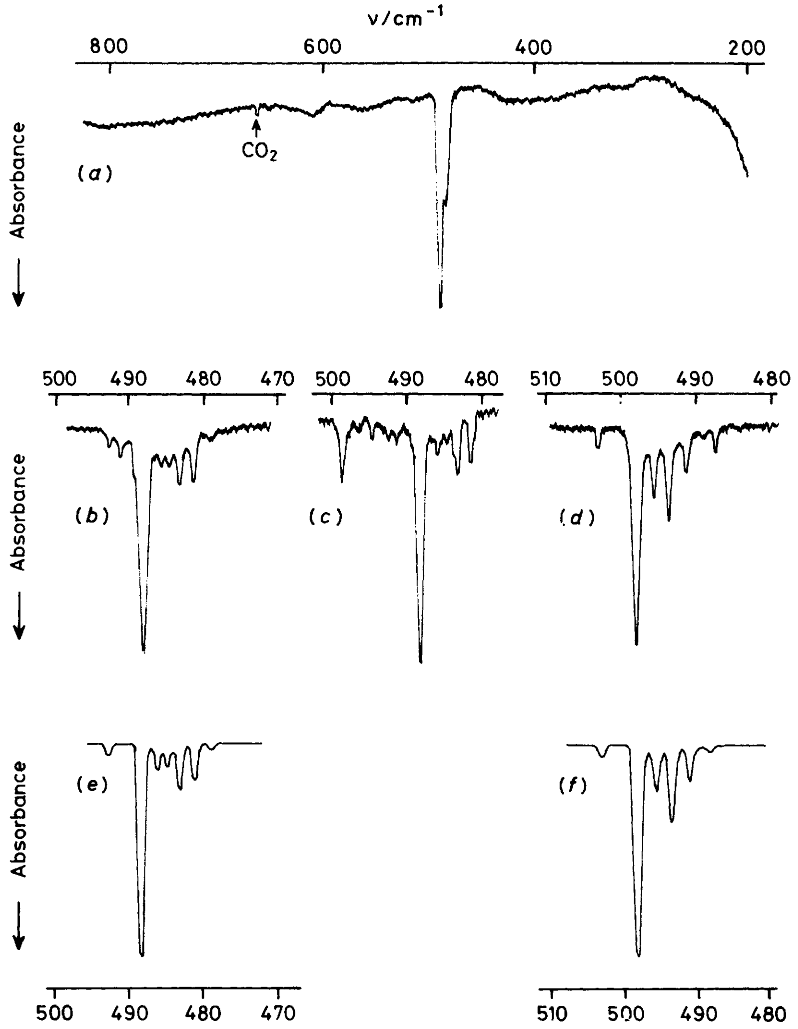


Figure 1. Argon matrix i.r. spectra obtained from the vaporisation of chromium(III) chloride. (*a*) Low-resolution spectrum obtained from a narrow-orifice sample holder at *ca.* 560 °C; (*b*) the prominent band in (*a*) under higher resolution (0.5 cm^{-1}); (*c*) high-resolution spectrum obtained from a narrow orifice at *ca.* 590 °C; (*d*) high-resolution spectrum obtained from a wide orifice at *ca.* 620 °C; (*e*) spectrum calculated for T_d $CrCl_4$; (*f*) spectrum calculated for D_{3h} $CrCl_3$

and the ionization efficiency curves for $CrCl_3^+$ and $CrCl_4^+$ both showed marked discontinuities at *ca.* 20 eV consistent with the onset of extensive fragmentation. Attempts to record the mass spectrum at the higher temperature of *ca.* 620 °C were abandoned due to the higher pressures generated by increased chlorine evolution.

Numerous matrix isolation studies were carried out on this system, using a wide variety of sample holders and deposition conditions. However, only six of these need be referred to in detail. Figure 1(*a*) shows part of an argon matrix i.r. spectrum (800—200 cm^{-1}) obtained from the vaporisation of anhydrous chromium(III) chloride under conditions identical to those employed in the mass spectrometric study. One prominent band is observed, centred at *ca.* 487 cm^{-1}, and the only other features present were weak absorptions due to small amounts of HCl, CO_2, and H_2O. Figure 1(*b*) shows this band under high resolution, where it is seen to consist of one intense component at 487.5 cm^{-1} and a number of weaker satellites. In nitrogen matrices under the same conditions, the low-resolution spectrum [Figure 2(*a*)] is very similar to that in argon, showing one prominent absorption at *ca.* 486 cm^{-1}, but on higher resolution, a different complex pattern is revealed, and this is shown in Figure 2(*d*).

