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A study of the reactions of fluorine with chromium and iron at high temperatures by matrix isolation IR spectroscopy

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Abstract

Apparatus suitable for characterising the molecular species produced when fluorine reacts with a high-temperature metal surface is described and its use illustrated by identifying the species formed when fluorine is passed over heated chromium or iron within a temperature range up to 1000 °C. The species so formed are isolated in argon matrices and characterised by infrared spectroscopy. Metal isotope frequency shifts were used to support identification and the molecular species thus identified included CrF_4, CrF_3, CrF_2, FeF_3 and FeF_2. For each of the systems studied, it was found that the distribution of reaction products was markedly dependent on temperature. The technique could be generally applicable to the study of any high-temperature metal–fluorine system.

Keywords: Fluorine; Chromium; Iron; High-temperature reactions; Matrix isolation IR spectroscopy

1. Introduction

The spectra and structures of high-temperature transition-metal halides in the vapour phase have been the object of numerous experimental studies, and a considerable body of information has been produced over the last 20 years concerning such molecules. In a large majority of these studies, the basic method involves the preliminary synthesis of the parent solid compound, followed by vaporisation from an appropriate cell. Characterisation of the species then takes place via, typically, mass spectrometric, spectroscopic or diffraction methods, either directly in the vapour or in low-temperature matrices. For some systems, the initial vaporisation products have been superheated or allowed to react at high temperatures with another solid, usually a metal, to produce lower valency species.

In contrast, very few systems have been studied in which metal halide molecules are generated in the vapour phase as a result of **direct reaction** between a halogen and the surface of a transition metal at elevated temperatures. Such in situ studies are essential to the understanding of the thermodynamic behaviour of heated metals in strongly corrosive atmospheres, and may also provide evidence of novel chemical species formed in the initial stages of reaction. As part of our continuing programme [1–5] on the characterisation of a wide range of transition-metal fluorides, this present study is concerned with identifying the molecular species formed when molecular fluorine reacts with heated transition metals over a wide temperature range at a variety of partial pressures. Considerable effort was directed into the design of equipment suitable for the generation and detection of the molecular species formed under these conditions, and this paper describes our experimental system in detail together with our results on the reactions F_2+Cr and F_2+Fe at high temperatures.

Matrix isolation IR spectroscopy was selected as the principal method of species detection and identification, in view of its cumulative sampling method and its ability to discriminate easily between different molecular species. The metals iron and chromium were selected partly for their industrial importance, and partly because data already exist for some of the possible products of these fluorination reactions. Thus, for chromium, characteristic IR bands have been established for the species CrF_2, CrF_3 and CrF_4 [6–10], and assignments also proposed for CrF_5/CrF_6 [11–13].

In the case of iron, FeF_2 has similarly been characterised [10] and presumed to be linear, and although FeF_3 has been established as an independent vapour species from mass spectrometric [14,15] and electron diffraction [16,17] studies, its vibrational spectrum is not well established.

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2. Experimental details

The matrix isolation and IR spectroscopic equipment used for this work consist of an Air Products closed-cycle 'Displex' refrigerator and a Perkin-Elmer 983 IR spectrometer, and have been described elsewhere [18]. The specialised furnace, in which the high-temperature reaction between fluorine and the metal takes place, is shown in Fig. 1.

The iron samples used in these experiments were in the form of small pieces of metal packed into a medium-wall, 5-mm diameter Fe tube. This tube was located inside an alumina tube furnace which could be heated to 1300 °C using molybdenum resistance windings. In the Cr/F_2 system, the metal reactor consisted of lumps of high purity chromium (Fluka, >99.99%) packed inside a 5-mm diameter Ni tube. This furnace assembly was surrounded by radiation shields made of nickel and molybdenum, and the furnace jacket and end flanges were water-cooled.

