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VIBRATIONAL SPECTRA OF THE BINARY FLUORIDES OF THE MAIN GROUP ELEMENTS

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I. Introduction

Vibrational spectroscopy is an important tool for the characterization of various chemical species. Valuable information regarding molecular structures as well as intra- and intermolecular forces can be extracted from vibrational spectral data. Recent advances, such as the introduction of laser sources to Raman spectroscopy, the commercial availability of Fourier transform infrared spectrometers, and the continuing development and application of the matrix-isolation technique to a variety of chemical systems, have greatly enhanced the utility of vibrational spectroscopy to chemists.

Inorganic fluorine compounds are of considerable interest and importance not only because fluorides of nearly all known elements, including some of the rare gases, have been synthesized, but because a number of these compounds are quite different from other halides. Consider, for example, compounds SF_4 and SF_6 and their chloro analogs. The SF_6 is chemically a very inert and a very stable compound, whereas SF_4, also quite stable, is quite reactive. The corresponding tetrachloride molecule is stable only at low temperatures, whereas the hexachloride molecule is nonexistent.

Many fluorides, particularly the interhalogens, are very reactive and require special handling techniques. Matrix isolation has proven to be a very useful technique in the study of inorganic fluorides; it is particularly helpful in the study of very reactive species, such as

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the free radicals and high-temperature vapor species. Such molecules can be stabilized in a low-temperature matrix environment that effectively prevents reaction with cell and window materials. Because the molecules are effectively isolated from each other, problems involving molecular association are minimized. There is generally a good correlation between matrix and gas phase spectral data except in cases where strong interaction between the matrix material and the isolated molecule exists. Narrow bandwidths are a characteristic feature of matrix spectra, making it frequently possible to obtain structural information from bands involving different isotopes. Matrix-isolation data will be utilized, wherever possible, throughout this paper.

In this review we summarize and attempt to correlate vibrational spectral data amassed from the literature for the main group, inorganic binary fluorides. In addition, a brief review of the matrix-isolation studies of both reactive intermediates and high-temperature fluoride vapor species is included, placing particular emphasis on the interhalogen molecules.

II. Inorganic Binary Fluorides

In this section available vibrational data for the main group binary fluorides will be reviewed in an attempt to establish trends in both structures and bond-stretching force constants. The review is restricted primarily to molecular entities that were observed either in the gas phase or in inert matrices. The emphasis on the matrix data in this review is in contrast with the more general approach taken by Reynolds in an earlier review of the vibrational spectra of inorganic fluorides (*1*).

Vibrational spectra, besides being utilized to establish molecular structures, can be used in the evaluation of molecular force constants. Considerable effort has been expended to relate bond-stretching force constants to bond order. Although no specific theoretical model has been found that will cover all types of chemical bonds, there exists a qualitative relationship between bond-stretching force constants and bond orders, permitting a comparison of bond strengths for molecules such as the binary fluorides. In making such a comparison, a consistent force field model must be adhered to. The general valence force field (GVFF) or an approximation of this field generally referred to as the modified valence force field (MVFF) are the potential models that have become increasingly popular with chemists. Valence force constants normally exhibit good transferability between molecules possessing similar types of bonds. Valence stretching force constants further bear a close relationship to the chemical bonding forces. Force constants utilizing the valence force field were, therefore, chosen for comparison in this paper for the reasons just mentioned and because of the wealth of data available in the literature. Although a unique set of force constants rarely exists for a given polyatomic molecule, one preferred set can normally be chosen on a physical basis. Relating stretching force constants to bond energies should be treated with caution, particularly for molecules exhibiting a large percentage of ionic bonding, since the magnitude of the force constant is primarily a reflection of only the covalent character of a particular bond.

Table I lists the symmetry point groups and X—F-stretching force constants for those main group binary fluorides for which the oxidation state of the element combined with fluorine corresponds to the group number. In Tables II–VI vibrational spectral data (using matrix-isolation results if available), including the X—F-stretching force constants, are presented for the main group binary fluorides having formulas ranging from XF to XF_5, respectively. Two force constant trends are apparent. First, the force constants decrease in magnitude from top to bottom for a given group in each of these tables with certain exceptions, as noted in the following. For molecules that possess both equatorial and axial X—F bonds, the axial stretching force constant exhibits the top-to-bottom trend opposite to that previously mentioned. Going from left to right, the force constants in the periodic table first increase, reaching a maximum in a given period somewhere in the vicinity of the transition point from metal to nonmetal; this is followed by a decrease in the force constant. These force constant trends are much more apparent for Tables I–III where a more complete set of data is available.