Low-resolution argon matrix spectra obtained from a sample of chromium(III) chloride contained in a wider bore silica tube (diameter *ca.* 6 mm) and heated to *ca.* 620 °C, were very similar in appearance to Figure 1(*a*). However, the main feature was now centred at *ca.* 498 cm^{-1}, and on closer examination was found to consist of a prominent pattern of new bands at 503.1, 498.1, 495.7, 493.8, and 491.6 cm^{-1} together with the feature at 487.5 cm^{-1}. This spectrum is shown in Figure 1(*d*). Several experiments were carried out in which the orifice size and vaporisation temperature for the system were varied within the limits indicated above, and these generally resulted in spectra containing different proportions of the features shown in Figure 1(*b*) and (*d*). A typical example illustrating this behaviour is shown in Figure 1(*c*), in which the absorptions of Figure 1(*b*) predominate, but where the most intense component of the higher frequency group (*ca.* 498 cm^{-1}) is also present. Controlled diffusion studies on this system showed that this higher frequency group decreased significantly in intensity on warming the matrix to *ca.* 30 K, whilst the group at *ca.* 487 cm^{-1} was relatively unaffected.

On the basis of these experiments, we therefore conclude that two quite distinct species may be isolated in argon matrices when chromium(III) chloride is vaporised over the temperature

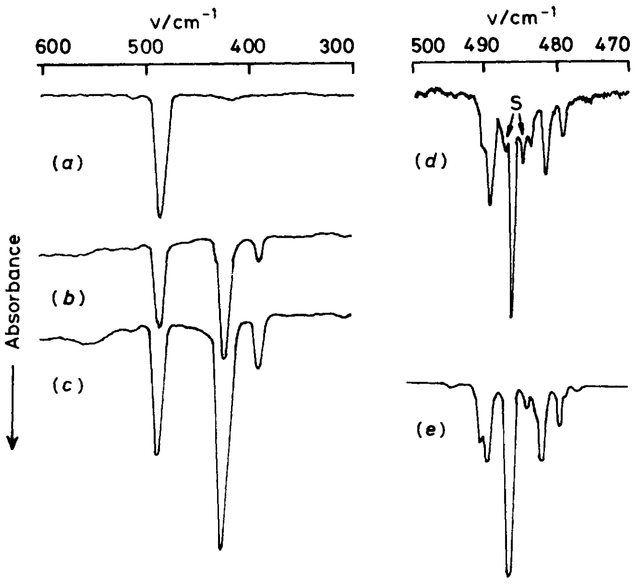


Figure 2. Nitrogen matrix i.r. spectra obtained from the vaporisation of chromium(III) chloride. (*a*) Low-resolution spectrum obtained from a narrow orifice at *ca.* 560 °C; (*b*) low-resolution spectrum obtained from a wide orifice at *ca.* 610 °C; (*c*) as (*b*), but with continued deposition at *ca.* 620 °C; (*d*) high-resolution spectrum of the prominent band in (*a*); (*e*) spectrum calculated for D_{2d} $CrCl_4$

Table 1. Observed and calculated vibration frequencies (cm^{-1}) for the most abundant isotopic $CrCl_4$ species isolated in argon matrices

Observed[a]	Calculated[b]	Assignments[c]
492.1	492.1	T_2 $^{50}Cr^{35}Cl_4$
490.8		Site effect (?)
487.5	487.5	T_2 $^{52}Cr^{35}Cl_4$
	485.9	A_1 $^{52}Cr^{35}Cl^{37}Cl_3$
485.2	485.3	T_2 $^{53}Cr^{35}Cl_4$
484.4	484.1	A_1 $^{52}Cr^{35}Cl_2{}^{37}Cl_2$
482.9	483.2	T_2 $^{54}Cr^{35}Cl_4$
	482.4	A_1 $^{52}Cr^{35}Cl_3{}^{37}Cl$
479.9	480.5	T_2 $^{52}Cr^{37}Cl_4$
	480.2	A_1 $^{53}Cr^{35}Cl_3{}^{37}Cl$
478.7	478.3	T_2 $^{53}Cr^{37}Cl_4$

[a] Frequency accuracy ±0.4 cm^{-1}. [b] Assuming ν_1 at 375 cm^{-1}, and stretching constants $F_r = 2.66$, $F_{rr} = 0.079$ mdyn $Å^{-1}$ respectively for tetrahedral geometry. [c] All T_2 modes are overlapped by E, B_1, or B_2 modes of lower symmetry isotopic species (see text).

Table 2. Observed and calculated vibration frequencies (cm^{-1}) for the most abundant isotopic $CrCl_3$ species isolated in argon matrices

Observed[a]	Calculated[b]	Assignment[c]
503.1	503.1	E' $^{50}Cr^{35}Cl_3$
498.1	498.1	E' $^{52}Cr^{35}Cl_3$
495.7	495.9	A_1 $^{52}Cr^{35}Cl^{37}Cl_2$
	495.7	E' $^{53}Cr^{35}Cl_3$
493.8	493.7	A_1 $^{53}Cr^{35}Cl_2{}^{37}Cl$
	493.4	E' $^{54}Cr^{35}Cl_3$
491.6	491.4	E' $^{52}Cr^{37}Cl_3$

[a] Frequency accuracy ±0.4 cm^{-1}. [b] Assuming symmetric stretch at 360 cm^{-1}, and stretching constants $F_r = 2.587$ and $F_{rr} = 0.042$ mdyn $Å^{-1}$ respectively for planar geometry. [c] All E' modes are overlapped by B_2 modes of lower symmetry isotopic species (see refs. 13 and 14).