Fluorine gas was admitted to the system through a medium-wall copper tube sealed hermetically into the detachable end flange, and this tube was connected to the reactor tube in the hot zone by a length of thin-wall (0.2 mm) Ni tubing which minimised thermal conduction losses. Fluorine flow rates were adjusted using a fine-control needle valve, precalibrated with air, and were ultimately optimised by the growth of product bands. The partial pressure of fluorine within the reaction zone was estimated to be ca. 10^{-2} mbar, significantly in excess of the vapour pressure of possible reaction products at the deposition temperature — indeed, we believe that the reactions within the heated tube were close to thermodynamic equilibrium. The matrix gas was admitted through an independent inlet system in an estimated 1000-fold excess, and there was no evidence for secondary co-condensation reactions involving metal fluorides and unreacted fluorine. Argon (99.999%) was obtained from BOC, and the fluorine was supplied by Matheson (>99%).

In a typical experimental sequence, the reactor and inlet system were prefluorinated at low temperatures and then outgassed at ca. 1000 °C for 20 min. During part of this period, the water cooling was disconnected to permit limited outgassing of the inner surfaces of the reactor. The deposition window was then cooled to ca. 12 K and pure argon deposited for several minutes to protect the window from subsequent attack. Fluorine was then passed through the reactor at increasing temperatures and spectra recorded after each deposition period, which varied between 0.5 and 10 h depending on the temperature and flow rate.

Some experiments also involved recording successive spectra with a *decreasing* temperature profile, and these gave essentially the same results as from an increasing profile. Controlled diffusion experiments were also performed up to ca. 35 K.

Survey spectra were obtained at a resolution of typically 5 cm^{-1}, and a resolution of 0.6 cm^{-1} was used to obtain isotopic features. A few argon matrix experiments were carried out on the direct vaporisation of anhydrous FeF_3 (98%, Aldrich). In these experiments, the sample was contained either in an alumina holder, which was heated inductively using a tantalum susceptor [19], or in a resistively-heated platinum holder [5].

3. Results and discussion

The general strategy followed for each set of experiments was first to monitor the temperature dependence of the reaction by recording sequential low resolution spectra and to relate the resulting difference spectra to the conditions of temperature and flow rate within the fixed period. The effect

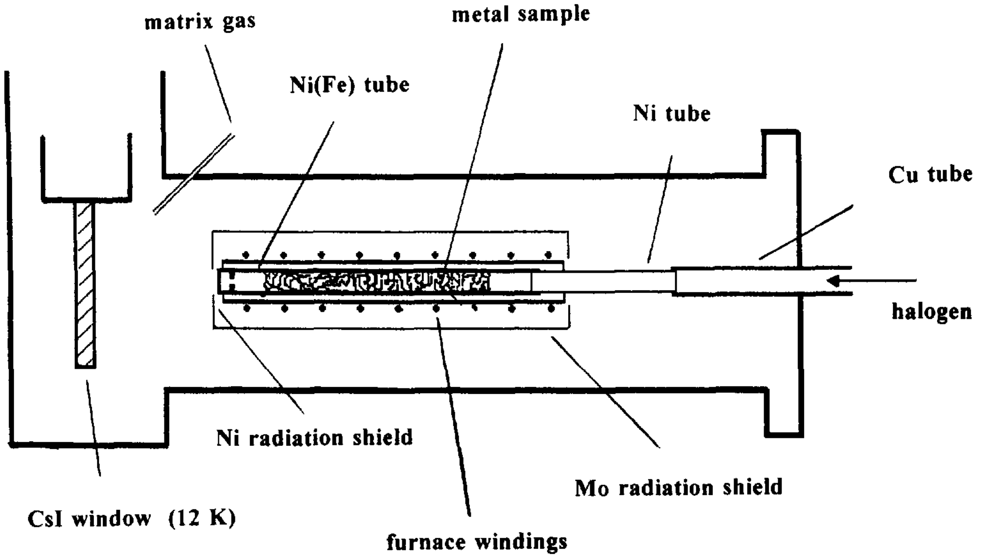

Fig. 1. Schematic diagram of high-temperature metal + F_2 reactor/evaporator.

of varying the F_2 flow rate at constant temperature was then explored and high resolution spectra were run at appropriate stages throughout the selected temperature/flow-rate regime. However, it soon became clear from a comparison of the chromium and iron systems that many of the resulting spectral features were common to both systems *and could also be observed in blank experiments, when neither of these metals was present.* In the description of a typical experimental sequence, as presented below, the positions of these 'impurity' bands are given in *italics* and the system-specific features in **bold** type. The results are most conveniently discussed by considering three temperature regions.

