Articles

Vibrational and Electronic Spectra of Molecular Chromium Tetrafluoride, CrF_4, and Chromium Pentafluoride, CrF_5. Comments on the Existence of Chromium Hexafluoride, CrF_6

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As a contribution to the chemistry and spectroscopy of higher chromium fluorides pure samples of CrF_4 and CrF_5 are reinvestigated by their FTIR and UV/vis spectra. It is shown here that an infrared band previously assigned to CrF_6 is due to CrF_5 and that earlier reports on CrF_6 are doubtful. For the colorless monomeric $^{52}CrF_4$ isolated in a Ne matrix fundamental vibrations at 790.17 (ν_3) and 200.68 (cm^{-1} (ν_4) as well as four combination bands and several isotopic shifts have been observed. The findings are consistent with T_d symmetry of the gaseous molecule. Gaseous CrF_5 shows no tendency to disproportionate into CrF_4 and CrF_6. Its IR and UV/vis spectra agree with those obtained from matrix-isolated CrF_5. For $^{52}CrF_5$ isolated in a Ne matrix, four fundamentals have been measured at 754.8 (ν_1), 767.71 (ν_7), 332.2 (ν_8), and 792.2 cm^{-1} (ν_{10}). In addition seven combination bands and several isotopic shifts were found. The data are in agreement with the known C_{2v} symmetry of gaseous CrF_5. Our results on CrF_5 and CrF_6 are confirmed by a high-resolution (ca. 0.003 cm^{-1}) infrared study of monoisotopic $^{52}CrF_5$ and $^{80}SeF_6$ in the gas phase. With a threshold of 610 nm, CrF_5 photodissociates into CrF_4 and F. The UV/vis spectrum of CrF_5 is compared with those of CrF_4, VCl_4, VF_5, WF_6, and MoF_6. Some properties of the elusive CrF_6 molecule are predicted.

Introduction

The first systematic investigation into binary chromium fluorides in higher oxidation states was reported by von Wartenberg 50 years ago. In the course of this study CrF_4, CrF_5, and CrO_2F_2 were obtained, but chromium hexafluoride, CrF_6, could not be detected.[1] Since then its synthesis has been a challenge for synthetic chemists. The first claim of the formation of CrF_6 was subsequently made in 1963 by Glemser et al., and the lemon-yellow material obtained was characterized by an elemental analysis[2] and by low-temperature infrared spectroscopy.[3] However the reported spectrum (cf. Table 4 in ref 3) is consistent with a mixture of solid CrF_5 (1492 (w), 800 (s), 785 (s) 730 (s), 680 (sh), 500 (m), 425 (m) cm^{-1}),[4,7] $CrOF_4$ (1005 (m), 730 (s)), CrO_2F_2 (965 (w), 610 (w)), and further compounds (1205 (w), 910 (w), 885 (w), 555 (m) cm^{-1}).[4]

The next claim of CrF_6 was made in 1985 by Hope et al.,[5,6] where in a matrix isolation study an infrared band, which exhibited the expected chromium isotopic pattern, was attributed to $\nu_3(f_{1u})$ of CrF_6. This prompted us to study the chemical, physical, structural, and spectroscopic properties of chromium hexafluoride. It was possible to reproduce the published IR band[5,6] and to measure three additional infrared bands.[7] When the chromium fluoride, used in the matrix experiments, was investigated in the gas phase by infrared spectroscopy, the excellent agreement between matrix and gas phase data led to the conclusion that in both phases the same species—chromium pentafluoride, CrF_5—was present. The identity of the yellow, gaseous chromium fluoride as CrF_5 was suggested by UV/vis and mass spectroscopy and a high-resolution infrared gas spectrum of monoisotopic $^{52}CrF_5$ and furthermore established by an electron diffraction study and a comparison of the properties of the neat compound with those described for CrF_5.[7]

In conclusion, all experimental findings provided conclusive evidence that the species studied by matrix isolation and in the gas phase was indeed CrF_5.[7]

In their recent communication[8] Hope et al. reaffirmed their belief in the existence of matrix-isolated CrF_6. Their principal evidence was based on the comparison of the calculated fine structure of the isotopic pattern with the only one observed CrF stretching band.

In order to settle the dispute on CrF_6, we have now repeated some of our earlier experiments, have extended the investigation to CrF_4, and are now presenting more novel findings on CrF_5.

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(2) Glemser, O.; Roesky, H.; Hellberg, K. H. *Angew. Chem.* **1963**, *75*, 346.
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Experimental Section

Materials. The syntheses of CrF_5 and CrF_4 were adopted from a method of Christe et al.[9] The reaction was carried out in a nickel reactor (internal volume 7.5 mL) of 6 mm inner diameter, 1 mm wall thickness, and 150 mm length equipped with Cajon fittings and a stainless-steel bellows valve (Nupro, SS-4 HTW). Prior to use it was passivated with 20 bar fluorine at 300 °C. The reactor was charged with 105 mg (2 mmol) of chromium granulate (0.04–0.15 mm, 99.99%, Cerac) and two batches of 1.5 mmol of fluorine each (99.99%, MAN Technology AG) at −196 °C. The strongly exothermic formation of CrF_3 was noted by careful thermal activation and recooling of the reactor. Progress of the reaction was monitored by consumption of fluorine. Subsequently an additional 3 mmol of F_2 was added, and after 1 day at 260 °C the reaction to produce CrF_5 was allowed to continue for 2 days with further addition of 3 mmol of F_2. Excess fluorine and small amounts of impurities (HF and $CrOF_4$) were removed in vacuo at −196 and −20 °C respectively. $^{52}CrF_5$ (99.8% ^{52}Cr, Chemotrade) was prepared in the same manner.

After the use of CrF_5 vapor from the reactor for all spectroscopic investigations, the remaining CrF_5 was reduced to CrF_4 with 2 mmol of Cl_2 at 100 °C, where the reduction was complete within 5 min.

For comparison purposes millimolar quantities of VF_5, MoF_6, WF_6, and $^{80}SeF_6$ were prepared. VF_5 was obtained from VCl_3 (Merck) in a similar way as described for CrF_5. MoF_6, WF_6, and $^{80}SeF_6$ were prepared by burning the metal powders (Cerac) and ^{80}Se (99.2%, Chemotrade) respectively in an excess of fluorine.