Table 3. Observed and calculated vibration frequencies (cm^{-1}) for the most abundant isotopic $CrCl_2$ species isolated in argon matrices

Observed		Calculated			
a	*b*	*c*	*d*	Assignment	Site
458.5	457.4	457.4	457.4	$^{52}Cr^{35}Cl_2$	A
455.9	454.8	454.8	454.2	$^{52}Cr^{35}Cl^{37}Cl$	
453.4	452.3	452.1	450.8	$^{52}Cr^{37}Cl_2$	
444.1	443.8	443.8	443.8	$^{52}Cr^{35}Cl_2$	B
441.5	441.4	441.3	440.7	$^{52}Cr^{35}Cl^{37}Cl$	
439.1	438.8	438.7	437.4	$^{52}Cr^{37}Cl_2$	

[a] Hastie *et al.*;[8] frequency accuracy ±1.0 cm^{-1}. [b] This work; frequency accuracy ±0.4 cm^{-1}. [c] Assuming a linear structure, with ν_1 at 330 cm^{-1}. [d] Assuming a bent structure (110°) with ν_1 at 330 cm^{-1}. The assumption regarding the value of ν_1 only affects the calculated band positions for $^{52}Cr^{35}Cl^{37}Cl$.

range *ca.* 550—650 °C. A group of bands close to 487 cm^{-1} is most prominent at lower temperatures when the orifice size is small, whilst higher vaporisation temperatures and large orifice sizes yield spectra which become dominated by a higher frequency group close to 498 cm^{-1}.

Nitrogen matrix studies using wider orifice samples tubes also reveal the presence of two distinct sets of bands. Figure 2(*b*) shows part of a low-resolution spectrum obtained in the initial stages of an experiment, whilst Figure 2(*c*) shows the same spectral region after further deposition at a higher temperature. Three bands are observed at *ca.* 486, 422, and 388 cm^{-1}. The feature at 486 cm^{-1} is prominent in the early stages of deposition: it corresponds to the single band shown in Figure 2(*a*), and exhibits the same fine structure under high resolution [*cf.* Figure 2(*d*)]. The two lower frequency bands increase in relative importance at higher temperatures, and were not observed at all in Figure 2(*a*). Unfortunately, they usually remained broad (*ca.* 5 cm^{-1}) at higher instrument resolution, but their constant intensity ratio over several experiments indicates that they arise from the same trapped species. Although shifted considerably in frequency, their occurrence under these experimental conditions indicates that they originate from the same *vapour phase* molecule as the species responsible for the argon matrix absorptions at *ca.* 498 cm^{-1}. Tables 1 and 2 summarise the frequency data obtained under the different experimental conditions.

Finally a number of argon matrix experiments were carried out on the vaporisation of the white residue remaining after the above experiments, and on prepared samples of chromium(II) chloride. At a temperature of *ca.* 780 °C, both materials sublimed to give i.r. spectra consisting of a complex pattern of sharp absorptions in the frequency range 430—470 cm^{-1}. In particular, the most intense components were found at 457.4 and 443.8 cm^{-1}, and these results are very similar to the spectra previously reported by Hastie *et al.*,[8] for matrix isolated $CrCl_2$. Our results are summarised in Table 3.

Spectral Interpretation for $CrCl_4$.—As indicated in the Introduction, the thermodynamic data on the chromium(III) chloride–chlorine system at elevated temperatures are consistent with the formation of molecular $CrCl_4$, and subsequent Raman studies on this system revealed features attributed to this species. In particular, five Raman-active bands were observed at 224, 375, 116, 486, and 126 cm^{-1} and although these were too broad for any isotope structure to be resolved, they were assigned[5] as the overtone $2\nu_2$ and fundamentals ν_1—ν_4 of tetrahedral $CrCl_4$ by comparison with known fundamentals of $TiCl_4$.

The mass spectrometric studies reported here clearly indicate that both molecular $CrCl_4$ and Cl_2 are present when anhydrous chromium(III) chloride is heated *in vacuo* at *ca.* 560 °C. Matrix isolation i.r. studies carried out under identical vaporisation conditions yield only one prominent band in the spectral range 1 000—200 cm^{-1}. This lies at *ca.* 487 cm^{-1} in argon matrices, and at *ca.* 486 cm^{-1} in nitrogen, and the initial aim of our spectral interpretation is to show this feature is due to matrix isolated $CrCl_4$.

The fundamental modes of a tetrahedral XY_4 species may be described as ν_1 (A_1 stretch), ν_2 (E bend), ν_3 (T_2 stretch), and ν_4 (T_2 bend). All four modes are Raman active, but only the T_2 modes are i.r. active; and these have been identified from the gas-phase Raman data as occurring at 486 (ν_3) and 126 cm^{-1} (ν_4). In the spectral range accessible to us in the i.r., we should therefore expect to see only one band at *ca.* 486 cm^{-1}, and this is in excellent agreement with the observed results. It also argues in favour of the *tetrahedral* geometry for $CrCl_4$, in so far as the occurrence of this feature in both i.r. and Raman studies effectively rules out the square-planar (D_{4h}) model. However, further proof of the identity of this isolated species as tetrahedral $CrCl_4$ comes from a consideration of the multiplet structure revealed under higher resolution.