From the data presented in Tables I–VI, it appears that a particular structure is maintained for molecules of the same formula and within a given group with the exception of BeF_2 and MgF_2, which are linear whereas the remaining members of that group have bent (C_{2v}) structures. The vibrational data for the diatomic fluorides presented in Table II are taken from gas-phase electronic and matrix-isolation spectral studies; both sets of data are available for a number of the diatomic molecules in this table. The gas-phase frequencies have all been corrected for anharmonicity except in the case of fluorine; this is apparently the reason for its force constant being lower than that for ClF. If the matrix data for the diatomic molecules of Group VIIA are examined, however, the expected top-to-bottom trend is observed. The apparent reversal in the magnitudes of the gas phase and matrix frequencies for MgF is a rather unusual occurrence that is also worth noting.

TABLE I

STRETCHING FORCE CONSTANTS AND SYMMETRY FOR MAIN GROUP BINARY FLUORIDES[a]

Parameter[b]	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
	LiF* (*23, 24*)	BeF_2* (*26*)	BF_3* (*29, 30*)	CF_4* (*33, 34*)	—	—	—	—
Sym.	$C_{\infty v}$	$D_{\infty h}$	D_{3h}	T_d	—	—	—	—
K_{F-X}	2.12	5.15	7.29	6.70	—	—	—	—
	NaF* (*9*)	MgF_2* (*8, 27, 28*)	AlF_3* (*31, 32*)	SiF_4* (*35, 36*)	PF_5 (*39*)	SF_6* (*40, 41*)	—	—
Sym.	$C_{\infty v}$	$D_{\infty h}$	D_{3h}	T_d	D_{3h}	O_h	—	—
K_{F-X}	1.51	3.23	4.91	6.11	6.32,[c] 4.47[d]	5.26	—	—
	KF* (*25*)	CaF_2* (*27*)	—	GeF_4* (*37, 38*)	AsF_5* (*4, 39*)	SeF_6 (*42*)	—	—
Sym.	$C_{\infty v}$	C_{2v}	—	T_d	D_{3h}	O_h	—	—
K_{F-X}	1.18	2.21	—	5.45	5.47,[c] 4.51[d]	5.01	—	—
	RbF* (*9*)	SrF_2* (*27*)	—	—	SbF_5* (*3, 4, 39, 152*)	TeF_6 (*43*)	IF_7 (*44–46*)	—
Sym.	$C_{\infty v}$	C_{2v}	—	—	D_{3h}	O_h	D_{5h}	—
K_{F-X}	1.01	1.97	—	—	5.38,[c] 4.75[d]	5.07	3.01,[c] 4.10[d]	—
	CsF* (*9*)	BaF_2* (*27*)	—	—	—	—	—	—
Sym.	$C_{\infty v}$	C_{2v}	—	—	—	—	—	—
K_{F-X}	0.95	1.59	—	—	—	—	—	—

[a] Asterisk (*) indicates that matrix data are available; references are given in parentheses.

[b] Units for force constants are in millidynes per angström.

[c] Equatorial fluorine atoms.

[d] Axial fluorine atoms.

TABLE II

VIBRATIONAL DATA FOR MAIN GROUP BINARY FLUORIDES WITH FORMULA XF[a]