Preparation of the Matrices. The Ni reactor described above containing CrF_5 or CrF_4 was attached to the inlet system of the matrix apparatus. The inlet system consisted of a stainless steel T-joint (Cajon) connected with the sample container, a spray nozzle (a Ni-tube with 4 mm inner diameter and 1 mm wall thickness), and a capillary of 1 mm inner diameter and 0.5 mm wall thickness leading to the matrix gas reservoir. Prior to use the inner surface of the complete inlet system was dried with ClF_3, passivated with fluorine (3 bar, 100 °C), and treated with CrF_5 vapor. Subsequently the inlet system was flushed with high purity argon (99.999%, Messer-Griesheim) and mounted in front of the matrix support. The matrix support consisted of a copper block with two diamond-cut surfaces coated with aluminum, thus acting as highly reflecting UV-grade mirrors. A gas stream of neon or nitrogen was swept through the inlet system, while the open container with CrF_5 was held at a constant low temperature. The resulting gas mixture was immediately quenched onto the matrix support at 4.5 (Ne) or 10 K (N_2). Cooling was achieved by a liquid helium continuous flow cryostat (Cryovac). During deposition of the matrix gas (rate: 4 mmol h^{-1} for Ne; 2 mmol h^{-1} for N_2), the CrF_5 container was held at −15, −20, and −25 °C respectively in different experiments. The vapor pressures of CrF_5 at these temperatures are 0.14, 0.08, and 0.05 mbar respectively.[7] Fourteen experiments with neon and two with nitrogen were performed. The amount of matrix gas was in the range 0.4–4 mmol. In some instances the temperature of the complete inlet system was kept at −20 °C during matrix deposition.

Four matrices containing pure CrF_4 were prepared in a similar way. However to achieve the desired concentration, the complete inlet system had to be heated during matrix decomposition to 60 °C and the sample container was held in the temperature range 40–60 °C.

Instrumentation. Matrix IR spectra were recorded on a Bruker IFS 66 v FT spectrometer at apodized resolutions of 1.2 and 0.3 cm^{-1}. A mid- and a far-IR DTGS detector were used together with a KBr and a 6-μm Mylar beam splitter respectively and were employed in the 4000–400 and 550–80-cm^{-1} spectral regions respectively. A total of 256/64 scans were coadded for 1.2/0.3-cm^{-1} resolution, respectively, in each case. The precision of band positions listed in Tables I and III with quoted 0.01, 0.1, or 1 cm^{-1} are ± 0.02, ±0.1, or ±0.5 cm^{-1}, respectively.

A reflectance device in the sample compartment of the interferometer directed the beam to the cold remote mirror holding the matrix. From here it was reflected to reenter the standard optical path. In addition to the inlet system, a KBr, a polyethylene, and a quartz glass window were attached in the vacuum shroud of the matrix chamber.

Photolysis of matrix-isolated CrF_5 was carried out with a medium-pressure mercury arc lamp, model TQ 150 (Heraeus), or a 150-W tungsten halogen lamp combined with a water cooled quartz lens optic (*f*-number = 1) and various cut-off filters (Schott).

High-resolution IR spectra of $^{52}CrF_5$ and $^{80}SeF_6$ were recorded at Giessen, Germany and Wuppertal, Germany, respectively, employing Bruker 120 HR interferometers. For the CrF_5 spectrum the instrument was equipped with a KBr beamsplitter and a Cu:Ge detector; the resolution for full apodization was adjusted to 2.8×10^{-3} cm^{-1}, but the effective resolution for trapezoidal apodization was on the order of 2.5×10^{-3} cm^{-1}. The $^{80}SeF_6$ spectrum registered for comparison was recorded using a KBr beamsplitter and a MCT detector. The nominal resolution was 3×10^{-3} cm^{-1}, effective line widths being slightly smaller. A stainless-steel cell measuring 11.5 cm in length outfitted with AgCl windows was employed for CrF_5, with a pressure adjusted to ca. 1 mbar. A glass cell of 28 cm length equipped with KBr windows was used for SeF_6, and a pressure of ca. 0.2 mbar was chosen.

Table I. Vibrational Wavenumbers (cm^{-1}), Relative Intensities *I*, and Assignment for CrF_4 Isolated in a Ne Matrix

ν^a	I^b	assignt^c
1586.76 1576.41 1571.51 1566.78	1.5	$2\nu_3$
1507.28 1502.06 1499.62 1497.27	1.4	$\nu_1 + \nu_3$
994.10 988.87 986.22 983.56	1.2	$\nu_3 + \nu_4$
916.47^d	0.5	$\nu_1 + \nu_4$
795.37 790.17 787.70 785.30	100	$\nu_3\ (f_2) = \nu_{as}(CrF)$
200.68^d	17	$\nu_4\ (f_2) = \delta_{as}(CrF)$

[a] Most intense components of the ^{50}Cr, ^{52}Cr, ^{53}Cr, and ^{54}Cr isotopomers; for precision, see text. [b] Integrated intensity over isotopic and matrix splittings; $I(\nu_3) = 100$. [c] According to T_d symmetry. [d] Isotopic splittings are obscured by matrix splittings of the ^{52}Cr isotopomer; see Figure 1 and text.

Matrix UV/vis spectra between 230 and 800 nm were recorded with a 1024 diode array spectrometer system (Spectroscopy International) in a reflection mode with spectral resolutions of 0.1–1 nm using a Y-fiber optic (fused silica) and a CLD 30W deuterium lamp (Zeiss) operating between 230 and 500 nm or a tungsten halogen lamp operating between 400 and 800 nm as the light source. The uncertainties are ca. ±1 in the last quoted digit for wavelengths and <15% for absorption cross sections.

For UV/vis measurements of gaseous samples a stainless steel cell (9.3 cm optical path length) equipped with sapphire windows (Saphikon) and a Baratron (221 AHS-A-10) capacity manometer was used.