Isotope patterns. There are several examples in the literature of matrix isolation i.r. studies on tetrahedral MCl_4 molecules.[9,10] Under high resolution, the T_2 stretching mode (ν_3) typically appears as a complex multiplet consisting of one intense component and four weaker, sharp shoulders to lower frequency. This multiplet is due to the five isotopically distinct species $M^{35}Cl_4$ (T_d), $M^{35}Cl_3{}^{37}Cl$ (C_{3v}), $M^{35}Cl_2{}^{37}Cl_2$ (C_{2v}), $M^{35}Cl^{37}Cl_3$ (C_{3v}), and $M^{37}Cl_4$ (T_d) present as a result of the natural abundance of chlorine isotopes ^{35}Cl (*ca.* 75%) and ^{37}Cl (*ca.* 25%). When the central atom M also possesses a number of isotopes, the resulting pattern is more complex, but can usually be recognised as a superposition of overlapping MCl_4 patterns.

Although the exact spacings and relative intensities within a particular MCl_4 multiplet are dependent both on the mass M and the positions of *all* the fundamental modes, the essential features of the multiplet may be derived from a relatively simple vibrational analysis which requires a knowledge only of the mass of M and the positions of the A_1 and T_2 stretching modes in $M^{35}Cl_4$. The essential features of this analysis have been described elsewhere,[10] and the general conclusions which emerge may be summarised as follows. For the species MCl_4 containing the two chlorine isotopes in natural abundance (^{35}Cl:^{37}Cl, 3:1), the isotope structure expected for ν_3 should consist of five approximately equally spaced components with intensity ratios close to 171:4:18:36:27.* These ratios arise as a result not only of the relative abundances of the five species present, but from the effect of removal of the T_2 degeneracy in the C_{3v} and C_{2v} isotopic species. This in turn may be shown to result in the *overlapping* of a number of components,[10] and it is this overlap which is responsible for the prediction of one very intense feature characteristic of tetrahedral geometry.

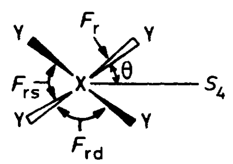
Infrared spectra of $CrCl_4$ *in argon matrices.* The high-resolution argon matrix spectrum shown in Figure 1(*b*) consists of a prominent absorption at 487.5 cm^{-1} and at least seven weaker features. The presence of only one intense component initially suggests a T_d MCl_4 structure, but the overall pattern clearly contains more than the five components predicted for such a species. However, in addition to the principal isotope, ^{52}Cr (83.8%), chromium in natural abundance contains small proportions of ^{50}Cr (4.5%), ^{53}Cr (9.4%), and ^{54}Cr (2.3%), and one might therefore anticipate three further peaks in this spectral region arising from the most intense components of the $^{n}CrCl_4$ quintets (n = 50, 53, 54).

As indicated above, it is possible to simulate the expected isotope pattern for $CrCl_4$ using only the values of the A_1 and T_2 stretching modes in $^{52}Cr^{35}Cl_4$. We have therefore taken the argon matrix frequency of 487.5 cm^{-1} as the T_2 mode and combined this with the gas-phase Raman value of 375 cm^{-1} for the A_1 mode to calculate the frequencies and relative intensities of all the isotopic components contributing to the 'T_2 region' (470—510 cm^{-1}). Calculations were also performed in which the position of the A_1 stretch was arbitrarily varied by ± 20 cm^{-1} from the gas-phase value, but this had a negligible effect on the isotope pattern. The result of this spectral simulation is shown in Figure 1(*e*), and the frequencies of the most intense components are included in Table 1.

The agreement between the observed high-resolution spectrum and this simulation is very satisfactory, and demonstrates beyond reasonable doubt the tetrahedral geometry of $CrCl_4$ in argon matrices. Only one weak component in the observed spectrum remains unassigned. This lies on the high frequency side of the intense 487.5 cm^{-1} component, and is believed to arise from $^{52}CrCl_4$ molecules trapped in a different matrix site. This phenomenon has previously been noted for $SnCl_4$ and $PbCl_4$ in argon matrices,[10] and similar evidence for site effects was found in matrix isolated CrF_4.[11]

Infrared spectra of $CrCl_4$ *in nitrogen matrices.* The isotope structure for the 'T_2' mode of $CrCl_4$ isolated in nitrogen is significantly different. Although the pattern [Figure 2(*d*)] is still dominated by one intense feature (486.5 cm^{-1}) it now contains two medium intensity components (*ca.* 490 and 482 cm^{-1}) in addition to weaker shoulders. It is now well established that isolation in nitrogen matrices often results in a lifting of vibrational degeneracy,[12] and an obvious starting point for the interpretation of this pattern is to consider the effects of small distortions of the $^{52}Cr^{35}Cl_4$ molecule to produce, for example, C_{2v}, C_{3v}, or D_{2d} structures. It should then be possible to compute theoretical patterns for all the isotopic tetrachloride species, and to compare the results with the observed spectrum. In practice, this approach is unsatisfactory for all but the D_{2d} distortion, because lower symmetry structures generally allow too much flexibility in the choice of force constant and bond angle parameters. Even for the D_{2d} distortion, three stretching constants and one bond angle will in general need to be specified within the framework of our simple model. Rather than attempting an unequivocal assignment of this isotope pattern, we therefore set out to show whether its principal features are consistent with a D_{2d} distortion.