Parameter[b]	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	LiF (*23, 24, 47*)	BeF (*47*)	BF (*47*)	CF (*53*)	NF (*55, 56*)	OF (*5, 25, 59*)	F_2 (*6, 47*)
K_{F-X}	2.48 2.12*	5.77	8.05	7.09*	6.18 5.90*	5.42*	4.45^c 4.43*
ω_e	906 840* [Ar]	1266	1400	1279* [Ar]	1141 1115* [Ar]	1029* [Ar]	892^c 890* [N_2]
	NaF (*9, 47*)	MgF (*47, 48*)	AlF (*31, 47*)	SiF (*54*)	PF (*57*)	—	ClF (*6, 47*)
K_{F-X}	1.76 1.51*	3.22 3.41*	4.36 4.05*	4.91	4.98	—	4.56 4.24*
ω_e	536 496* [Ar]	718 738* [Kr]	815 785* [Ne]	858	847	—	793 764* [N_2]
	KF (*25, 47*)	CaF (*47*)	GaF (*49, 50*)	GeF (*47*)	AsF (*58*)	—	BrF (*47, 60*)
K_{F-X}	1.37 1.18*	2.62	3.25*	3.93	4.20	—	4.07 3.93*
ω_e	426 396* [Ar]	587	609* [Ne]	665	686	—	671 660* [Ar]
	RbF (*9, 47*)	SrF (*47*)	InF (*51*)	SnF (*47*)	SbF (*47*)	—	IF (*61*)
K_{F-X}	1.30 1.01*	2.30	2.75	3.28	3.65	—	3.62
ω_e	376 332* [Ar]	500	535	583	614	—	610
	CsF (*9, 47*)	BaF (*47*)	TlF (*47, 52*)	PbF (*47*)	BiF (*47*)	—	—
K_{F-X}	1.22 0.95*	2.16	2.31 1.99*	2.64	2.68	—	—
ω_e	353 312* [Ar]	469	475 441* [Ar]	507	511	—	—

[a] Asterisk (*) indicates that matrix data are available; references are given in parentheses; matrix material is indicated within brackets.

[b] Force constant units are in millidynes per angström, and frequency is expressed per centimeter.

[c] Uncorrected for anharmonicity.

TABLE III

Vibrational Data for Main Group Binary Fluorides with Formula XF_2[a]

Parameter[b]	IA	IIA	IVA	VA	VIA	VIIA	VIIIA
	$^6LiF_2$* (*9*)	BeF_2* (*26*)	CF_2* (*33*)	NF_2* (*33, 65, 66*)	OF_2* (*5, 25*)	—	—
Sym.	C_{2v}	$D_{\infty h}$	C_{2v}	C_{2v}	C_{2v}	—	—
K_{F-X}	—	5.15	6.00	4.83	4.10	—	—
Obs. freq.	ν_1, 452	ν_2, 330	ν_1, 1222	ν_1, 1070	ν_1, 925	—	—
	ν_2, 708 [Ar]	ν_3, 1542 [Ne]	ν_2, 668	ν_2, 573	ν_2, 446	—	—
			ν_3, 1102 [Ar]	ν_3, 931 [N_2]	ν_3, 826 [Ar]	—	—
	NaF_2* (*9*)	MgF_2* (*8, 27, 28*)	SiF_2* (*37, 62*)	PF_2* (*36*)	SF_2* (*67*)	ClF_2* (*6, 20*)	—
Sym.	C_{2v}	$D_{\infty h}$	C_{2v}	C_{2v}	C_{2v}	C_{2v}	—
K_{F-X}	—	3.23	4.90	4.93	—	2.48	—
Obs. freq.	ν_1, 475	ν_1, 550	ν_1, 843	ν_1, 831	ν_3, 847 [Ar]	ν_1, 500	—
	ν_2, 454 [Ar]	ν_2, 249	ν_2, 343	ν_3, 852 [Ar]	—	ν_2, 242	—
		ν_3, 842 [Ar]	ν_3, 855 [Ar]	—	—	ν_3, 578 [N_2]	—
	KF_2* (*9*)	CaF_2* (*27*)	GeF_2* (*7, 37*)	—	—	BrF_2* (*21*)	KrF_2* (*5, 68, 69*)
Sym.	C_{2v}	C_{2v}	C_{2v}	—	—	C_{2v}	$D_{\infty h}$
K_{F-X}	—	2.21	4.16	—	—	—	2.46
Obs. freq.	ν_1, 464	ν_1, 485	ν_1, 685	—	—	ν_3, 569 [Ar]	ν_1, 452
	ν_2, 342 [Ar]	ν_2, 163	ν_2, 263[d]	—	—	—	ν_2, 236
		ν_3, 554 [Kr]	ν_3, 653 [Ne, N_2]	—	—	—	ν_3, 580 [Ar, Xe]