Results and Discussion

(a) Infrared, Ultraviolet, and Visible Spectra of Monomeric CrF_4. In order to obtain both vibrational band positions for molecular CrF_4 as close as possible to the yet unknown gas phase values and transparent matrices for UV/vis measurements, neon was used as matrix host. The observed infrared bands for CrF_4 deposited from the gas phase are illustrated in Figure 1 in expanded scale, and the measured wavenumbers are summarized in Table I. All bands attributed to CrF_4 were confirmed independently by generation of CrF_4 through photodissociation of CrF_5 (see next section); the band positions and matrix splittings of CrF_4 produced in this manner in the matrix cage are only slightly different from those displayed in Figure 1. The strongest band of $^{52}CrF_4$ at 790.17 is in good agreement with the band at 784.3 cm^{-1} reportedly observed in Ar matrix;[6] however, no band was observable in our spectra at 303 cm^{-1} (cf. ref 6). It is noteworthy that spectra of CrF_4 and CrF_5 displayed in ref 6 and described as "very similar" do not contain the main features of CrF_5 and are thus due only to CrF_4.

The molecular structure of gaseous chromium tetrafluoride,

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(9) Bougon, R.; Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1985**, *24*, 2286.

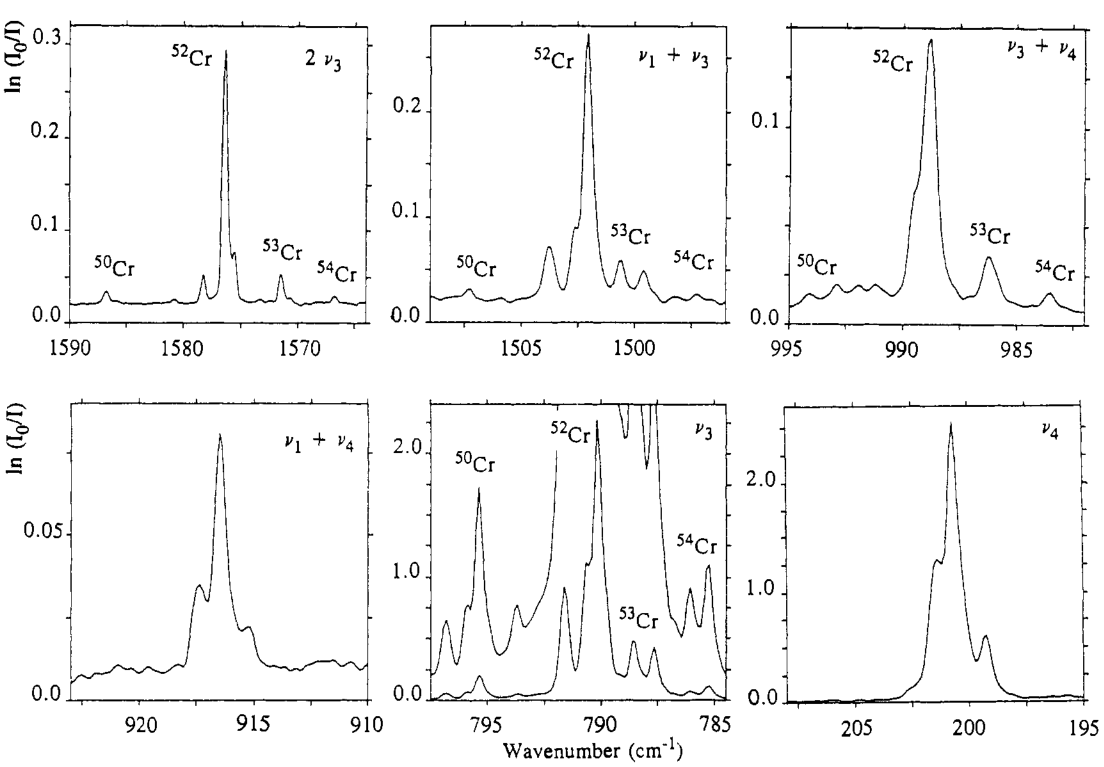

Figure 1. Infrared spectrum of CrF_4 isolated in a Ne matrix. Note the different scales; the most prominent isotopic band of each isotopomer is indicated.

studied by electron diffraction, is found to be tetrahedral.[10] The normal modes of vibration are described by the following irreducible representation:

$$\Gamma_{\text{vib}} = a_1\ (\text{Ra p}) + e\ (\text{Ra dp}) + 2\ f_2\ (\text{IR; Ra dp})$$

Strong bands at 790 and 201 cm^{-1} are assigned unambigously to the infrared active fundamentals ν_3 and ν_4 respectively. According to Figure 1 the band at 790 cm^{-1} is split into four components due to the four CrF_4 isotopomeres with the expected intensity ratio $^{50}Cr/^{52}Cr/^{53}Cr/^{54}Cr$ of 5/100/11/3. In addition each isotopomer shows an identical matrix splitting. It is interesting to note that the ν_3 mode at 799.4 cm^{-1} due to $^{48}TiF_4$, isolated in a Ne matrix, exhibits a similar pattern for the matrix splitting[11] as $^{52}CrF_4$. For the deformation mode ν_4 at 201 cm^{-1} the small isotopic effects (ca. 1.0 cm^{-1} for $^{50/52}Cr$, as calculated from the force field) are obscured by matrix splittings. All additional bands observed are due to combination modes. Their assignments are based on the selection rules and their isotopic and matrix patterns. The wavenumber of the infrared inactive mode ν_1 was deduced from the combination $\nu_1 + \nu_4$. With a small anharmonicity correction included ($x_{14} = -2 \pm 3$ cm^{-1}) it is estimated to be 717 ± 3 cm^{-1}. No combination band involving ν_2 was detected, but in comparison to the bending modes ν_2 and ν_4 of TiF_4 and GeF_4, it is expected to be below 200 cm^{-1} (see Table II). In order to complete the vibrational analysis of CrF_4, we intend to record its Raman spectrum.

Table II. Fundamental Vibrations (cm^{-1}) and Force Constants (10^2 N m^{-1}) of CrF_4 and Related Molecules

	$^{48}TiF_4$	$^{52}CrF_4$	$^{74}GeF_4$[d]
ν_1	712[b]	717	735
ν_2	185[b]		203
ν_3	799[b]	790	800
$\Delta\nu_3$[a]	12.6 (46/50)[c]	5.2 (50/52)	5.7 (70/74)
ν_4	209[b]	201	273
f_r	4.74[e]	4.99	5.57
f_{rr}	0.31[e]	0.26	0.16

[a] Isotopic shift. [b] Reference 14. [c] Reference 15; TiF_3 bands assigned to TiF_4 according to ref 11. [d] Reference 16. [e] This work, from data given above; see also text.

