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GAS-PHASE STRUCTURES AND MASS SPECTRA OF BINARY PENTAFLUORIDES

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SUMMARY

Most known non-radioactive pentafluorides have been examined by molecular-beam mass spectrometry and by the deflection of molecular beams in inhomogeneous electric fields. Extensive association of the vapors occurs for all but the lighter pentafluorides and the interhalogens. The interhalogen pentafluorides are strongly polar, consistent with the accepted C_{4v} symmetry. The transition-metal and Group V pentafluorides are all non-polar, except VF_5 and CrF_5 for which temperature-dependent polarity is observed. However, uncertainty exists as to whether these observations are applicable to monomeric pentafluorides in all cases. Mass-spectral cracking patterns are presented for all species.

INTRODUCTION

The gas-phase structures of the Group VB and halogen pentafluorides have been studied reasonably extensively, but understanding of the structures of the transition-metal pentafluoride series is less developed. For PF_5 and AsF_5, vibrational spectroscopic results[1–8] indicate the presence of a monomeric gaseous phase

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containing molecules of D_{3h} symmetry, consistent with the interpretation of electron-diffraction studies on PF_5[9] and AsF_5[10]. The SbF_5 molecule was originally interpreted as having D_{3h} symmetry on the basis of its vibrational spectrum in the liquid and vapor phases[11–13], but the results of a recent re-investigation of the liquid phase by Beattie *et al.*[14] have been interpreted in terms of *cis*-bridged polymers with the fluorine atoms octahedrally distributed about the antimony atom. Although Aljibury and Redington[15] had assigned a C_{4v} structure to SbF_5 based on the infrared spectra of SbF_5 in Ar and Ne matrices, Alexander and Beattie[16,17] have shown that these spectra are essentially the same as those of liquid and gaseous SbF_5 under conditions where little or no monomer is present. Mass-spectrometric measurements of SbF_5 vapor[18–21] indicate substantial association. Thus there exists some question as to the correct structural assignment for monomeric SbF_5, although the most consistent interpretation of the vibrational spectra would favor a trigonal-bipyramidal D_{3h} structure. BiF_5 has been considerably less studied in the gaseous phase, but like SbF_5 is associated in the vapor[19,21].

Analyses of the vibrational spectra of the halogen pentafluorides ClF_5, BrF_5 and IF_5 indicate that all have square-pyramidal structures with C_{4v} symmetry[22–25]. For BrF_5 and IF_5, this assignment is supported by ^{19}F NMR studies[22] and analysis of microwave and electron-diffraction data[26–28].

Of all the transition-metal pentafluorides, only those of Group VA, *i.e.* VF_5, NbF_5 and TaF_5, have been studied in the gaseous phase. The vibrational spectrum of VF_5 in the liquid phase at elevated temperatures and in the gaseous phase has been interpreted in terms of a molecule of D_{3h} symmetry[5,29,30]. Electron-diffraction data for gaseous VF_5 are consistent with this bipyramidal structure[31]. However, the electric deflection of molecular beams of VF_5 has shown the presence of a temperature-dependent dipole moment[32]. These properties may be confidently ascribed to monomeric VF_5 based on vapor density[33,34] and mass-spectrometric[20] measurements. By contrast, NbF_5 and TaF_5 vapors are now known to be associated[16,20,31,35–37]. Although Blanchard[38] made an initial assignment of the infrared spectrum of NbF_5 vapor to D_{3h} monomers, her material was probably polymeric. Gas-phase vibrational spectra[16,35] of NbF_5 and TaF_5 monomers and gas-phase electron-diffraction data[31] at 200–240 °C are consistent with D_{3h} symmetry. Recently, on the basis of gas-phase and matrix-isolation infrared spectra, Acquista and Abramowitz[37] have proposed the alternative C_{4v} structure for monomeric NbF_5.

Although solid structures have been reported for all of the remaining transition-metal pentafluorides[39,40], a structure for the isolated molecule has only been proposed for MoF_5. From the infrared spectrum of matrix-isolated MoF_5, Acquista and Abramowitz[41] have assigned D_{3h} symmetry to the monomer. This is consistent with the conclusions of Ouellette *et al.*[42] obtained from vibrational spectra of liquid MoF_5.

Characterization of inorganic pentafluorides in the gaseous phase requires a knowledge of the structure of free MF_5 molecules, an understanding of the degree of association of the discrete monomers and the formation of low molecular weight oligomers as a function of temperature and pressure, and characterization of the associated species, if any. Investigation of these structural properties is complicated by the reactivity of many pentafluorides, including in some cases bimolecular disproportionation. In an attempt to understand further the gas-phase structures of these pentafluorides, we have studied many molecules of this class using molecular-beam mass-spectrometric techniques coupled with electric-deflection measurements. These combined techniques minimize complications due to impurities or reaction products and offer a less ambiguous interpretation than is often possible from the use of conventional spectroscopy.

If gas-phase polymers of the pentafluorides are stable they will be detected most readily in the saturated vapor, and their concentration in the saturated vapor is unlikely to be very largely temperature-dependent. The pentafluorides were therefore examined for polymers under conditions approaching the saturated vapor state to determine which species associate in the gaseous phase and which do not.