	RbF_2* (*9*)	SrF_2* (*27*)	SnF_2* (*63*, *64*)	—	—	—	XeF_2* (*5*, *68*, *69*)
Sym.	C_{2v}	C_{2v}	C_{2v}	—	—	—	$D_{\infty h}$
K_{F-X}	—	1.97	3.41	—	—	—	2.84
Obs. freq.	ν_1, 462	ν_1, 441	ν_1, 605	—	—	—	ν_1, 512
	ν_2, 266[c] [Ar]	ν_2, 82	ν_2, 201	—	—	—	ν_2, 213[e]
		ν_3, 442 [Kr]	ν_3, 584 [Ne]	—	—	—	ν_3, 547 [Ar, Xe]
	CsF_2* (*9*)	BaF_2* (*27*)	PbF_2* (*63*, *64*)	—	—	—	—
Sym.	C_{2v}	C_{2v}	C_{2v}	—	—	—	—
K_{F-X}	—	1.59	2.92	—	—	—	—
Obs. freq.	ν_1, 459	ν_1, 390	ν_1, 546	—	—	—	—
	ν_2, 248[c] [Ar]	ν_3, 413 [Kr]	ν_2, 170	—	—	—	—
			ν_3, 523 [Ne]	—	—	—	—

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[a] There are no data for Group IIIA XF_2 compounds. Asterisk (*) indicates that matrix data are available; references are given in parentheses; matrix material is indicated within brackets.

[b] Stretching force constants units are in millidynes per angström, and frequency is expressed per centimeter.

[c] These assignments are subject to uncertainty.

[d] Estimated from electronic spectra.

[e] Gas-phase frequency.

TABLE IV

VIBRATIONAL DATA FOR MAIN GROUP BINARY FLUORIDES WITH FORMULA XF_3[a]

Parameter[b]	IIIA	IVA	VA	VIA	VIIA
	BF_3^* (*29, 30, 70*)	CF_3^* (*33*)	NF_3^* (*60, 72, 73*)	—	—
Sym.	D_{3h}	C_{3v}	C_{3v}	—	—
$K_{\mathrm{F-X}}$	7.29	5.48	4.16	—	—
Obs. freq.	ν_1, 888[c] ν_3, 1439 [Kr]	ν_1, 1087 ν_3, 1251 [Ar]	ν_1, 1029 ν_3, 898 [Ar]	—	—
	ν_2, 680 ν_4, 480	ν_2, 703 ν_4, 512	ν_2, 649 ν_4, 495	—	—
	AlF_3^* (*31, 32*)	SiF_3^* (*71*)	PF_3^* (*36, 74*)	SF_3^* (*67*)	ClF_3^* (*77*)
Sym.	D_{3h}	C_{3v}	C_{3v}	C_s	C_{2v}
$K_{\mathrm{F-X}}$	4.91	5.49	5.34	—	4.19,[e] 2.70
Obs. freq.	ν_2, 280 ν_4, 252 [Ne]	ν_1, 832 ν_3, 954 [Ar]	ν_1, 887 ν_3, 850 [Ar]	ν_5, 682 [Ar]	ν_1, 751 ν_4, 677 [Ar]
	ν_3, 949	ν_2, 406 ν_4, 290	ν_2, 484 ν_4, 349	—	ν_2, 523 ν_5, 431
					ν_3, 328 ν_6, 332
	GaF_3^* (*49*)	—	AsF_3 (*75*)	—	BrF_3^* (*77, 78*)
Sym.	D_{3h}	—	C_{3v}	—	C_{2v}
$K_{\mathrm{F-X}}$	—	—	4.64	—	4.08[e] 3.01
Obs. freq.	ν_2, 190 ν_4, 190 [Ne]	—	ν_1, 740[d] ν_3, 702[d]	—	ν_1, 674 ν_4, 597 [Ar]
	ν_3, 759	—	ν_2, 336[d] ν_4, 262[d]	—	ν_2, 547 ν_5, 347
					ν_3, 238 ν_6, 253
	—	—	SbF_3^* (*76*)	—	IF_3(*79*)
Sym.	—	—	C_{3v}	—	C_{2v}
$K_{\mathrm{F-X}}$	—	—	3.89	—	—
Obs. freq.	—	—	ν_1, 654 ν_3, 624 [N_2]	—	ν_1, $\left\{\begin{matrix}640^f\\628\end{matrix}\right.$ ν_4, 480[f]
			ν_2, 259	—	ν_2, 550[f] ν_5, 331[f]
					ν_3, 228[f] ν_6, $\left\{\begin{matrix}245^f\\240\end{matrix}\right.$

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[a] Asterisk (*) indicates that matrix data are available; references are given in parentheses; matrix material is indicated within brackets.