From the secular equation for tetrahedral molecules[12] and the vibrational data in Table II, the symmetry force constants of TiF_4/CrF_4 are calculated to be $F_{11} = 5.67/5.75$, $F_{22} = 0.13/...$, $F_{33} = 4.43/4.73$, $F_{34} = -0.065/0.069$ and $F_{44} = 0.151/0.136$ respectively. The force constants of TiF_4 agree well with those of ref 13 within their quoted uncertainties.

The deduced internal force constants f_r and f_{rr} are collected in Table II. As expected the X–F (X = Ti, Cr, Ge) force constant f_r increases with increasing nuclear charge of the elements and f_{rr} decreases with increasing nuclear mass.

The Ne matrix containing pure CrF_4 is colorless, and no absorption is observed in the visible region. In the UV region an increasing absorption is noted from ca. 400 nm to 230 nm, which is much weaker than that of the mother molecule CrF_5 (see Figure 6a). The fine structure >400 nm may be due to uncompensated background and sample spectra.

(b) Infrared, Ultraviolet, and Visible Spectra of Monomeric CrF_5. As for CrF_4, neon is used as matrix material for the same reason and in order to minimize gas phase/matrix wavenumber shifts. In addition nitrogen is used as matrix gas in order to compare our spectrum with that attributed previously to CrF_6.[6] In the course of our experiments, the conditions for matrix isolation of the material, which we show convincingly to be pure CrF_5, are

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(10) Hedberg, L.; Hedberg, K.; Gard, G. L.; Udeaja, J. O. *Acta Chim. Scand.* **1988**, *A42*, 318.

(11) Beattie, I. R.; Jones, P. J.; Young, N. A. *Angew. Chem.* **1989**, *101*, 322; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 313.

(12) See, for example: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, Chicester, England, Brisbane, Australia Toronto, Canada, 1977.

(13) Girichev, G. V.; Petrov, V. M.; Giricheva, N. I.; Krasnov, K. S. *Zh. Strukt. Khim.* **1982**, *23*, 55; *J. Struct. Chem.* (*Engl. Transl.*) **1982**, *23*, 45.

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Table III. Vibrational Wavenumbers (cm^{-1}), Intensities, *I*, and Assignments for CrF_5

	neon matrix		nitrogen	
gas phase ν^a	ν^a	I^b	matrix ν^a	assignts^c
	1486.2	vw, br		$\nu_2 + \nu_{10}$ (B_2)
1466	1469.7 1463.5 1460.7 1457.7	0.7	1456.2	$\nu_2 + \nu_7$ (B_1)
	1399	vvw, br		$\nu_3 + \nu_{10}$ (B_2)
1372	1370.3	1.1	1359.7	$\nu_3 + \nu_7$
	887	9.4, br	890	$\nu_3 + \nu_{11}$ (B_2)
	864	6.3, br		$\nu_3 + \nu_{12}$ (B_2)
	819	1.5		$\nu_3 + \nu_9$ (B_1)
~800	797 792.2	sh 80, br	789	ν_{10} (b_2) = $\nu_{as}(CrF_e)$
779 R 772 Q 771 Q′ ~763 P	774.23 767.71 764.63 761.67	100	765.26 758.85 755.83 752.90	ν_7 (b_1) = $\nu_{as}(CrF_a)$
	754.8	1.4	746.8	ν_1 (a_1) = $\nu_{op}(CrF_e)^d$
	333.4 332.2 331.5 330.9	8		ν_8 (b_1) = $\delta_{op}(CrF_a)^d$

[a] Most intense components of the ^{50}Cr, ^{52}Cr, ^{53}Cr, and ^{54}Cr isotopomers; for precision: see text. [b] Integrated intensity over isotopic and matrix pattern; $I(\nu_7)$ = 100. [c] According to C_{2v} symmetry; see also text. [d] op: out of phase.

improved further. Compared to our previous report,[7] knowledge of both the photochemical behaviour of CrF_5 and the spectrum of pure CrF_4 has made it possible to correlate more bands to CrF_5 than previously.[7] The results are summarized in Table III, and the CrF stretching region is displayed in an expanded scale in Figure 2a.

The most important novel feature in the spectrum of CrF_5 is the unusual broad band at 792 and 789 cm^{-1}, respectively (half-widths 5 and 12 cm^{-1}), in Ne and N_2 matrices, which is also present in the matrix spectrum published by Hope et al.[5,6] However this band extends from 795 to 775 cm^{-1} in Figure 2d of ref 6. Therefore, its absorbance is fairly low, which might be the reason why this band was overlooked by the authors of refs 5 and 6. In all matrix spectra of CrF_5 interference is caused by the very intense ν_3 absorption of CrF_4. Since CrF_5 is an extremely strong oxidative fluorinator, partial reduction occurs by the metal surface of the inlet system employed for matrix deposition. This undesirable side reaction is minimized by keeping the inlet system at a temperature of −20 °C during matrix deposition. By means of CrF_4 spectra it is also possible to subtract its contribution in the spectra of CrF_5. Afterward in all different experiments the ratio of integrated band intensities for the bands at 792 and 768 cm^{-1} is about 0.8. The fact that *both* bands are due to CrF_5 is confirmed by the photolysis experiments with light of wavelengths <610 nm, which causes an identical decrease in intensity for all CrF_5 bands, as reported in Table III.

Besides bands of CrF_5, CrF_4, and traces of $CrOF_4$ which are assigned by comparison with published spectra,[17] some additional bands are observed in the matrix spectra of CrF_5 at 816.2 and 735.4 (Ne-matrix) and 813.8 and 733.8 cm^{-1} (N_2-matrix). The relative intensity of these bands, compared to the band intensities of CrF_5, increases with increasing concentration of CrF_5. The species causing these bands is stable with respect to irradiation with light of wavelengths >320 nm and is tentatively suggested to be Cr_2F_{10} or another oligomer of CrF_5.