The pentafluorides were also studied under similar conditions using molecular-beam electric deflection. This technique is a sensitive method for detecting the presence of electric dipoles and hence is a valuable probe of molecular symmetry[43, 44]. Pentafluorides with D_{3h} symmetry and non-degenerate electronic ground states should be non-polar and hence any evidence of polar behavior in these molecules may be interpreted in terms of distortion from D_{3h} symmetry. Molecules with C_{4v} symmetry, however, should be quite polar and exhibit a first-order Stark effect characteristic of an oblate symmetric top. Double-fluorine-bridged dimers would be non-polar as would higher polymers with closed symmetric ring structures. Higher chain polymers would either exhibit a double-fluorine-bridged structure with all the metal atoms except those at terminal positions 7-coordinate or alternatively be octahedrally coordinated with one double-fluorine bridge per chain, regardless of the chain length. The double-fluorine bridge might occur at any position in the chain. For odd chains, and for even chains with the double bridge not in the center, the polymer would be electrically asymmetric. The magnitude of a possible dipole moment would be further dependent on the linearity of the structure.

EXPERIMENTAL

Apparatus

Electric-deflection studies were made using the molecular-beam resonance apparatus at Harvard University[45] which has also been used for related studies of volatile, high-oxidation-state fluorides[32, 46, 47]. The range of the mass analyzer associated with this apparatus was limited to about 400 a.m.u., thus enabling fragment ions containing a single metal atom to be monitored but restricting the study of fluoride agglomerates to metals of the first transition series. The pressures of VF_5, PF_5, AsF_5, SbF_5, ClF_5, BrF_5 and IF_5 in cylinders or Monel storage cans were regulated by means of a single needle valve into an effusion source from which the molecular beam originated. The pressures of the vapors behind the source slit for these species were below their saturation values and were generally less than 1 Torr. Samples of other pentafluorides were contained in Monel tubes of 6 mm outside diameter with crimped ends provided with a 0.25 mm × 6 mm slit from which the beam originated. These tubes were electrically heated to provide adequate beam intensities, the resulting vapor pressures approaching their saturation values.

To extend the mass range to enable the general study of the pentafluoride oligomers, the Bell Laboratories molecular-beam mass spectrometer has been constructed[48]. This apparatus consists of a differentially-pumped molecular-beam source and a quadrupole mass analyzer. The beam originates from a controlled-temperature effusion source and is collimated by a slit which separates the analyzer and source chambers. The beam is directed through an open Pierce-type ionizer so as to avoid contact both with the walls and the filaments. Contributions to the mass spectra from decomposition products are thus minimized. Ions are withdrawn perpendicularly to the plane of the molecular beam to minimize ion–molecule reactions.

Fluorides whose vapor pressures were sufficiently high were metered into a controlled-temperature effusion source, as shown in Figure 2 of ref. 48. Solid pentafluoride could be condensed in this source and the equilibrium vapors sampled. Beams of less volatile species were generated from Monel cells fitted into small, electrically-heated copper blocks. These sources had interchangeable orifices ranging from 0.125–1.0 mm in diameter.

Materials

The use of mass spectrometers to monitor beam intensities coupled with a knowledge of the physical properties in most cases provided positive identification of the species under study. At the same time, the use of mass-spectrometric detection methods provided some insight into the impurities present in the samples and reduced the need for working with samples of high purity.

It was found that a common contaminant was the oxide tetrafluoride. Mass peaks corresponding to this compound could be readily resolved from those of the pentafluoride with the quadrupole mass analyzer, but the deflection apparatus has only sufficient resolution to separate MOF_n^+ peaks from MF_{n+1}^+ peaks below a mass value of 150. For higher molecular weights, the presence in the focusing pattern for a given ion peak of a small component with a strong first-order Stark effect behavior was taken as indicative of an unresolved oxide fluoride component. Gentle heating generally removed such contamination. Similarly, small amounts of the more volatile hexafluorides were also readily removed by heating. The corresponding lower fluorides are of much lower volatility and therefore do not enter the beam; consequently, even if present, they would not perturb the results reported here.

ClF_5

In order to prepare ClF_5, a complex was first formed by heating ClF_3 and CsF together at *ca.* 80 °C. This complex was then heated for 20 h at 175 °C in F_2 at a pressure of *ca.* 21 atm. Excess F_2 was removed at −196 °C and ClF_5 distilled at −78 °C.

BrF_5

A commercial sample (Matheson) was vacuum-distilled and used without further purification.

IF_5

A commercial sample (Matheson) was treated with NaF in a Kel-F container, then vacuum-distilled prior to use.

PF_5

A commercial sample (Matheson) was used without purification. It contained *ca.* 1% POF_3.

AsF_5

A commercial sample (Ozark–Mahoning) was used without purification. It contained *ca.* 1% $AsOF_3$.

SbF_5

A commercial sample (Ozark–Mahoning) was degassed and heated for 2 h at 250 °C in the presence of F_2 at *ca.* 1.5 atm pressure. Excess F_2 was removed at −196 °C, volatile materials pumped off for 5 min at 0 °C and the resulting sample used without further purification. No $SbOF_3$ could be detected ($<0.1\%$ present).

BiF_5

A commercial sample (Ozark–Mahoning) was used without purification. It contained a substantial involatile component but no impurities were found in the vapor.

VF_5

1 g of 30 mesh vanadium metal (Gallard–Schlesinger, 99.9%) was heated in the presence of F_2 at *ca.* 6 atm pressure for 5 h at 290 °C, when virtually complete conversion of the metal to VF_5 occurred.