[b] Stretching force constant units are in millidynes per angström, and frequency is expressed per centimeter.

[c] Calculated from combination bands in the gas-phase IR spectrum.

[d] Gas-phase frequencies. [e] Unique fluorine atom. [f] Solid-state frequencies.

TABLE V

VIBRATIONAL DATA FOR MAIN GROUP BINARY FLUORIDES WITH FORMULA XF_4[a]

Parameter[b]	IVA	VIA	VIIIA
	CF_4* (*33, 34, 80*)	—	—
Sym.	T_d	—	—
K_{F-X}	6.70	—	—
Obs. freq.	ν_1, 909^c ν_3, 1267 ν_2, 435^c ν_4, 631 [Ar]	— —	— —
	SiF_4* (*35, 36, 81*)	SF_4* (*77, 83, 84*)	—
Sym.	T_d	C_{2v}	—
K_{F-X}	6.11	5.51,^{d} 3.30^e	—
Obs. freq.	ν_1, 800^c ν_3, 1022 ν_2, 268^c ν_4, 384 [Ar]	ν_1, 884 ν_4, 228^c ν_7, 529 ν_2, 552 ν_5, 474^c ν_8, 858 [Ar, N_2] ν_3, 360 ν_6, 707 ν_9, 357	— — —
	GeF_4* (*37, 38, 82*)	SeF_4* (*85*)	—
Sym.	T_d	C_{2v}	—
K_{F-X}	5.45	5.04,^{d} 3.38^e	—
Obs. freq.	ν_1, 740^c ν_3, 799 ν_2, 200^c ν_4, 260^c [Ne]	ν_1, 743 ν_4, ~160^c ν_8, 723 ν_2, 589 ν_5, 596 ν_9, 254 [N_2] ν_3, 406 ν_7, 364	— — —
	SnF_4* (*64*)	TeF_4* (*85*)	XeF_4* (*69, 86, 87*)
Sym.	T_d	C_{2v}	D_{4h}
K_{F-X}	—	4.62,^{d} 3.53^e	3.00
Obs. freq.	ν_3, 687 [Ar]	ν_1, 695 ν_6, 587 ν_2, 572 ν_7, 273 [N_2] ν_3, 333 ν_8, 682	ν_1, 554^c ν_4, 216^{c,f} ν_7, 161^{c,f} ν_2, 290 ν_5, 524^c [Ar] ν_3, 218^c ν_6, 568
	PbF_4* (*64*)	—	—
Sym.	T_d	—	—
K_{F-X}	—	—	—
Obs. freq.	ν_3, 663 [Ar]	—	—

[a] There are no data for Groups VA and VIIA XF_4 compounds. Asterisk (*) indicates that matrix data are available; references are given in parentheses; matrix material is indicated within brackets.

[b] Stretching force constants units are in millidynes per angström, and frequency is expressed per centimeter.

[c] Gas-phase frequencies.

[d] Equatorial fluorine atoms.

[e] Axial fluorine atoms.

[f] Evaluated from overtone observed in the Raman spectrum.

In Table III there are several points to be considered. For both Groups VA and VIIIA, there appear to be deviations from the apparent normal top-to-bottom trend with PF_2 and XeF_2 having slightly larger force constants than NF_2 and KrF_2, respectively. All molecules in Table III have bent (C_{2v}) structures with the exception of KrF_2 and

TABLE VI

VIBRATIONAL DATA FOR THE MAIN GROUP BINARY FLUORIDES WITH FORMULA XF_5[a]