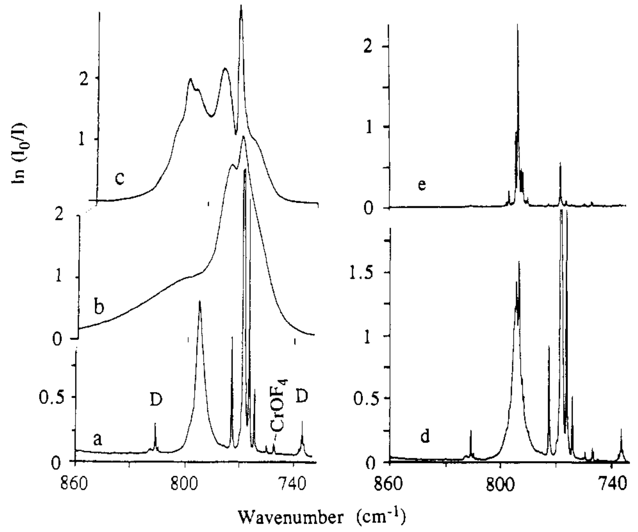

Figure 2. Infrared spectra of CrF_5 and VF_5 in the region of the MF stretching region. Note: the wavenumber scale is centered at $\nu_{as}(MF_a)$. (a) Spectrum of CrF_5 isolated in a Ne matrix, with minor bands of CrF_4 subtracted and peak D being due to Cr_2F_{10}; resolution 0.3 cm^{-1}. Note: The band of $^{52}CrF_5$ at 767.71 cm^{-1} in the isotopic pattern of $\nu_{as}(CrF_a)$ is cut off. (b) Spectrum of 10^{-4} mol L^{-1} CrF_5 in the gas phase, optical path length 20 cm, resolution 2 cm^{-1}. (c) Spectrum of 6 × 10^{-4} mol L^{-1} VF_5 in the gas phase, optical path length 20 cm, resolution 1 cm^{-1}. (d) Original spectrum of a 4 mmol neon matrix containing CrF_5, which was used for computer subtraction with spectrum e resulting in spectrum a. The estimated molar ratio CrF_5/Ne is 1/1000 as concluded from the UV absorbance of CrF_5 (cf. Figure 6a,b) and the thickness of the matrix. (e) Original spectrum of a 0.4 mmol neon matrix containing CrF_4, which was used for computer subtraction resulting in spectrum a. The estimated CrF_4/Ne ratio is 1/500. This ratio was concluded from comparison of spectra d and e with the relative integrated absorbance ratio CrF_4/CrF_5 in the spectral region 810–780 cm^{-1} (1.8), determined from the photolysis experiment (see text).

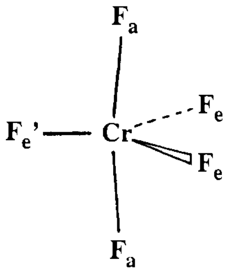

Figure 3. Structure of CrF_5. Structural parameters of CrF_5[18,19] $r(Cr-F_e)$ = 168.9 (5) pm, $\angle(F_eCrF_e)$ = 129.6 (11)°, $r(Cr-F_a)$ = 173.2 (8) pm, and $\angle(F_e'CrF_a)$ = 95.2 (4)°.

The wavenumbers in the region of ν_7 of CrF_5 isolated in a nitrogen matrix due to the well-resolved chromium isotopic pattern are in complete agreement with the published data attributed to CrF_6.[5,6,8]

The molecular structure of gaseous chromium pentafluoride was determined by electron diffraction. The symmetry is slightly distorted from D_{3h} toward C_{2v} symmetry.[18] All reported structural parameters, displayed in Figure 3, have been confirmed by Oberhammer[19] employing our material.[7] The experimental radial distribution curve is incompatible with a mixture of CrF_4 and CrF_6.[19] The normal modes of vibration for CrF_5 with C_{2v} symmetry are described by the following irreducible representation:

$$\Gamma_{vib} = 5\ a_1\ (IR;\ Ra\ p) + a_2\ (Ra\ dp) + 3\ b_1\ (IR;\ Ra\ dp) + 3\ b_2\ (IR;\ Ra\ dp)$$

The observed vibrational wavenumbers in Table III are assigned

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(17) Christe, K. O.; Wilson, W. W.; Bougon, R. *Inorg. Chem.* **1986**, *25*, 2163.

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Table IV. Fundamental Vibrations (cm^{-1}) of CrF_5 in Comparison to VF_5

VF_5^{a}	assignts (D_{3h})	CrF_5	assignts (C_{2v})
719	ν_1 (a_1') = $\nu_s(VF_e)$	696^b	ν_2 (a_1) = $\nu_{ip}(CrF_e)$^{c}
608	ν_2 (a_1') = $\nu_s(VF_a)$	603^b	ν_3 (a_1) = $\nu_s(CrF_a)$
784	ν_3 (a_2'') = $\nu_{as}(VF_a)$	768	ν_7 (b_1) = $\nu_{as}(CrF_a)$
331	ν_4 (a_2'') = $\delta_{op}(VF_e)$	332	ν_8 (b_1) = $\delta_{op}(CrF_e)$^{c}
810	ν_5 (e') = $\nu_{as}(VF_e)$	792	ν_{10} (b_2) = $\nu_{as}(CrF_e)$
		755	ν_1 (a_1) = $\nu_{op}(CrF_e)$^{c}
282	ν_6 (e') = $\delta(VF_e)$	284^b	ν_{11} (b_2) = $\delta(CrF_e)$
		...	ν_4 (a_1) = $\delta(CrF_e)$
~200	ν_7 (e') = $\delta(VF_a)$	261^b	ν_{12} (b_2) = $\delta(CrF_a)$
		...	ν_5 (a_1) = $\delta(CrF_a)$
350	ν_8 (e'') = ρ	216^b	ν_9 (b_1) = $\rho(CrF)$
		...	ν_6 (a_2) = $\rho(CrF_e)$

^{a} Reference 20. ^{b} Tentative, deduced from combinations; see text. ^{c} ip, in phase; op, out of phase.

by comparison with the vibrational spectrum of VF_5.[20] Lowering of the D_{3h} symmetry of VF_5 to the symmetry C_{2v} of CrF_5 removes degeneracy of each e-mode resulting in a split into a and b modes (see Table IV).