3.1. Cr + F_2 reaction products isolated in solid argon

(i) *25 °C to 550 °C*

No spectral features were observed as a result of passing F_2 over chromium at room temperature, but on heating the sample to 250 °C two prominent bands appeared at *737* and *707* cm^{-1} [Fig. 2(a)]. Further heating to 390 °C resulted in the growth of the *707* cm^{-1} band, the appearance of new bands at **784** and *689* cm^{-1}, and a relative decrease in the *737* cm^{-1} band. At 460 °C [Fig. 2(b)], the **784** cm^{-1} band was quite prominent, the *689* cm^{-1} band well-established while the *737* cm^{-1} was diminishing, and by 515 °C [Fig. 2(c)] the band at **784** cm^{-1} had become the most intense feature in the spectrum. At this stage, minor changes could be detected in certain of the band contours and peak maxima, and a new feature appeared at *811* cm^{-1} together with additional bands at *631* cm^{-1}, and at *1053*, *1022* and *384* cm^{-1} (not shown). Further heating to 540 °C and a reduction in the F_2 flow rate yielded a spectrum in which essentially only the **784** cm^{-1} band had grown.

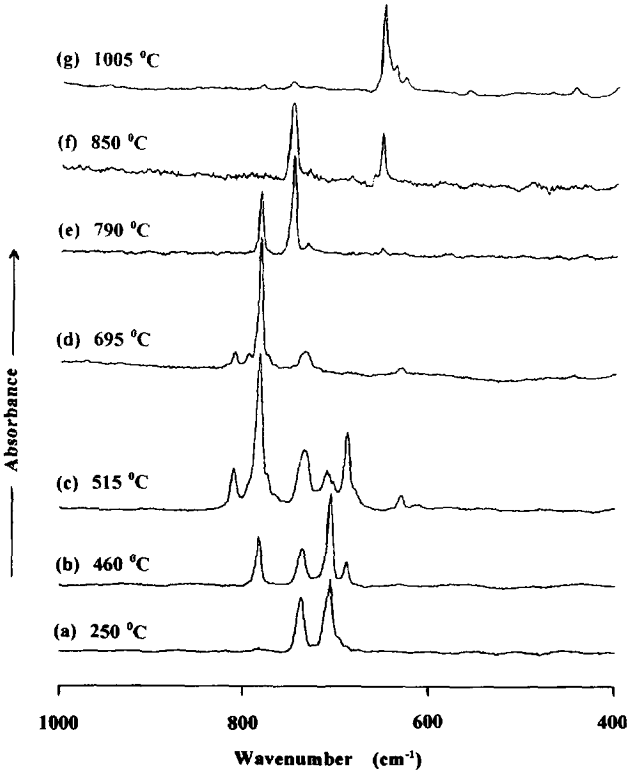

Fig. 2. Sequential argon matrix spectra obtained from the Cr + F_2 system.

(ii) *550 °C to 750 °C*

Relatively few spectral changes were observed in this intermediate temperature range, and Fig. 2(d), which characterises the reaction products at 695 °C shows a typical spectrum. Spectral features below 760 cm^{-1} and the band at *811* cm^{-1} have become less prominent in comparison with the **784** cm^{-1} band, but with an enhanced F_2 flow rate a number of very weak bands: *972; 941; 933; 903; 820; 794; 774; 732; 641; 559; 446; 398; 301; 243* cm^{-1} could be detected with varying degrees of reproducibility.