NbF_5

A commercial sample (Allied Chemicals) was used for the deflection experiments. For the association study, however, a sample prepared by the direct fluorination of Nb metal at 300 °C was used. No impurities were apparent in the mass spectra of either sample.

TaF_5

A commercial sample (Allied Chemicals) was used for the deflection experiments. For the association study, however, a sample prepared by the direct fluorination of Ta metal at 300 °C in excess F_2 at *ca.* 18 atm pressure was used. No impurities were detected in the mass spectra of either sample.

CrF_5

CrF_5 was prepared[49] by the thermal decomposition of the complex, which probably contains variable proportions of CrF_4 and CrF_5, formed by the fluorination of Cr metal powder in the presence of F_2 gas at, for example, *ca.* 360–430 atm pressure at 385 °C. Any CrF_6 present in the complex was first removed at −80 °C. For the electric-deflection experiments, however, the complex itself was loaded into the tube oven and decomposed *in situ* to provide a beam of CrF_5.

MoF_5

A commercial sample of MoF_6 (Allied Chemicals) was reduced with excess PF_3 (Ozark–Mahoning) for 12 h at room temperature[50]. The resulting crystalline yellow product was recovered after removal of remaining volatiles from the reactor. Traces of oxide fluorides were observed mass spectrometrically.

WF_5

A commercial sample of WF_6 (Varlacoid Chemical Co.) was condensed over NaF to remove HF impurities and then reduced on a W or Ni filament to form the pentafluoride[51–53]. In a typical experiment, purified WF_6 was condensed into a Pyrex tube maintained at a temperature of −64 °C. Tungsten wire of 0.5 mm diameter was suspended as a coil in the tube and heated to the glow point. Yellow WF_5 was recovered from the walls of the reactor.

ReF_5

In order to prepare this compound, ReF_6 was first obtained by the fluorination of excess rhenium metal by heating in fluorine at 400 °C for 4 h. This material was then condensed over NaF to remove HF and distilled into a Pyrex reactor in which was suspended a 30 cm loop of rhenium wire. The reactor was maintained at −23 °C and the wire heated to the glow point until conversion to ReF_5 was complete[53].

RuF_5

Green RuF_5 was prepared by the direct fluorination of dried ruthenium powder by heating the latter in excess F_2 at a pressure of 6.5–7 atm for 4 h at 370 °C. Trace amounts of oxide fluoride were found in the mass spectra.

OsF_5

In order to prepare this compound, OsF_6 was first obtained by the fluorination of osmium powder in excess fluorine at 400 °C for 4 h followed by subsequent purification over NaF. Excess OsF_6 was condensed on to $W(CO)_6$ contained in a glass tube at −196 °C and the mixture allowed to warm slowly with nitrogen gas continuously purging the system according to the method of Hargreaves and

Peacock[54]. The resulting blue-green, crystalline product was purified by sublimation. A small amount of oxide fluoride was detected.

RhF_5

Dark red RhF_5 was prepared[55] by reacting rhodium sponge with excess fluorine at a pressure of 5.5–6.5 atm and a temperature of 400 °C for 12 h. No evidence was found for the presence of impurities.

IrF_5

Iridium metal was reacted with slightly more than the stoichiometric amount of fluorine at *ca.* 400 °C for 2 h[56]. The IrF_6 contaminant was removed by sublimation, leaving yellow-green IrF_5 powder. No impurities were detected.

PtF_5

Platinum sponge was reacted with excess fluorine at 6.5–7.5 atm pressure for 12 h at 350 °C. Deep red PtF_5 was obtained after small amounts of PtF_6 were removed at room temperature. No impurities were detected.

UF_5

Excess UF_6 was reduced for 12 h at 200 °C with HBr[57] to produced bluish-white UF_5. No impurities were detected.

RESULTS

Association studies

The presence of association and lower limits to the extent of association can be inferred directly from the relative abundances of ions containing one, two, three, *etc.* metal atoms. The observed mass-spectrometric ion intensities may be corrected for quadrupole discrimination effects, and it can be shown that ion–molecule reactions and free-jet expansion make negligible contributions to the higher molecular weight clusters[48]. For a given metal, as the electron-impact energy of the ion gun is reduced below *ca.* 20 eV the relative intensities of higher molecular weight ions increase, although the total ion current decreases. This is most probably a result of reduced fragmentation of the larger neutral clusters, with the lower energy data representing more closely the neutral abundances in the beam. However, a more rapid decrease in the ionization cross-section with decreasing energy for the monomeric species would give a similar behavior. Since neither the cross-sections nor the fragmentation patterns are known, a quantitative assessment of the population of neutral species in the vapor cannot be made from the existing data.

The relative abundances of ions with varying numbers of central nuclei for vapors approaching saturation are presented in Table 1. To ensure that sampling was effusive and that the vapor was in equilibrium with the condensed phase, sampling orifice diameters were varied in some cases, as shown for example for IrF_5. No significant variations in abundances occurred.