The secular equations for the stretching modes of the D_{2d} XY_4 unit are summarised below, and the parameters defined in the accompanying diagram. In the case of $CrCl_4$, the only frequencies which can initially be estimated with any confidence are the three fundamentals of $^{52}Cr^{35}Cl_4$, and it is evident that there will be no unique solution for the four parameters F_r, F_{rd}, F_{rs}, and θ. However, there are at least two additional constraints



$$\lambda_{A_1} = (F_r + F_{rs} + 2F_{rd})(1/M_Y)$$

$$\lambda_{B_2} = (F_r + F_{rs} - 2F_{rd})[(1/M_Y) + (4\cos^2\theta/M_X)]$$

$$\lambda_E = (F_r - F_{rs})[(1/M_Y) + (2\sin^2\theta/M_X)]$$

---

* These particular ratios are obtained by assuming an abundance ratio of 3:1 for ^{35}Cl:^{37}Cl, and an equal distribution of intensity between all components of the (split) T_2 mode. No account has therefore been taken of the slightly lower intensity expected for ^{37}Cl atom motion compared with ^{35}Cl.

which can be applied to narrow down the range of possible solutions. First, the values obtained for any set of parameters should be 'reasonable', and preferably fairly close to the corresponding values for T_d geometry, and secondly, they should give a satisfactory frequency and intensity fit for the whole isotope pattern.

On the basis of intensity considerations, we assign the B_2 and E stretching modes of (D_{2d}) $^{52}Cr^{35}Cl_4$ at 490.5 and 486.5 cm^{-1} respectively, and assume the same value for the (inactive) A_1 mode as in the T_d model (375 cm^{-1}). As was noted previously, the appearance of the isotope pattern in the 470—510 cm^{-1} region is not sensitive to the exact position of this mode. The angle 2θ was varied between 100 and 114°, and each angle value thus yielded a set of stretching constants, F_r, F_{rd}, and F_{rs} from the secular equations. For values of 2θ outside the range 104—112°, negative values for either F_{rd} or F_{rs} were obtained, and these solutions were rejected. Within this range of angles, several calculations were carried out to simulate the appearance of the complete isotope pattern. Although varying in minor details, these calculations all gave acceptable agreement with the observed spectrum, and Figure 2(*e*) summaries the result of one particular simulation, in which $2\theta = 108°$.

Two relatively minor features in the observed spectrum, denoted 'S' in Figure 2(*d*), remain unassigned for this D_{2d} model. It might be possible to accommodate these by resorting to a lower symmetry structure, but these additional features could alternatively be due to a small proportion of $^{52}CrCl_4$ species trapped in a different matrix site. Apart from this uncertainty, the main conclusion of this analysis is that the principal features of the nitrogen matrix spectrum of $CrCl_4$ can be accounted for in terms of a relatively small perturbation to D_{2d} geometry in which the T_2 stretching mode is split into components $B_2 + E$ at 490.5 and 486.5 cm^{-1} respectively. Both the magnitude and ordering of this splitting are comparable to the effect produced by a nitrogen matrix environment on CrF_4.[11] If the interaction constants F_{rd} and F_{rs} have similar values, this splitting order ($\nu_{B_2} > \nu_E$) is consistent with an elongation of the tetrahedron along the S_4 axis (*i.e.* $2\theta < 109°28'$).

Spectral Interpretation for $CrCl_3$.—Matrix isolation studies on chromium(III) chloride at higher vaporisation temperatures (typically 600—620 °C) yield a number of new features in addition to those assigned to $CrCl_4$, and when vaporisation takes place from a wide-bore tube, these new features dominate the spectrum. However, unlike $CrCl_4$, for which only relatively minor differences were found between the different matrix materials, these new features show significant differences between argon and nitrogen environments.

Infrared spectra of $CrCl_3$ *in argon matrices.* Figure 1(*d*) shows a typical argon matrix spectrum in the region 470—510 cm^{-1} obtained from the vaporisation of chromium(III) chloride at *ca.* 620 °C from a wide-bore (diameter *ca.* 6 mm) silica tube. The feature at 487.5 cm^{-1} corresponds to the most intense component of the $CrCl_4$ multiplet, but there is also a much stronger quartet at 498.1, 495.7, 493.8, and 491.6 cm^{-1}, and a weaker absorption at 503.1 cm^{-1}.