(iii) *790 °C to 1100 °C*

At ca. 790 °C, a new band begins to appear to **749** cm^{-1}, and a reduction of the F_2 flow rate at this temperature results in a spectrum in which this new feature is of comparable intensity to that at **784** cm^{-1} [Fig. 2(e)], with all other bands in the spectrum being much weaker. By 850 °C the band at **749** cm^{-1} dominates the spectrum while the **784** cm^{-1} has decreased dramatically, and a new band has begun to grow at **652** cm^{-1}.

Fig. 2(f) shows a typical spectrum at 850 °C for normal F_2 flow rates. Under conditions of reduced F_2 flow at this temperature, the **749** cm^{-1} band is considerably less prominent. Above 860 °C, this **749** cm^{-1} band diminishes in importance and by ca. 1000 °C [Fig. 2(g)] the **652** cm^{-1} band dominates the spectrum, and is accompanied by weak shoulders at 641 and 630 cm^{-1}. Both the bands at **784** and **749** cm^{-1} are by now very weak, even at high F_2 flow rates. Two additional weak bands were also observed at this stage, at *1047* and *850* cm^{-1}.

3.1.1. Spectral analysis

The total number of IR bands which appeared during these studies was quite large, and although attention was focused primarily on the **chromium-specific** features, the identity and possible origin of some of the *impurity* bands could be established from previous studies. Thus, the features at *1022* and *384* cm^{-1} are assigned to SiF_4 [20] and those at *737* and *631* cm^{-1} to MoF_6 [21] and CF_4 [22], respectively. The presence of SiF_4 and MoF_6 arise, we believe, as a result of reaction between hot F_2 and the interior construction materials of the cell: silica-based ceramics were employed in the electrical heating system and the resistance heater was made of molybdenum. The other bands, many of which are only present in the initial stages of reaction, are attributed to traces of perfluorohydrocarbons formed from the residual grease in the system.

The chromium-specific features were initially identified by comparison with blank runs, but a second criterion was the **positive identification of the chromium isotope structure.** Chromium in natural abundance possesses four isotopes: ^{50}Cr, 4.31%; ^{52}Cr, 83.76%; ^{53}Cr, 9.55%; and ^{54}Cr, 2.38%, and all IR-active Cr–F vibrations are expected to show a

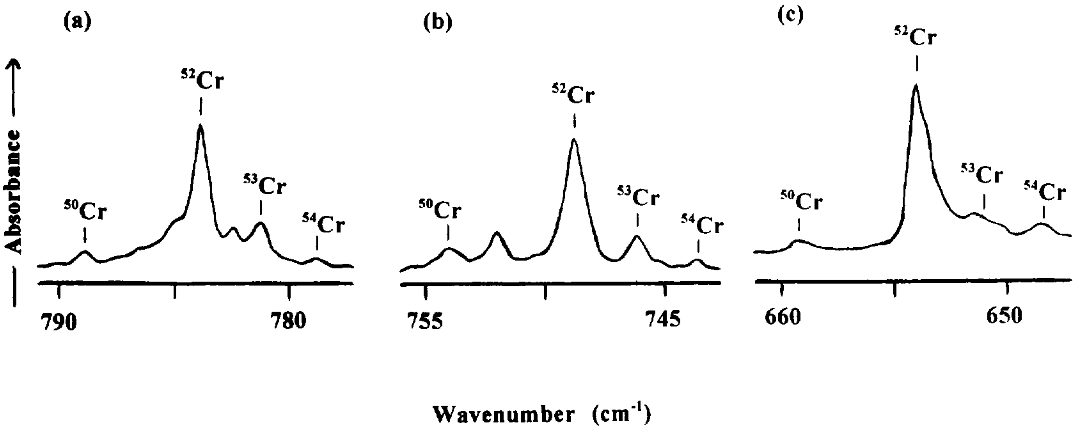

Fig. 3. Argon matrix spectra of (a) CrF_4, (b) CrF_3 and (c) CrF_2, obtained at a resolution of 0.6 cm^{-1}.