TABLE 1

RELATIVE ABUNDANCES OF PENTAFLUORIDE OLIGOMER IONS[a, b]

Pentafluoride	Source temperature/°C	Orifice diameter/cm	Electron energy/V	Ion abundances				
				Monomer	Dimer	Trimer	Tetramer	Pentamer
NbF_5	66	0.025	70	1.0	0.60	0.02	3.0 E-6	—
MoF_5	48	0.10	70	1.0	0.20	0.013	4.0 E-4	—
RuF_5	115	0.10	70	1.0	0.46	0.11	0.03	—
RhF_5	90	0.051	70	1.0	0.51	0.12	2.0 E-3	—
RhF_5	90	0.051	16	0.07	1.0	0.28	—	—
TaF_5	93	0.025	70	1.0	0.30	0.033	1.0 E-5	—
ReF_5	100	0.025	70	1.0	0.30	0.022	—	—
OsF_5	83	0.051	70	1.0	0.13	0.02	—	—
OsF_5	163	0.051	70	1.0	0.08	5.0 E-3	—	—
IrF_5	65	0.012	70	1.0	0.15	0.01	8.0 E-4	1.0 E-6
IrF_5	69	0.10	70	1.0	0.13	0.01	2.0 E-4	..
PtF_5	93	0.025	70	1.0	0.14	5.0 E-3	—	—
SbF_5	25	0.025	70	1.0	0.21	8.0 E-3	1.0 E-4	1.0 E-6
BiF_5	87	0.025	70	1.0	0.45	5.0 E-3	—	—

[a] — = not detected.

[b] 1.0 E-X = 1.0×10^{-x}.

An example of the effect of the variation of electron energy is provided by the results given for RhF_5 in Table 1. Unlike the null effect of orifice size, significant changes occur in the relative abundances of the species. The effect of temperature (and hence pressure) with constant orifice size is shown by the results quoted for OsF_5. Increasing the source temperature by 80 °C resulted in a 38% and 75% decrease in the intensities of the dimer and trimer relative to that of the monomer.

Polymeric ions were not found for VF_5, CrF_5, PF_5, AsF_5, ClF_5, BrF_5, or IF_5 in the saturated vapors at 263, 298, 161, 191, 208, 218 and 273 K, respectively, the detection limits for oligomers in these cases being between 1 part in 10^4 and 1 part in 10^5. Excessive disproportionation of WF_5 and UF_5 prevented the observation of associated clusters in these systems. Lesser but substantial disproportionation was also noted for PtF_5 and RhF_5.

Electric-deflection studies

In electric-deflection experiments, either focusing or defocusing of a molecular beam about a stop-wire may be observed on the application of an inhomogeneous electrical field[43,44]. Molecules possessing an electric dipole moment will exhibit focusing behavior, whereas non-polar molecules will exhibit only defocusing behavior brought about by the polarizability interaction. The magnitudes of focusing or defocusing may be related qualitatively to the magnitudes of the dipole moment or polarizability, respectively, but the numerous variables present in any given experiment make it impossible to provide quantitative estimates of these parameters. However, the sensitivity of the method for electric dipoles is excellent, being *ca.* 0.02 D for molecules possessing a first-order Stark effect.

Since parent ion peaks for fluorides of the type MF_n are generally weaker than MF_{n-1}^+ ions, most data were obtained employing the latter peaks. The resulting spectral behavior was corroborated with other masses, including the parent, whenever possible.

ClF_5, BrF_5 and IF_5

The room-temperature focusing behavior of all three halogen pentafluorides is typical of that for an oblate symmetric-top molecule with a reasonably large dipole moment. With no voltage on one quadrupole field and 3 kV applied to the other, the ClF_4^+ ion peak had a refocused beam intensity 57% of that with the beam stop removed. The intensities of the BrF_4^+ and IF_5^+ ion peaks with 1 kV applied to one quadrupole field were respectively 54% and 57% of the straight-through beam. The total focusing curves for all three molecules are similar.

PF_5, AsF_5 and SbF_5

No observable parent MF_5^+ ion peaks were observed with PF_5 or AsF_5. For the MF_4^+ peaks, only defocusing behavior was observed for PF_5 from room temperature down to −145 °C and for AsF_5 from room temperature to −65 °C.

Although SbF_5 vapor is substantially polymerized, the fragmentation pattern of ions containing one Sb atom is similar to that of PF_5 and AsF_5. In the deflection studies, an attempt was made to dissociate polymeric species by heating the vapor at constant pressures. Only defocusing behavior was observed for the SbF_4^+ ion peak from room temperature to 235 °C.

VF_5 and CrF_5

The focusing observed with the higher purity VF_5 sample used in this study was similar to that previously reported for commercial samples[32]. Focusing was observed at 217 K, the lowest temperature at which a satisfactory beam could be obtained. Upon increasing the temperature the extent of focusing decreased, until at a temperature of 530 K and above only defocusing was observed.

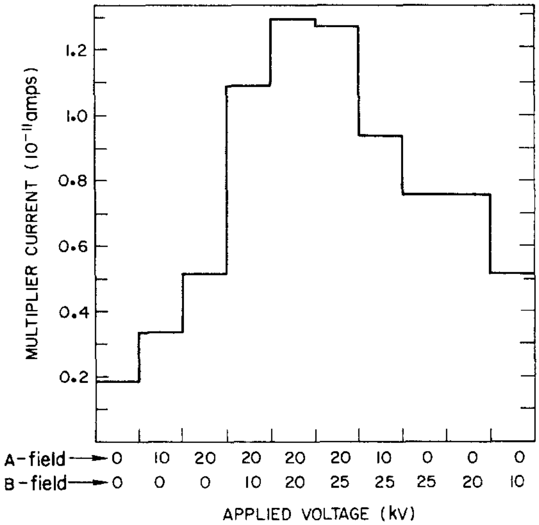

Fig. 1. Focusing behavior of the CrF_5^+ fragment from CrF_5 at 80 °C. The multiplier current with the beam stop removed was 2.2×10^{-10} A.