The intensity pattern of this quartet is characteristic of the chlorine isotope structure expected for the doubly degenerate stretching mode of a trichloride.[13,14] The parent species is therefore provisionally identified as molecular $CrCl_3$. Both pyramidal (C_{3v}) and planar (D_{3h}) parent geometries would be expected to show this pattern, but as no evidence was found in these spectra for an i.r.-active symmetric stretch, we assign this pattern to the antisymmetric stretching mode of the planar $CrCl_3$ molecule. Isotopic patterns characteristic of this geometry have now been observed for several metal trichlorides, including $AlCl_3$,[13] $InCl_3$,[13,15] $FeCl_3$,[16] and $CoCl_3$,[16] and confirmation of this assignment comes from a detailed comparison between the observed spectrum and the pattern expected for planar $CrCl_3$, taking into account both chlorine and chromium isotope abundances. The calculated isotope pattern requires a knowledge of the frequencies of the E' and A_1' stretching modes of the parent $^{52}Cr^{35}Cl_3$ molecule, together with the isotope masses and abundances of the atoms involved, and the procedure adopted here is identical to that described elsewhere.[13,14]

The position of the E' mode is identified by the most intense component of the quartet (498.1 cm^{-1}) and the frequency of the (unobserved) A_1' mode was initially set at 360 cm^{-1}. This was subsequently varied by up to ± 40 cm^{-1} in a series of calculations of the expected pattern. As was found earlier for $CrCl_4$, these calculated patterns were relatively insensitive to the exact position of this A_1' mode, and satisfactory agreement with the observed spectrum could be achieved over a wide range of A_1' positions. However, negative values of the interaction constant F_{rr}[13] were obtained for $\nu_{A_1'} < 350$ cm^{-1}, and a reasonable estimate for this mode was therefore considered to be *ca.* 360 cm^{-1}. Figure 1(*f*) shows the isotope pattern predicted for planar $CrCl_3$ in the region 470—510 cm^{-1}, and comparison with the observed spectrum [Figure 1(*d*)] is very satisfactory.

The basic components of the characteristic quartet are reproduced almost exactly, and the weak higher frequency feature is identified as arising from $^{50}CrCl_3$. The numerical data are included in Table 2.

Infrared spectra of $CrCl_3$ *in nitrogen matrices.* As indicated above, nitrogen matrix studies under these vaporisation conditions yielded a quite different pattern of absorption. In addition to the $CrCl_4$ feature at *ca.* 486 cm^{-1}, these i.r. spectra typically showed an intense absorption at *ca.* 422 cm^{-1} and a weaker, associated absorption at *ca.* 388 cm^{-1}. These two latter features were always present in the same relative intensity, and almost certainly arise from molecular $CrCl_3$. However, it is evident that they can no longer arise from a D_{3h} structure, and we believe that an adduct such as $N_2{\cdot}CrCl_3$ has been formed resulting in a pyramidal $CrCl_3$ unit. Both the symmetric (A_1) and antisymmetric (E) Cr–Cl stretching modes would now be i.r. active, and one might also hope to see evidence of the bound N_2 unit. However, despite a careful search over a wide frequency range, no evidence could be found for an i.r.-active N_2 stretch. Nevertheless, the observed spectrum is qualitatively similar to that previously found by Shirk[17] for monomeric $AlCl_3$ isolated in low-temperature matrices containing N_2, and we provisionally assign the 422 and 388 cm^{-1} features as the E and A_1 modes respectively of a pyramidal $CrCl_3$ unit.

High-resolution studies could in principle confirm these assignments by revealing chlorine isotope patterns characteristic of these different symmetry fundamentals. However these absorptions generally remained broad, although some spectra did reveal partially resolved structure on the lower frequency (A_1) band at 389.1, 386.5, and (perhaps) 383 cm^{-1}. Nevertheless, if our pyramidal model for $CrCl_3$ in nitrogen is correct, it would be possible to estimate the bond angle Cl–Cr–Cl from the relative intensities of the E and A_1 stretching modes, and hence solve the secular equations for the stretching modes of the $CrCl_3$ unit. This in turn would allow one to calculate the chlorine isotope structure expected for the A_1 mode, and to compare the result with the observed spectrum.

Measurement of several spectra similar to Figure 2(*c*) gave an estimate of 5.5 ± 0.5 for the intensity ratio I_E/I_{A_1}. Using the 'stretch-only bond dipole' model,[18] this ratio corresponds to a bond angle Cl–Cr–Cl of $102 \pm 2°$, and solution of the appropriate secular equations[18] yields values of 2.09 and 0.05 mdyn Å^{-1} for the principal and interaction stretching constants. The A_1 isotope pattern is expected to show four components under high resolution, with approximate intensity ratios 27:27:9:1, and using the above parameters, the frequency separations between the three most intense components are calculated to be 2.8 and 2.6 cm^{-1}. Although the A_1 band observed in our spectra was only partially resolved, the splittings of *ca.* 2.6 and 2.5 cm^{-1} are similar to the calculated values. This analysis also yields reasonable values for the Cl–Cr–Cl angle and for the two force-constant parameters, and therefore is consistent with the pyramidal model.

Effect of orifice size. None of the conditions used in these experiments could be described as 'ideal' in terms of the criteria necessary for Langmuir or Knudsen vaporisation.[19] In the latter case, sampling takes place from an established equilibrium, and demands not only a very small orifice size, but also a suitable geometric correction for orifice shape. Langmuir 'free vaporisation,' on the other hand, ideally takes place from a surface directly into a high vacuum, and is independent of any vapour species impinging on the surface. However, despite being non-ideal, our experiments using narrow- and wide-bore orifices could be regarded as approximating to Knudsen and Langmuir conditions respectively, and the i.r. spectra obtained from these differing conditions thus rationalised.