The five stretching modes of CrF_5 are distributed among 3 a_1 + b_1 + b_2, which are all infrared allowed. Of these, the b modes are expected to have high intensities in the IR spectrum. Accordingly the bands at 792 and 768 cm^{-1} are assigned to ν_{10} (b_2) = $\nu_{as}(CrF_e)$ and ν_7 (b_1) = $\nu_{as}(CrF_a)$, respectively. (The subscripts "e" and "a" denote equatorial and axial, respectively; cf. Figure 3.) The unusual broad appearance of ν_{10} may either be due to coupling of ν_{10} with pseudorotation motions or to the dynamic Jahn–Teller distortion.[21] It should be pointed out that, in the infrared spectrum of matrix-isolated VF_5, the respective mode ($\nu_{as}(VF_e)$) is also rather broad.[22] The corresponding band envelope of gaseous CrF_5 (cf. Figure 2b) now becomes comprehensible: The strong band in the range 790–750 cm^{-1} is mainly due to $\nu_7 = \nu_{as}(CrF_a)$. It exhibits a PQR contour similar to that of $\nu_{as}(VF_a)$ in VF_5 with PR separations of ~16 and ~18 cm^{-1} for CrF_5 and VF_5, respectively. The extremely broad feature at higher wavenumbers is due to $\nu_{10} = \nu_{as}(CrF_e)$. In contrast, the corresponding vibration of VF_5 exhibits a Q branch (cf. Figure 2c), and some fine structure is resolved at a resolution of 0.5 cm^{-1}. These differences are suggested to be due to the different symmetries of CrF_5 and VF_5.

It should be pointed out that the observation of more than one stretching vibration in the matrix and gas-phase IR spectra argues convincingly against the identification of the molecule as CrF_6. Additional, independent evidence comes from electron diffraction and high-resolution IR studies.

Of the two equatorial a_1 stretching vibrations, the out of phase vibration ($\nu_{op}(CrF_e)$) is expected at higher wavenumbers than the in phase vibration ($\nu_{ip}(CrF_e)$). In comparison to the stretching vibrations of VF_5, the vibration $\nu_s(CrF_a)$ of CrF_5 should also be the lowest one. While $\nu_{op}(CrF_e)$ should exhibit significant IR intensity and Cr isotopic shifts, the intensities of bands due to $\nu_{ip}(CrF_e)$ and $\nu_s(CrF_a)$, which correlate with infrared inactive a_1 modes of VF_5, should be much lower.

In agreement with these expectations $\nu_1 = \nu_{op}(CrF_e)$ is observed at 754.8 cm^{-1}. The observation of this vibration is consistent with CrF_5 to be distorted from D_{3h} to C_{2v} symmetry in the matrix as well as in the gas phase. An isotopic shift could not be determined. The fundamentals $\nu_2 = \nu_{ip}(CrF_e) \approx 696$ cm^{-1} and $\nu_3 = \nu_s(CrF_a) \approx 603$ cm^{-1} were not observed directly, but could be evaluated from combination bands, found in the 1350–1500-cm^{-1} region (cf. Table III). For VF_5 the corresponding modes have also been observed with similar intensities.[20] Additional support for the proposed assignments stems from the observation that $\nu_2 + \nu_{10}$ and $\nu_3 + \nu_{10}$ are broad, just like ν_{10}, whereas $\nu_2 + \nu_7$ and $\nu_3 + \nu_7$ are much sharper. Finally it appears that the calculated wavenumbers for ν_2 and ν_3 are very close to the corresponding ones of VF_5 (cf. Table IV).

In the deformation mode region, 400–80 cm^{-1}, only one band, which exhibits a chromium isotopic pattern, is observed at 332 cm^{-1}. In comparison to VF_5 the band is assigned to ν_8 (b_1). The remaining combinations at 887, 864, and 819 cm^{-1} can be attributed to $\nu_3 + \nu_{11}$, $\nu_3 + \nu_{12}$, and $\nu_3 + \nu_9$, respectively, due to their half-widths, again in comparison to the spectrum of VF_5. However, the latter assignments are tentative and must be confirmed by Raman measurements of the respective fundamentals.

For an additional proof, that the vibrational properties of CrF_5 described above are incompatible with those of CrF_6, a high-resolution IR spectrum of monoisotopic $^{52}CrF_5$ in the gas phase was recorded. It is illustrated in Figure 4 with an insert showing the water line at 525.96 cm^{-1} due to residual water vapor in the instrument and observed in the same spectrum to prove the experimental resolution. The CrF_5 band consists of two components, of which the stronger one reveals a Q branch at 772 cm^{-1} and a second, broad one whose band center cannot be determined exactly. Both bands do not show any rotational fine structure and are nearly identical with the low-resolution spectrum displayed in Figure 2b.

Resolved fine structure would be expected under the given experimental conditions, if the sample were rigid $^{52}CrF_6$ with octahedral (O_h), prismatic (D_{3h}), or antiprismatic (D_{3d}) shape, the latter two being expected to show K and even J details typical of symmetric top molecules.

That at least *some* structure of the $\nu_3(f_{1u})$ band of octahedral MF_6 molecules can be resolved, admittedly employing (slightly) different experimental conditions, has been shown in the past for several species. We cite $^{239}PuF_6$, FTIR, resolution 0.006 cm^{-1}, 205 K,[23] monoisotopic MoF_6, tunable diode laser, resolution 0.002 cm^{-1}, 195 K,[24] and there are other examples. Since the quoted spectra were recorded at lower temperature, we have searched for a more comparable example with a similar B_0 value and a similar band position, thus ensuring a comparable partition function and rovibrational pattern. We believe that (monoisotopic) $^{80}SeF_6$ mimics the rovibrational properties of the hypothetical CrF_6 perfectly. Therefore, we have recorded the ν_3 band of monoisotopic $^{80}SeF_6$ located at 780 cm^{-1} at room temperature with a resolution (fwhm) which was slightly worse than that employed for CrF_5. Figure 5 shows the complete band and a 0.2 cm^{-1} detail of the R branch plotted with the same transmission scale. Undoubtedly ample rotational structure is evident here.