The polar behavior for CrF_5 was observed by monitoring the parent CrF_5^+ ion peak. A typical focusing curve for the CrF_5^+ peak of a CrF_5 beam with a source temperature of 80 °C is show in Figure 1. For this configuration, the intensity of the refocused beam was 5.0% of that observed with the beam stop removed. Focusing of CrF_4^+ and CrF_3^+ peaks was similar to that of CrF_5^+, except that the maximum percentages were 6.3% and 8.2%, respectively. These differences are probably the result of substantial CrF_4 being present in the CrF_5 sample. The mass spectrum of CrF_5, obtained with the Harvard apparatus and given in Table 2, is different from that obtained at Bell Laboratories. Whilst the relative magnitudes of the CrF_5^+ and CrF_4^+ ion peaks are as expected, the ratio of the CrF_4^+ to the CrF_3^+ peak is not typical of a pentafluoride. CrF_4 is present in the initial sample and may also result from disproportionation. The increased focusing behavior of the CrF_4^+ and CrF_3^+ peaks would then imply that CrF_4 focuses more strongly than

CrF_5. The focusing behavior for CrF_4 is expected in view of the polar behavior observed[58] for TiF_4 and VF_4.

NbF_5, MoF_5, RuF_5 and RhF_5

Only defocusing of beams associated with the second transition series was observed. For NbF_5, NbF_4^+ was monitored at room temperature and 40 °C. For MoF_5, parallel behavior was observed for MoF_4^+, MoF_5^+ and $Mo_2F_9^+$ between room temperature and 55 °C. For RuF_5 beams at 50 °C and 90 °C, similar defocusing was observed for RuF_4^+, RuF_5^+ and $Ru_2F_9^+$. The behavior of RhF_4^+, RhF_6^+ and $Rh_2F_9^+$ peaks at room temperature, and of $Rh_2F_9^+$ and $Rh_2F_{11}^+$ peaks at 80 °C has also been examined. Despite changes in the mass-spectral cracking patterns over this temperature range, only defocusing was observed.

TaF_5, WF_5, ReF_5, OsF_5, IrF_5 and PtF_5

As for the second transition series, only defocusing of molecular beams of these species was observed. No parent ion was observed for TaF_5, hence TaF_4^+ was used to monitor TaF_5 between room temperature and 70 °C. The results obtained for WF_5 are questionable. The mass spectrum observed at 25 °C and 40 °C closely resembles that of WF_6. However, any WF_6 initially present in the sample must be removed by pumping, and the reported rate of disproportionation[52] at room temperature is too small to produce an observable WF_6 beam. Both WF_4^+ and WF_5^+ defocused in a similar manner. For ReF_5, ReF_4^+ and ReF_5^+ were studied at 25 °C and 80 °C, well below the reported onset of disproportionation[59]. OsF_5^+ was employed to monitor the OsF_5 beam at 80 °C and 110 °C while for IrF_5, IrF_5^+ was examined at 50 °C and IrF_5^+ and IrF_6^+ at 80 °C. The PtF_5 observations were obscured by disproportionation, the mass spectrum at 60 °C approaching that of PtF_6. However, the ready observation of oligomers on the Bell Laboratories mass spectrometer at 93 °C under conditions which give higher than usual MF_5^+ to MF_4^+ ratios suggests that at this temperature some PtF_5 and its polymers are present in the vapor. Only defocusing was observed for the PtF_4^+ fragment ion.

UF_5

This was the only actinide pentafluoride studied. Its relative involatility precluded obtaining a strong beam below 175 °C, at which temperature the sample was apparently disproportionating rapidly to give a predominantly UF_6 beam. The UF_5^+ peak defocused at this temperature, and also at 130 °C where a weak beam, possibly richer in UF_5, was examined.

Mass spectra

The mass spectra obtained both with the Harvard apparatus and with the Bell Laboratories mass spectrometer are tabulated in Tables 2–4. The latter intensities have been corrected for non-uniform transmission of the quadrupole mass filter[48]. Although peaks due to different isotopes could be resolved, their contributions have been summed for clarity. A high current, Weiss-type[45,60] ionizer at 120 V potential was used for the Harvard spectra; the Bell Laboratories data are reported for 70 eV electron energies from a Pierce ionizer[48]. Ion peak intensities are given relative to the most intense ion found. Double dots indicate that the intensity of the specified ion peak was not measured; a dash indicates the intensity was too low to be observed. The precision of these mass spectra is not great since their observation was a secondary objective of this research.

DISCUSSION

Extensive association of the vapors occurs for all but the lighter pentafluorides, *i.e.* VF_5, CrF_5, PF_5 and AsF_5, and the interhalogens ClF_5, BrF_5 and IF_5. Although we have not observed association for WF_5 or UF_5 for which disproportionation is excessive, the fact that oligomers are the rule for the transition metals suggests that WF_5 may also be associated. Effusion and transport experiments indicate that at room temperature the gaseous phase consists of $(WF_5)_4$ tetrameric units[52].