Table 1
Observed and calculated isotopic frequencies (cm^{-1}) for chromium tetra-, tri- and di-fluorides isolated in argon matrices

(i) CrF_4

Observed	Calculated	Observed	Assignment
Cr + F_2 (this work [a])	T_d	CrF_4 (solid vaporisation) [6]	
788.9	788.92	789.5 788.2	$^{50}CrF_4$
784.9		786.6	
783.8	783.80	784.3	$^{52}CrF_4$
782.4			
781.2	781.37	781.8 780.5	$^{53}CrF_4$
778.8	779.03	779.5 778.3	$^{54}CrF_4$

(ii) CrF_3

Observed	Calculated	Observed	Assignment
Cr + F_2 (this work [a])	D_{3h}	CrF_3 (solid vaporisation) [9]	
754.0	753.98	754.7	$^{50}CrF_3$
752.0			
748.7	748.70	749.3	$^{52}CrF_3$
746.1	746.19	746.9	$^{53}CrF_3$
743.7	743.77	744.4	$^{54}CrF_3$

(iii) CrF_2

Observed	Calculated	Observed	Assignment
Cr + F_2 (this work [a])	$D_{\infty h}$	CrF_2 (solid vaporisation) [7]	
659.3	659.29	659.8	$^{50}CrF_2$
653.8	653.80	654.4	$^{52}CrF_2$
651.5	651.19	652.7 (651.8 [b])	$^{53}CrF_2$
650.2 sh			
648.4	648.66	649.5	$^{54}CrF_2$

[a] Frequency accuracy, ±0.3 cm^{-1}.
[b] Corrected as per Ref. [21].

corresponding isotope pattern under high resolution. The magnitude of the isotope splitting depends on the frequency and geometric factors, but for Cr–F terminal modes the ^{50}Cr–^{54}Cr splitting is expected to lie within a frequency range ca. 8–14 cm^{-1}. Sharp features which do not show the expected isotope pattern are unlikely therefore to arise from Cr–F modes.

The three bands at **784**, **749** and **652** cm^{-1}, previously identified as chromium-specific features, exhibited the expected isotopic structure and are shown under high resolution in Fig. 3. From previous argon matrix studies on the vaporisation of the anhydrous solids, these bands may be unequivocally assigned as 784, ν_3 CrF_4 (T_d) [6]; 749, ν_3 CrF_3 (D_{3h}) [9]; and 652, ν_3 CrF_2 ($D_{\infty h}$) [7]. Table 1 compares the bands observed in these present studies with the earlier work, and also includes the results of isotope shift calculations. The overall agreement is very satisfactory, the small differences in frequency between this work and previous studies being attributed to the presence of unreacted fluorine in our matrices.

3.2. Fe + F_2 reaction products isolated in solid argon

3.2.1. Results and spectral analysis

When fluorine was passed over heated iron, the initial matrix IR spectra at low temperatures showed the characteristic 'impurity' features noted in the chromium system above, but at temperatures in excess of ca. 700 °C a prominent new feature was observed centred at ca. **730** cm^{-1} which was unique to the iron system. Under high resolution, this band appeared as a partially resolved doublet, with components at 730.2 and 728.4 cm^{-1}, and weaker additional features could also be observed at 735.6, 733.0 and 725.2 cm^{-1}. When the temperature of the reaction zone was raised to 850 °C, only the absorptions at 730.2 and 735.6 cm^{-1}, together with a very weak additional feature at 727.5 cm^{-1} were observed. Fig. 4(a) shows a typical spectrum obtained at a reaction temperature of 850 °C, while Fig. 4(b) shows the IR bands obtained at 720 °C.