As indicated earlier, two mechanisms have been proposed for the production of molecular $CrCl_4$ from these systems. These are disproportionation, reaction (3), and oxidation, reaction (2). The finite partial pressure of chlorine necessary for reaction (2) is presumed to originate *via* reaction (1).

The most significant feature of our experiments is that under conditions approaching Langmuir vaporisation (*i.e.* wide-bore tubes) the matrix i.r. spectrum was dominated by molecular $CrCl_3$. Indeed, the weak $CrCl_4$ features present in these spectra [see *e.g.* Figure 1(*d*)] were originally assigned to $CrCl_3$ molecules trapped on different sites. Only when a smaller diameter orifice was used did the proportion of $CrCl_4$ increase significantly. This behaviour is not consistent with reaction (3), which might be expected to yield $CrCl_4$ under conditions which are *independent* of the nature of the vapour above the heated solid, but is entirely consistent with reaction (2) which demands an equilibrium pressure of Cl_2 for the formation of $CrCl_4(g)$. No attempt was made to measure either the pressure or composition of the vapour directly above our heated chromium(III) chloride samples, but it is possible that under our pseudo-Knudsen conditions, the partial pressure of chlorine could be *ca.* 10^{-2}—10^{-3} Torr. In contrast, the pressure is unlikely to exceed *ca.* 10^{-4}—10^{-5} Torr using wide-bore sample tubes, and under these conditions of pseudo-Langmuir vaporisation, we propose that molecular $CrCl_3$ is formed *via* $CrCl_3(s) \longrightarrow CrCl_3(g)$.

Spectral Interpretation for $CrCl_2$.—The vaporisation of chromium(II) chloride has been studied by a number of techniques including mass spectrometry,[6] matrix isolation,[8,20] and electron diffraction,[21,22] and there is general agreement that under high-vacuum conditions, the predominant vapour species is monomeric $CrCl_2$. However, there is disagreement in the literature concerning first the shape of the monomer in the vapour phase, and secondly the values of the vibrational fundamentals for the matrix isolated species.

Argon matrix i.r. spectra for this system have been reported by Jacox and Milligan[20] and by Hastie *et al.*[8] The former authors observed a pattern of bands at *ca.* 490 cm^{-1} which showed the splittings and intensities expected for linear $CrCl_2$ species. In contrast, Hastie *et al.* reported a complex pattern of absorptions between 430 and 470 cm^{-1} which they interpreted in terms of a linear $CrCl_2$ species isolated in more than one matrix site. Our spectrum which consists essentially of two triplets is very similar to that reported by Hastie *et al.*, and calculations based on these isotope patterns (Table 3) support the linear geometry of $CrCl_2$ in argon matrices.

However, before comparing this result with the proposed vapour phase structures, it is important to investigate the discrepancy of *ca.* 40 cm^{-1} between the two sets of argon matrix data. One possible explanation for this difference may arise from the fact that Jacox and Milligan used a welded nickel sample holder. The most intense component in their isotope pattern was at 493.5 cm^{-1}, only 0.3 cm^{-1} higher than the most intense absorption of matrix isolated $FeCl_2$.[20] Most welding materials contain at least some iron, and the original mass spectrometric studies on $CrCl_2$ specifically drew attention to the presence of $FeCl_2^+$ in their spectra when iron was present in the system.[6] Moreover, simulation of the isotope patterns for (linear) $FeCl_2$ and $CrCl_2$ reveals a very close similarity. This arises primarily from the fact that the lightest isotopes for iron and chromium are not only of similar abundances, relative to the dominant isotopes (^{50}Cr, 4.5%; ^{52}Cr, 83.8%; ^{54}Fe, 5.8%; ^{56}Fe, 91.7%) but that they are both lighter by two mass units. The presence of chlorine isotopic structure effectively masks the differing contribution made by ^{53}Cr and ^{54}Cr compared with ^{57}Fe and '^{58}Fe'. We therefore suggest that the 493.5 cm^{-1} assigned by Jacox and Milligan to $^{52}Cr^{35}Cl_2$ could be due to $^{56}Fe^{35}Cl_2$.

Confusion over the shape of monomeric $CrCl_2$ in the vapour phase lies in the different conclusions reached by two independent electron diffraction studies. The most recent study[21] proposed a significantly bent structure (Cl–Cr–Cl *ca.* 110°) but drew attention to an earlier study[22] in which a linear model was preferred, after suitable correction for shrinkage. We are unable to comment on the detailed interpretation of these data, but note that a significant proportion of dimer (Cr_2Cl_4) was present in the latest experiments.[21] Our matrix results, although complicated by what we believe is a multiplicity of trapping sites, yield isotope splittings inconsistent with such an acute angle. Thus, for a bond angle of 110°, the outer components of the $^{52}CrCl_2$ triplet(s) should be separated by *ca.* 6.4 cm^{-1}, which is significantly larger than the value of 5.2 ± 0.2 cm^{-1} found both here and by Hastie *et al.*[8] These authors also found no evidence for the symmetric stretch (ν_1), which should be relatively intense if the bond angle is indeed *ca.* 110°.