The experiments reported here show that electron impact on the neutral species sampled from the saturated vapor leads to an abundant concentration of monomer, dimer and trimer ions whereas ions with four or more metal atoms are scarce or absent. The neutral cluster from which an observed ion is formed cannot be identified at this time; the extent of fragmentation on electron impact is not known. However, the observation of pentameric ions for SbF_5 and IrF_5, and the relatively weak tetrameric ion peaks observed in many cases, suggest that the vapors are not composed predominantly of tetrameric rings as is usual in the solids[40].

The uncertainties in composition of the saturated vapors complicate the interpretation of the electric-deflection data. Association may be considered as consisting of a series of equilibrium steps

$$MF_5 + (MF_5)_n \underset{k_{-(n+1)}}{\overset{k_{n+1}}{\rightleftharpoons}} (MF_5)_{n+1}$$

for which the individual k values are not known. However, our observations are not inconsistent with $k_2 >> k_{-2}$, at least for some of the associating systems, in which case the concentration of monomer may be too small for the deflection experiments to provide a sensitive indication of dipole moments.

For the lighter pentafluorides, small concentrations of dimers, *etc.* greater than the *ca.* 10^{-5} sensitivity limits may be expected from the forces that give rise to non-ideal gas behavior. For PF_5 and AsF_5, which were driven through 0.25 mm diameter holes at pressures exceeding 100 Torr, association as a result of isentropic expansion might be anticipated. The non-detectability of dimers in these systems could result from the unimolecular decomposition of the weakly bound polymers

TABLE 2

MASS SPECTRA OF MONOMERIC PENTAFLUORIDES[a]

Compound:	PF_5	AsF_5		CrF_5		VF_5		ClF_5	BrF_5		IF_5	
Spectrometer:	BL[b]	H[c]	BL	H	BL	H	BL	BL	H	BL	H	BL
Temperature/°C:	—110	25	—76	90	25	25	—8	—65	25	—42	25	0
M^+	0.30	0.97	0.22	. .	0.38	. .	0.24	0.54	. .	0.49	. .	0.17
MF	0.49	0.41	0.20	. .	0.32	. .	0.21	0.50	. .	0.40	. .	0.10
MF_2	0.16	0.27	0.17	0.50	0.25	0.73	0.30	1.00	0.60	0.56	. .	0.06
MF_3	0.33	0.16	0.17	1.0	0.85	0.36	0.37	0.15	0.26	0.36	. .	0.19
MF_4	1.00	1.00	1.00	0.52	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
MF_5	—	—	—	0.026	0.048	—	—	—	0.003	0.009	0.10	0.16
MF_6	—	—	—	—	—	—	—	—	—	—	—	—

[a] Contributions from all isotopes are summed. Intensities relative to most intense peak ≡ 1.00. Not detected, —. Not searched for, . . .

[b] Bell Laboratories apparatus, 70 eV impact energy.

[c] Harvard apparatus, 120 eV impact energy.

TABLE 3

MASS SPECTRA OF SECOND ROW TRANSITION-METAL PENTAFLUORIDES[a]

Compound:	NbF_5		MoF_5		RuF_5		RhF_5		SbF_5	
Spectrometer:	H[c]	BL[b]	H	BL	H	BL	H	BL	H	BL
Temperature/°C:	40	66	25–50	45	80	118	25	90	25	25
M^+	. .	—	. .	7.4 E-3	. .	0.06	. .	0.39	. .	0.04
MF	0.27	9.5 E-3[d]	. .	0.015	. .	0.36	1.0	0.29	0.35	0.23
MF_2	0.42	0.057	0.42	0.067	. .	0.48	0.85	0.80	0.51	0.47
MF_3	0.37	0.16	0.43	0.22	. .	1.0	0.62	0.62	0.14	0.26
MF_4	1.00	1.00	1.00	1.00	1.00	0.98	0.77	1.0	1.00	1.00
MF_5	—	—	0.06	0.015	0.25	0.32	0.56	0.21	—	—
MF_6	—	—	—	—	—	—	0.16	0.06	—	—
M_2		—		—		—		7.4 E-3		—
M_2F		—		—		—		0.02		—
M_2F_2		—		—		—		6.8 E-3		—
M_2F_3		—		—		8.0 E-3		0.02		—
M_2F_4		—		—		0.011		0.03		—
M_2F_5		—		—		8.0 E-3		0.05		0.025
M_2F_6		—		—		0.022		0.02		0.017
M_2F_7		6.6 E-3		—		0.082		0.10		8.0 E-3
M_2F_8		0.02		2.2 E-3		0.21		0.36		0.023
M_2F_9		0.71	0.24	0.26	0.6	1.1	0.07	1.0		0.34
M_2F_{10}		—		—		0.055		0.1		—

M_3F_{11}	—	—	—	4.0 E-3	—
M_3F_{12}	—	—	—	0.02	—
M_3F_{13}	—	—	0.015	0.11	—
M_3F_{14}	0.027	0.017	0.27	0.21	0.017
M_3F_{15}	—	—	0.06	0.06	—
M_4F_{17}	—	1.5 E-4	—	—	—
M_4F_{18}	—	2.5 E-4	—	1.7 E-3	—
M_4F_{19}	3.6 E-6	1.5 E-4	—	2.3 E-3	1.7 E-4
M_4F_{20}	—	—	0.08	1.7 E-3	—

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[a] Contributions from all isotopes are summed. Intensities relative to most intense peak $\equiv$ 1.00. Not detected, —. Not searched for, . . .

[b] Bell Laboratories apparatus, 70 eV impact energy.