From the high-resolution study of CrF_5, we conclude that the presence of rigid octahedral, prismatic, or antiprismatic CrF_6 in our sample, which was checked to be identical with that producing the reported matrix spectra before and after the high-resolution measurement, can be ruled out.

The color of molecular CrF_5 is described as crimson and that of "CrF_6" as lemon yellow.[8] We measured the UV/vis spectrum of CrF_5, isolated in a Ne matrix, in order to compare it with the reported gas phase spectrum of CrF_5.[7] The same matrix was used to record the infrared (cf. Figure 2a) and UV/vis spectrum shown in Figure 6a. In comparison to the gas-phase spectrum (Figure 6b), λ_{max} of the two principal absorption bands are only shifted by a few nanometers, but all other features are completely identical. This finding confirms that our gas-phase and matrix species are identical. In the UV/vis spectrum of "CrF_6" reported in ref 6 the prominent bands at 260 and 375 nm can now be attributed to CrF_5, while additional features may be due to byproducts like $CrOF_4$, CrO_2F_2, and oligomeric CrF_5, as evident from the reported IR spectra.

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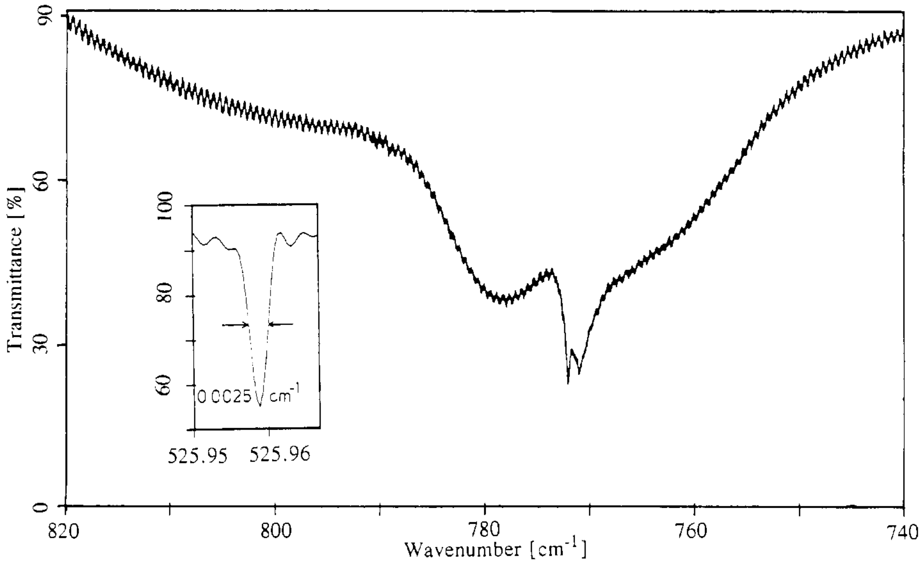

Figure 4. Infrared spectrum of 4×10^{-5} mol L^{-1} $^{52}CrF_5$ in the gas phase at 298 K, optical path length 11.5 cm, and resolution 2.5×10^{-3} cm^{-1}. The modulation of the band profile is due to interferences in the optical path.

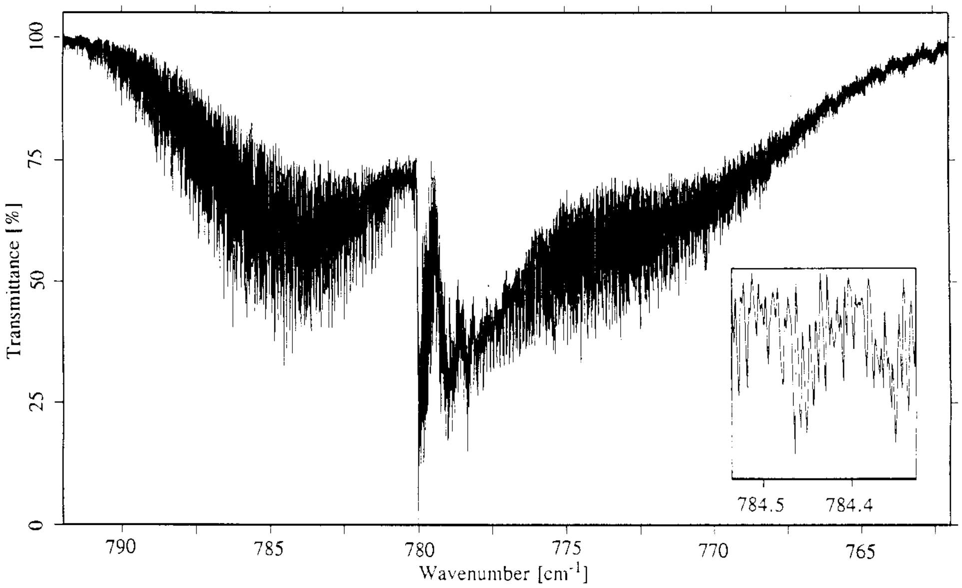

Figure 5. Infrared spectrum of 10^{-5} mol L^{-1} $^{80}SeF_6$ in the gas phase at 298 K, optical path length 28 cm, resolution 3×10^{-3} cm^{-1}.

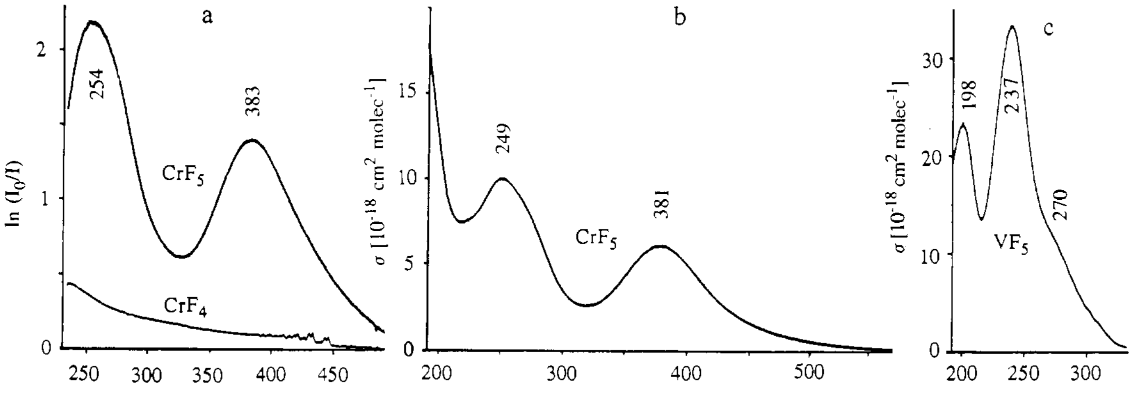

Figure 6. UV/vis spectra of (a) CrF_5 isolated in a Ne matrix (same matrix as used for recording the IR spectrum shown in Figure 2a) and CrF_4 obtained after complete photodissociation of CrF_5 in the same matrix, (b) gaseous CrF_5, and (c) gaseous VF_5.