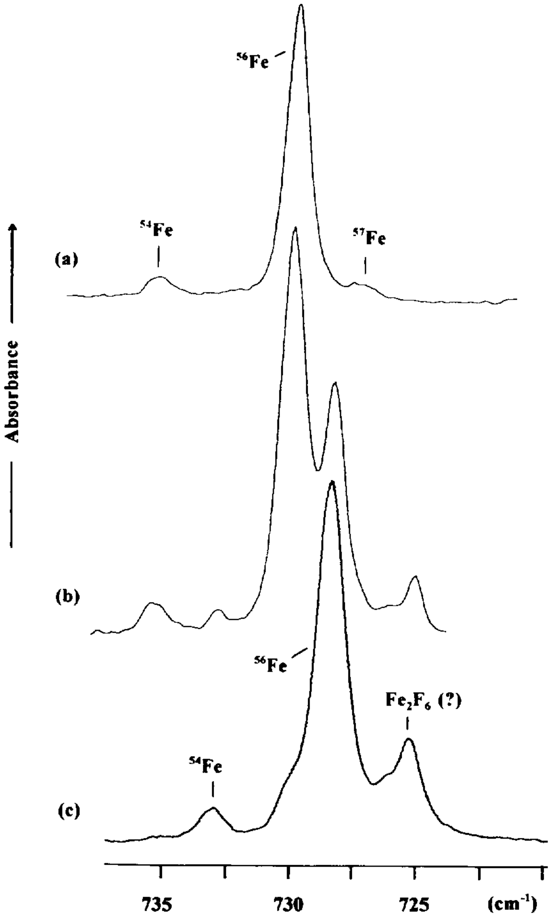

Fig. 4. High-resolution (0.6 cm^{-1}) argon matrix spectra obtained from: (a) Fe + F_2 at 850 °C; (b) Fe + F_2 at 720 °C; and (c) solid FeF_3 at ca. 700 °C.

The 730.2 cm^{-1} band is assigned as the antisymmetric stretching mode of molecular $^{56}FeF_2$ on the basis of the previous work by Hastie et al. [10] who observed a feature at 731.1 cm^{-1} under low resolution during the course of argon matrix studies on the vaporisation of solid FeF_2. In addition to this principal isotope ^{56}Fe (91.66%), iron in natural abundance also contains the isotopes ^{54}Fe (5.82%) and ^{57}Fe (2.19%), and the weaker features at 735.6 and 727.5 cm^{-1} in Fig. 4(a) are correspondingly assigned to $^{54}FeF_2$ and $^{57}FeF_2$. Fig. 4(b) shows that an additional reaction product is formed at lower temperatures, and by analogy with the Cr + F_2 system, we assign the additional bands at 733.0, 728.5, 726.3 and 725.2 cm^{-1} to iron(III) fluoride. In particular, the prominent feature at 728.5 cm^{-1} is assigned as the antisymmetric stretch in D_{3h} $^{56}FeF_3$, the weaker satellite at 733.0 cm^{-1} to $^{54}FeF_3$, and the very weak feature at 726.3 cm^{-1} to $^{57}FeF_3$. The lower frequency band at 725.2 cm^{-1} is provisionally assigned to a polymer.

There is currently no definitive vibrational characterisation of molecular FeF_3. However, bands at 728 and 725 cm^{-1} have previously been noted (but unassigned) by Huglen [23] during argon matrix studies on the vaporisation of NaF/FeF_3 and KF/FeF_3 systems, and Predtechenskii and Shcherba [24] have reported the appearance of a band at ca. 730 cm^{-1} under low resolution during an argon matrix study of the vaporisation of solid FeF_3. In order to support our assignments for FeF_3, we therefore carried out an independent study on the vaporisation of solid Fe(III) fluoride. Fig. 4(c) shows part of the argon matrix spectrum obtained from our vaporisation of solid Fe(III) fluoride at ca. 700 °C. The same prominent band was observed at 728.4 cm^{-1}, together with the weaker satellite at 732.9 cm^{-1} and the 'polymer' band at 725.2 cm^{-1}. Controlled diffusion studies on this deposit over the temperature range 12–35 K showed a significant decrease of the principal 728.4 cm^{-1} feature and the disappearance of the weaker satellite, but there was little change in the intensity of the 725.2 cm^{-1} feature. These results therefore confirm our above assignments, and by analogy with other metal(III) halide systems, we believe the 'polymer' feature can be assigned to the Fe_2F_6 dimer.