[c] Harvard apparatus, 120 eV impact energy.

[d] $1.0\text{ E-X} = 1.0 \times 10^{-x}$.

TABLE 4

MASS SPECTRA OF THIRD ROW TRANSITION-METAL PENTAFLUORIDES AND URANIUM PENTAFLUORIDE[a]

Compound:	TaF_5		WF_5		ReF_5		OsF_5		IrF_5		PtF_5		UF_5	
Spectrometer:	H[c]	BL[b]	H	BL	H	BL	H	BL	H	BL	H	BL	H	BL
Temperature/°C:	70	93	25–38	60	25	100	85	83	25	119	30–57	93	175	190
M^+	. .	0.01	. .	0.03	. .	0.04	. .	—	. .	0.036	. .	0.55	. .	0.13
MF	. .	0.01	0.35	0.05	0.44	0.04	0.45	0.03	. .	0.085	0.52	0.37	0.88	0.24
MF_2	. .	0.03	0.45	0.12	0.51	0.11	0.61	0.18	. .	0.44	. .	0.70	0.92	0.38
MF_3	0.37	0.19	0.39	0.14	1.00	0.80	. .	0.70	. .	1.00	. .	0.80	0.60	0.31
MF_4	1.00	1.00	0.32	0.14	0.91	1.00	1.00	1.00	1.00	1.00	0.65	1.00	0.40	0.32
MF_5	—	—	1.00	1.00	0.12	0.18	0.16	0.10	0.10	0.049	1.00	0.85	1.00	1.00
MF_6	—	—	—	—	1.8 E-3[d]	0.02	2.0 E-3	—	—	—	0.58	0.48	0.028	—
M_2		—				—		—		—		0.02		
M_2F		—				—		—		—		0.01		
M_2F_2		—				—		—		—		0.05		
M_2F_3		—				—		—		—		0.01		
M_2F_4		—				—		—		—		8.0 E-3		
M_2F_5		—				—		—		—		0.01		
M_2F_6		—				—		—		—		3.0 E-3		
M_2F_7		3.0 E-3				—		—		6.8 E-3		0.10		
M_2F_8		6.0 E-3				0.02		0.02		0.085		0.13		
M_2F_9		0.37				0.63		0.23		0.28		0.31		
M_2F_{10}		—				—		0.01		0.027		0.05		

M_3F_{12}	—	—	—	—	—
M_3F_{13}	—	—	—	—	4.0 E-3
M_3F_{14}	0.04	0.05	0.03	0.018	0.012
M_3F_{15}	—	—	0.01	0.010	8.0 E-3
M_4F_{18}	—	—			
M_4F_{19}	1.2 E-5	—		1.5 E-3	
M_4F_{20}	—	—		7.3 E-4	

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[a] Contributions from all isotopes are summed. Intensities relative to most intense peak ≡ 1.00. Not detected, —. Not searched for, . . .

[b] Bell Laboratories apparatus, 70 eV impact energy.

[c] Harvard apparatus, 120 eV impact energy.

[d] 1.0 E-X = 1.0×10^{-x}.

in the *ca.* 10^{-3} s flight time between the beam source and the detector. For the smaller molecules with less complex vibrational manifolds, redistribution of energy into the dissociative stretching mode will be slower and polymeric species will survive. For strongly interacting systems such as HF[61], H_2O[62], HCN[63], *etc.*, more energy is required for dissociation; hence their agglomerates are stable in the beam. However, unimolecular decomposition might also reduce the concentration of high, more weakly bound oligomers for these systems, thus shifting the observed distribution towards lower degrees of association.

The halogen pentafluorides could be studied as monomeric gases. The rapid and large Stark focusing observed for ClF_5, BrF_5 and IF_5 is typical of symmetric-top molecules and supports the well-established square-pyramidal C_{4v} structures assigned to these molecules[22–28].

In interpreting the weaker focusing observed for VF_5 and CrF_5 as evidence for the distortion of these presumed symmetric molecules, sources of slight polar behavior other than static distortion must be considered. Molecules with D_{3h} symmetry can have vibrationally-induced dipole moments in excited vibrational states of symmetry E' or E'', with second-order Stark energies resulting from these moments[58]. By comparison with observations second-order Stark interactions of T_d molecules whose symmetry has been lowered to C_{2v} by isotopic substitution, the Stark effect associated with vibrationally-induced moments in molecules of D_{3h} symmetry is not expected to be seen. Furthermore, this mechanism would not account for the significantly different behavior of VF_5 and CrF_5 on the one hand and PF_5 and AsF_5 on the other.

Although a vibrationally-induced dipole moment with a magnitude similar to that found for T_d molecules would not be observable in D_{3h} molecules, the possibility still remains that an anomalously large vibrationally-induced moment could be present in some pentafluorides. A vibrationally-induced dipole moment contains contributions from the anharmonicity of the vibration[64]. The molecular motion postulated to explain the NMR spectral equivalence of axial and equatorial fluorines in presumably D_{3h} pentafluorides could result in large anharmonicity for a vibration whose normal coordinates are closely related to this inversion motion. Selig *et al.*[5] have interpreted anomalies in the vibrational spectrum of VF_5 as indicating an inversion rate much faster than that for PF_5 or AsF_5. If this interpretation is correct, the induced dipole moment in excited vibrations of the normal mode related to the inversion motion might be large enough to give rise to observable polar behavior in VF_5. No evidence concerning either the presence or absence of rapid inversion in CrF_5 is available. It should be emphasized that an inversion motion does not itself give rise to any new non-zero electric-dipole matrix elements between the rotational–vibrational energy levels of a D_{3h} molecule[65].