Parameter[b]	VA[c]	VIA	VIIA
	—	—	—
	PF_5 (*39, 88*)	SF_5* (*89*)	ClF_5* (*90, 91*)
Sym.	D_{3h}	C_{4v}	C_{4v}
K_{F-X}	6.32,[d] 4.47[e]	—	2.75, 3.66[g]
Obs. freq.	ν_1, 817^f ν_4, 576^f ν_7, 175^f	ν_7, 812 ν_8, 552 [Ar]	ν_1, 722 ν_4, 480^f ν_8, 482
	ν_2, 640^f ν_5, 1026^f ν_8, 514^f	—	ν_2, 539 ν_6, 375^f ν_9, 299 [N_2]
	ν_3, 945^f ν_6, 533^f	—	ν_3, 493 ν_7, 726
	AsF_5* (*4, 39, 88*)	—	BrF_5* (*77, 78, 91*)
Sym.	D_{3h}	—	C_{4v}
K_{F-X}	5.47,[d] 4.51[e]	—	3.26, 4.01[g]
Obs. freq.	ν_1, 734^f ν_4, 397 ν_7, 130^f	—	ν_1, 681 ν_4, 535^f ν_8, 415
	ν_2, 644^f ν_5, 808 ν_8, 366 [Ar]		ν_2, 582 ν_6, 312^f ν_9, 240 [Ar]
	ν_3, 782 ν_6, 372^f	—	ν_3, 366 ν_7, 636
	SbF_5* (*3, 4, 39, 152*)	—	IF_5 (*91*)
Sym.	D_{3h}	—	C_{4v}
K_{F-X}	5.38,[d] 4.75[e]	—	3.64, 4.68[g]
Obs. freq.	ν_1, 683^f ν_4, 285 ν_8, 272^f	—	ν_1, 698^f ν_4, 575^f ν_8, 374^f
	ν_2, 636^f ν_5, 726 [Ar]		ν_2, 593^f ν_6, 273^f ν_9, 189^f
	ν_2, 726 ν_6, 263		ν_3, 315^f ν_7, 640^f

[a] There are no data for Group VIIIA XF_5 compounds. The asterisk (*) indicates that matrix data are available; references are given in parentheses; matrix material is indicated in brackets.

[b] Stretching force constant units are in millidynes per angström, and frequency is expressed per centimeter.

[c] See text for a discussion of SbF_5.

[d] Equatorial fluorine atoms.

[e] Axial fluorine atoms.

[f] Gas-phase frequencies.

[g] Unique fluorine atom.

XeF_2, which are linear ($D_{\infty h}$) as are BeF_2 and MgF_2, as previously noted, and the MF_2 molecules of Group IA, which are apparently triangular (C_{2v}). For the series of molecules, CF_2, NF_2, and OF_2, the ν_1 mode is observed to have a higher frequency than the ν_3 mode; this is an apparent deviation from normal trends. This behavior may be a result of dynamic effects due to the similarity in the masses of the various atoms making up this series of triatomic molecules (*2*). The assignment of the ν_1 mode to a higher frequency value than ν_3 has been made for a number of other molecules in Table III. In some cases, however, these assignments are subject to some uncertainty. Raman data, which could be utilized to clarify such situations, are largely unavailable for molecules in Table III because the majority of the data come from infrared matrix-isolation studies.

In Table IV, NF_3 appears to be an exception as its stretching force constant is lower than that for PF_3. It should be noted also that the force constants for CF_3 and SiF_3 are very nearly the same. The XF_3 compounds of Group VIIA possess two equivalent axial X—F bonds and one equatorial or unique bond. The equatorial-type bonds are stronger than the axial bonds for all molecules in Tables IV–VI that exhibit bonding of this type with the exception of the XF_5 molecules of Group VIIA. The range of point-group symmetry for the molecules in Table III is D_{3h} for Group IIIA, C_{3v} for Groups IVA and VA, C_s for Group VIA, and C_{2v} for Group VIIA. The frequency data for Group VA indicate that ν_1 is greater than ν_3 for each member of that series.

Vibrational data for the main group binary fluorides with the formula XF_4 are restricted to compounds of Groups IVA, VIA, and VIIIA as exemplified in Table V. Molecules of Group VIA possess two axial and two equatorial X—F bonds. The range of point-group symmetry for the molecules in Table V is T_d for Group IVA, C_{2v} for Group VIA, and D_{4h} for Group VIIIA.

The XF_5 molecules of Group VIIA possess C_{4v} symmetry and have four equivalent equatorial X—F bonds and one unique axial bond, as indicated in Table VI. The equatorial stretching force constant exhibits the reverse of the normal top-to-bottom trend previously noted for bonds of this type. The XF_5 molecules of Group VA have D_{3h} symmetry. It appears appropriate at this point to present a brief discussion of SbF_5, since there has been considerable uncertainty in the interpretation of the vibrational spectra and the assignment of a structure to the monomer. A recent report involving a temperature-dependent study (*3*) of the Raman gas-phase spectrum of SbF_5 indicates that previous vibrational assignments were apparently in error.* This study shows that SbF_5 is strongly associated in the gas phase even at temperatures as high as 250°C. The association apparently occurs through bonds involving *cis*-fluorine bridging. An assignment of a C_{4v} structure to the monomer for SbF_5 from a previous matrix-isolation study (*4*) appears to be negated, because the experimental conditions that were utilized could not preclude the predominance of the associated species. The force constants presented in Table VI for SbF_5 are based on an incorrect vibrational assignment. It would appear, however, that a corrected assignment might produce very little

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* Additional matrix studies of monomeric SbF_5 have been recently reported (*152*).