Table 2 compares our observed isotopic band positions for matrix-isolated FeF_3 and FeF_2 with those calculated for various geometries. For FeF_2, the linear model gives a better fit than the bent model, and for FeF_3, a D_{3h} geometry gives a better fit than a slightly pyramidal C_{3v} structure. However, although these equilibrium symmetries would appear to be the same as for the analogous chromium species, it is interesting to note that the antisymmetric stretching modes in FeF_2 and FeF_3 lie at almost the same frequency, whereas for CrF_3 and CrF_2 the corresponding modes are separated by almost 100 cm^{-1}. This represents a significant difference between the two systems, and mirrors the differences in bond length previously discussed by Hargittai [17].

The experimentally determined bond lengths in CrF_2 and CrF_3 are stated to be 1.795(3) and 1.732(2) Å, respectively, whereas for FeF_2 and FeF_3 the corresponding values are

Table 2
Observed and calculated isotopic frequencies (cm^{-1}) for iron tri- and difluorides isolated in argon matrices

(i) FeF_3

Observed	Calculated		Observed	Assignment
Fe + F_2 (this work)	D_{3h}	C_{3v} [a]	FeF_3 (solid vaporisation) (this work)	
733.0	733.03	732.88	732.9	$^{54}FeF_3$
728.5	728.50	728.50	728.4	$^{56}FeF_3$
726.3	726.34	726.41	726.2	$^{57}FeF_3$
725.2			725.2	Fe_2F_6

(ii) FeF_2

Observed	Calculated		Observed	Assignment
Fe + F_2 (this work)	$D_{\infty h}$	C_{2v} [b]	FeF_2 (solid vaporisation) [10]	
735.6	735.64	735.42		$^{54}FeF_2$
730.2	730.20	730.20	731.3	$^{56}FeF_2$
727.5	727.60	727.71		$^{57}FeF_2$

[a] Assuming a bond angle F–Fe–F = 115°.
[b] Assuming a bond angle F–Fe–F = 150°.

1.769(4) and 1.763(4). Numerous empirical relationships have been proposed linking bond lengths with principal stretching constants, and one might therefore anticipate that the principal M–F stretching constants in the four molecules follow the ordering: $CrF_3 > FeF_3 \sim FeF_2 > CrF_2$. The apparent ease by which the observed **frequencies** follow this order probably arises from the fact that for all four molecules, the dominant term in the relevant secular equations for both the di- and tri-halides takes the form $F_r - F_{rr}$, where F_r is the principal stretching constant and F_{rr} the interaction constant. Evidently, one must assume that the interaction constants do not change significantly within this group of molecules.

4. Conclusions

The work described here shows first that matrix isolation IR spectroscopy can be used successfully to monitor the reaction products formed in a particularly hostile chemical environment, and that it is possible to study variations in relative concentration as a function of temperature. Such variations, we believe, directly reflect changes in the equilibria in the system and can thus, in principle, provide one of the few sources of experimental verification of the predictions of thermodynamic modelling.

For the chromium system in particular, the relative importance of the species CrF_2, CrF_3 and CrF_4 as a function of temperature is very marked, and the excellent agreement between the frequencies observed here and those obtained previously from the vaporisation of solid samples suggests that this type of experiment can be extended meaningfully to a wide range of high-temperature metal–halogen reactions. In the case of the $Fe + F_2$ reaction, this work has provided supporting evidence for the linearity of FeF_2 and produced the first detailed vibrational characterisation of molecular FeF_3. The vapour-phase equilibria in this system are not well established, but our observations on the relative importance of FeF_2 and FeF_3 are qualitatively similar to the results recently obtained by mass spectrometry [15]. Work is currently in progress to refine existing thermodynamic models for both the high-temperature systems described here.

Acknowledgements

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