Finally, with the exception of VF_5, NbF_5 and TaF_5, all monomeric transition-metal pentafluorides may have ground electronic states of symmetry *E*, with dipole moments perpendicular to the symmetry axis. The second-order Stark energies associated with these moments for CrF_5 will not be observable unless the dipole moment associated with the dynamic Jahn–Teller distortion is large, *i.e.* at least 0.1 D.

The most probable explanation of the polar behavior of VF_5 and CrF_5, and of the anomalies in the vibrational spectrum[5] of VF_5, is that the equilibrium structures are distorted from D_{3h} symmetry. If the ground electronic state of CrF_5 is in fact of symmetry E, one explanation for a static distortion could be the Jahn–Teller effect. The distortion of VF_5 on the other hand cannot be the result of Jahn–Teller phenomena.

The non-polar, defocusing behavior observed for PF_5 and AsF_5 supports the assignment of a D_{3h} structure for these monomeric molecules[1–10]. Heating SbF_5 gas at pressures below 1 Torr shifts the equilibrium towards higher monomer concentrations. Nevertheless, the SbF_4^+ ion peak defocused uniformly between 25 °C and 235 °C, indicating that whatever neutral species were precursors for this fragment ion they were non-polar. If even a few percent of the gas molecules were monomeric, this observation strongly favors an approximately D_{3h} structure for the monomer over the proposed[15] C_{4v} structure. However, focusing behavior due to small distortions from D_{3h} symmetry might be obscured. The observations at room temperature indicate that the oligomer structures are predominantly electrocentrosymmetric.

The defocusing of pentafluorides of the second and third transition series indicates that monomers of these species possess non-polar D_{3h} structures, or are only slightly non-symmetric. However, although some monomer concentration in the molecular beams is likely, uncertainty as to the actual amount present makes it difficult to make precise statements regarding the structure of the monomer. For oligomers of these pentafluorides, which are abundant in all cases, electrically centrosymmetric structures are strongly favored. With octahedrally coordinated metals, double-bridged dimers and most cyclic ring structures fulfill this requirement, as do linear chains containing even numbers of MF_5 units and with a single double bridge at the center.

Certain generalities emerge which are representative of the mass-spectral cracking patterns of fluorides and which are useful for species identification, particularly for distinguishing amongst members of a series MF_n. The fragmentation patterns of the pentafluorides show a systematic variation of ion peak intensity—parent MF_5^+, weak or absent; MF_4^+, dominant; MF_3^+, weaker; MF_2^+, intermediate; MF^+, weak; M^+, strong or intermediate. If the central atom of the pentafluoride is in its highest oxidation state, the parent ion is not observed, *e.g.* with V, Nb, Ta, P, As, Sb, or Bi. Both these trends have been observed in other fluoride systems, such as hexafluorides[47], heptafluorides[46] and the rare-earth trifluorides[66]. A typical feature in electron-impact ionization of halides is that the most intense peak is that of the (parent-less-one-halogen)$^+$ ion[67]. These generalities are useful in identifying the dominant species in a beam, and the presence of a substantial parent peak for the highest known fluoride may suggest the possibility of a still higher fluoride. Similar behavior occurs amongst the higher molecular weight ions in pentafluoride systems; hence $M_2F_9^+$, $M_3F_{14}^+$ and $M_4F_{19}^+$ are the most intense of the ion agglomerates. This may suggest that the primary source of such ions is the corresponding neutral molecule, *i.e.* $M_2F_9^+$ originating from M_2F_{10}, *etc.* On the other hand, it is possible that these ion configurations are the most stable irrespective of the original neutral molecule.

Deviations from this regular behavior are observed for some samples. The atypical ratio of CrF_4^+ to CrF_3^+ in CrF_5 suggested contamination by CrF_4, which was later confirmed.

With the halogen pentafluorides, no parent ion was observed for ClF_5 whilst a weak parent was obtained for BrF_5; for IF_5, the peak intensity of IF_5^+ was about 10% that of IF_4^+ at 70–120 eV. This trend may be a reflection of the relative difficulty of synthesizing the various halogen heptafluorides; thus, to date, only IF_7 is known.

The relative intensities of RhF_4^+, RhF_5^+, RhF_6^+ and $Rh_2F_9^+$ changed markedly between room temperature and 80 °C. The room-temperature mass spectrum recorded in Table 3 is not typical of a pentafluoride, having an RhF_5^+ peak whose intensity is close to that of RhF_4^+. On increasing the temperature, RhF_6^+ and RhF_5^+ decrease relative to RhF_4^+ while $Rh_2F_9^+$ increases. This could be a result of the presence of trace amounts of RhF_6 in the RhF_5 sample, but in view of the high volatility of RhF_6, its difficulty of preparation and its thermal instability, RhF_6 is an unlikely impurity in the preparation and an improbable product of RhF_5 disproportionation. The mass spectrum of RhF_5 is relatively rich in ions containing more than one Rh atom.

The MF_6^+ peaks observed in the spectra of ReF_5, OsF_5 and IrF_5 probably result from fragmentation of higher neutral clusters. In the cases of PtF_5 and WF_5, disproportionation is a more likely origin.

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