Conclusions

These experiments demonstrate for the first time the existence of molecular $CrCl_3$, and also prove beyond doubt that this species, together with $CrCl_4$ and Cl_2, can be produced by vacuum sublimation of anhydrous chromium(III) chloride. All the molecular species demanded by the earlier thermodynamic studies[4] have been identified, and in particular, when conditions approach Knudsen effusion, the principal chromium vapour species at *ca.* 560 °C is $CrCl_4$.

Argon matrix i.r. spectra obtained for this molecule are in good agreement with previous high-temperature Raman studies, and are entirely consistent with a tetrahedral geometry. Nitrogen matrices appear to impose a small static distortion, possibly towards D_{2d} symmetry.

When conditions of vaporisation approach those of 'free evaporation,' the predominant chromium species is identified as monomeric $CrCl_3$. This molecule is found to be planar in argon matrices, and thus to be isostructural with $FeCl_3$ and $CoCl_3$. However, it appears to adopt a pyramidal geometry in nitrogen matrices, possibly as a result of specific co-ordination.

At significantly higher temperatures, molecular $CrCl_2$ may be identified, and although the argon matrix i.r. spectrum is complex, analysis of the isotope patterns indicates a linear or near-linear geometry.

Acknowledgements

We gratefully acknowledge the financial support of the S.E.R.C., and also the contributions made to this work by Professor I. R. Beattie, Dr. R. A. Gomme, Dr. S. N. Jenny, and Mr. G. K. Morgan.

References

1 H. A. Doerner, 'Chemistry of the Anhydrous Chlorides of Chromium,' U.S. Bureau of Mines Technical Papers 577, Washington D.C., 1937.

2 H. von-Wartenberg, *Z. Anorg. Allg. Chem.*, 1942, **250**, 122.

3 G. I. Novikov and N. V. Galitskii, *Russ. J. Inorg. Chem.*, 1965, **10**, 313.

4 H. Oppermann, *Z. Anorg. Allg. Chem.*, 1968, **359**, 51.

5 B. Cuoni, F. P. Emmenegger, C. Rohrbasser, C. W. Schlapfer, and P. Studer, *Spectrochim. Acta, Part A*, 1978, **34**, 247.

6 R. C. Schoonmaker, A. H. Friedman, and R. F. Porter, *J. Chem. Phys.*, 1959, **31**, 1586.

7 See, for example, G. Brauer (ed.), 'Handbook of Preparative Inorganic Chemistry,' Academic Press, London, 1963.

8 J. W. Hastie, R. H. Hauge, and J. L. Margrave, *High Temp. Sci.*, 1971, **3**, 257.

9 F. Koniger and A. Muller, *J. Mol. Spectrosc.*, 1975, **56**, 200; F. Koniger, R. O. Carter, and A. Muller, *Spectrochim. Acta, Part A*, 1976, **32**, 891; F. Koniger and A. Muller, *J. Mol. Struct.*, 1977, **37**, 199.

10 S. A. Arthers and I. R. Beattie, *J. Chem. Soc., Dalton Trans.*, 1984, 819.

11 E. G. Hope, P. J. Jones, W. Levason, J. S. Ogden, M. Tajik, and J. W. Turff, *J. Chem. Soc., Dalton Trans.*, 1985, 1443.

12 See, *e.g.* W. Levason, R. Narayanaswamy, J. S. Ogden, A. J. Rest, and J. W. Turff, *J. Chem. Soc., Dalton Trans.*, 1981, 2501; E. G. Hope, P. J. Jones, W. Levason, J. S. Ogden, M. Tajik, and J. W. Turff, *ibid.*, 1985, 529.

13 I. R. Beattie, H. E. Blayden, S. M. Hall, S. N. Jenny, and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1976, 666.

14 J. S. Ogden, *Ber. Bunsenges. Phys. Chem.*, 1978, **83**, 76.

15 R. G. S. Pong, A. E. Shirk, and J. S. Shirk, *J. Mol. Spectrosc.*, 1977, **66**, 35.

16 D. W. Green, D. P. McDermott, and A. Bergman, *J. Mol. Spectrosc.*, 1983, **98**, 111.

17 J. S. Shirk and A. E. Shirk, *J. Chem. Phys.*, 1976, **64**, 910; M. L. Lesiecki and J. S. Shirk, *ibid.*, 1972, **56**, 4171.

18 See, for example, E. B. Wilson, jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.

19 See, for example, J. L. Margrave (ed.), 'The Characterisation of High Temperature Vapors,' Wiley, New York, 1967.

20 M. Jacox and D. E. Milligan, *J. Chem. Phys.*, 1969, **51**, 4143.

21 M. Hargittai, O. V. Dorofeeva, and J. Tremmel, *Inorg. Chem.*, 1985, **24**, 3963.

22 A. V. Kupreev, unpublished work (quoted in ref. 21).

Received 25th April 1986; *Paper* 6/799