It is interesting to compare the electronic spectrum of CrF_5 with that of VF_5, which is shown in Figure 6c. The difference between the spectra of both molecules is caused by the d^1-electron configuration and lower symmetry of CrF_5. The strong charge transfer transitions in CrF_5 may be mixed with d–d transitions. For pure d–d transitions, weak bands are expected in the near-infrared region (too weak to be detected or out of the range of our spectrometer) in correspondence to the electronic spectrum of VCl_4.[25]

With the help of photolysis experiments of matrix-isolated CrF_5, the threshold for photodissociation of CrF_5 was determined using a tungsten halogen lamp in combination with different cut-off filters. Decay of all infrared bands by a few percent within 10 min was first observed when a cut-off filter for wavelengths >610 nm was used. Photolysis with a mercury arc lamp in combination with a 320-nm cut-off filter caused complete depletion of the CrF_5 bands within 5 min, and pure CrF_4 was formed (vide infra).

$$CrF_5 \xrightarrow[>610\ \mathrm{nm}]{h\nu} CrF_4 + F$$

The resulting UV spectrum of CrF_4 is shown in Figure 6a. The photolysis threshold of 610 nm represents an upper limit for the bond dissociation energy of 196 kJ/mol, because an activation energy for ejection of the fluorine atom from the matrix cage is necessary. This low bond dissociation energy, which is comparable with that for F_2 (158 kJ/mol), is in agreement with the high oxidative fluorinating power of CrF_5, which is able to fluorinate Xe to XeF_2 and XeF_4.[26]

During our earlier[7] and present studies we found no evidence for disproportionation of CrF_5 into CrF_4 and CrF_6 as claimed by Hope et al.[5,6] Both mass and gas-phase infrared spectra were measured repeatedly and simultaneously in a high-vacuum system at different vapor pressures and temperatures. No change in either spectrum was observed. After condensation of the vapor at low temperature, infrared and Raman spectra of the solid compound were very similar to the respective literature spectra of solid and liquid CrF_5.[7]

Judging by the chemical behavior of CrF_5[9,26] and the results of our study, we predict CrF_6 to be an extremely strong oxidizer with low thermal stability. Considering the bathochromic shift from WF_6 to MoF_6 (cf. Figure 7; for assignments see ref 27) and taking into account the UV spectrum of VF_5, we expect for CrF_6 an UV band with prominent vibrational fine structure (ca. 700–750 cm^{-1}) and at most a weak absorption tail >400 nm. Hence CrF_6 should be colorless or possibly pale yellow.

In a recent high level ab initio study, structural and spectroscopic properties for CrF_6 were predicted. The surprising result is that its ground-state geometry might be a trigonal prism.[28] The predicted vibrational wavenumbers should be helpful for the identification of CrF_6.

Conclusion

The present study and our earlier study[7] on binary chromium fluorides in high oxidation states has led to the conclusion that so far there is no definitive and unambiguous evidence for the existence of CrF_6, in contrast to earlier reports.[2,3,5,6,8]

The results of this study bring chemical, structural, and spectroscopic properties of chromium fluorides in higher oxidation states in agreement.

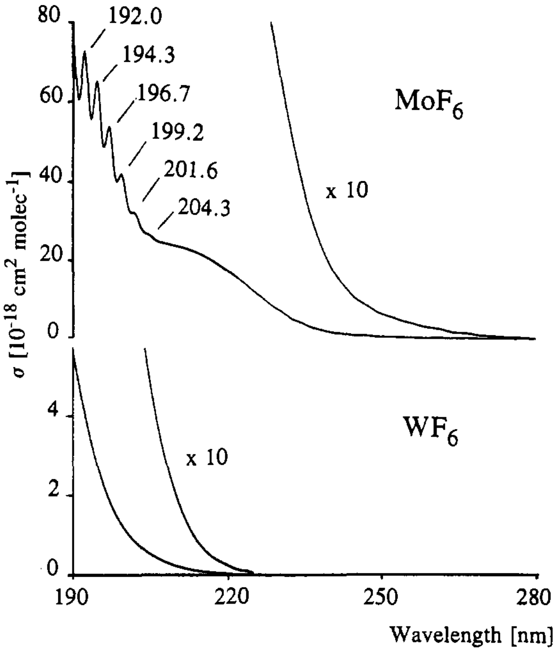

Figure 7. UV spectra of gaseous MoF_6 and WF_6.

Of these monomeric chromium tetrafluoride is colorless, and the molecule has T_d symmetry both in the gas phase as well as in a Ne matrix. Its spectroscopic and bonding properties fit well into the series TiF_4, CrF_4, and GeF_4.

Gaseous chromium pentafluoride is monomeric and shows no tendency to disproportionate into CrF_4 and CrF_6. In contrast, lower titanium fluorides, e.g. TiF_3, tend to disproportionate. This was the reason for a misinterpretation of vibrational spectra as in the case of "CrF_6": in ref 15, TiF_3 bands have been assigned to TiF_2 and TiF_4 bands to TiF_3.[11] Monomeric CrF_5 is yellow and has C_{2v} symmetry in the gas phase as well as in inert gas matrices.

Dimeric chromium pentafluoride, Cr_2F_{10}, can only be detected in matrices at higher CrF_5 concentrations. This is in contrast to the respective sulfur chemistry, where the SF_5 radical is short-lived and the S_2F_{10} molecule is well established.[29]

CrF_6 remains an unknown species. If it can be synthesized, it may be a transient species. Therefore, some of its predicted properties will be helpful for its identification.

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