TABLE VII

VIBRATIONAL DATA FOR VARIOUS ISOELECTRONIC BINARY FLUORIDE SERIES WITH FORMULA XF_4[a]

Parameter[b]	IIIA	IVA[d]	VA	VIA[d]	VIIA
	BF_4^- (*34, 92, 93*)	CF_4 (*33, 34, 80*)	NF_4^+ (*95, 96*)	—	—
Sym.	T_d	T_d	T_d	—	—
K_{F-X}	4.57	6.70	6.06	—	—
Obs. freq.	ν_1, 769 ν_3, 1084[c] ν_2, 353 ν_4, 524 [aqueous sol.]		ν_1, 849 ν_3, 1162 ν_2, 450 ν_4, 611 [solid $NF_4^+BF_4^-$]	— —	— —
	AlF_4^- (*94*)	SiF_4 (*35, 36, 81*)	—	SF_4 (*77, 83, 84*)	ClF_4^+ (*84, 97*)
Sym.	T_d	T_d		C_{2v}	C_{2v}
K_{F-X}	4.33	6.11		5.51,[e] 3.30[f]	4.78,[e] 3.73[f]
Obs. freq.	ν_1, 622 ν_3, 760 ν_2, 210 ν_4, 322 [MF–AlF_3 melts]	— —	— —	— —	ν_1, 800 ν_4, 250 ν_7, 515 ν_2, 571 ν_5, 475 ν_8, 829 ν_3, 385 ν_6, 795 ν_9, 385 [$ClF_5\cdot AsF_5$ $ClF_5\cdot SbF_5$ adducts]
	—	—	—	SeF_4 (*85*)	BrF_4^+ (*97*)
Sym.	—	—	—	C_{2v}	C_{2v}
K_{F-X}	—	—	—	5.04,[e] 3.38[f]	—
Obs. freq.	—	—	—	—	ν_1, 733 ν_4, 216 ν_8, 736 ν_2, 606 ν_6, 704 ν_9, 369 ν_3, 385 ν_7, 419 [$BrF_5\cdot 2SbF_5$ adduct]
	—	—	SbF_4^- (*76*)	TeF_4 (*85*)	IF_4^+ (*97*)
Sym.	—	—	C_{2v}	C_{2v}	C_{2v}
K_{F-X}	—	—	3.3,[e] 2.0[f]	4.62,[e] 3.53[f]	—
Obs. freq.	—	—	ν_1, 596 ν_4, 163 ν_7, 257 ν_2, 449 ν_5, ~220 ν_8, 566 ν_3, 285 ν_6, 431 ν_9, 180 [MeCN sol.]	— — —	ν_1, 704 ν_4, 151 ν_8, 720 ν_2, 609 ν_5, 655 ν_9, 316 ν_3, 341 ν_7, 385 [$IF_5\cdot SbF_5$ adduct]

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[a] References are given in parentheses; the state for which the frequencies were observed is denoted in brackets.

[b] Stretching force constant units are in millidynes per ångström, and frequency is expressed per centimeter.

[c] KBr matrix value.

[d] Observed frequencies are given in Table V.

[e] Equatorial fluorine atoms.

[f] Axial fluorine atoms.

effect on magnitudes of these reported stretching force constants, and so they are included for comparison.

Vibrational data for various isoelectronic binary fluorides with the formula XF_4 are listed in Table VII. For the first series in the upper left of this table, the force constant increases in going from BF_4^- to CF_4 and then decreases slightly for NF_4^+. It would appear that the next series beginning with AlF_4^- would follow a similar trend except that data for PF_4^+ are unavailable. The fluorides of these two series all have T_d symmetry. Very little can be said with regard to the three series in the lower right section of Table VII since the data are largely incomplete. The symmetry, however, for the various species in these series is C_{2v}.

Vibrational data are presented in Table VIII for various isoelectronic series of the formula XF_6. All the species in Table VIII possess O_h symmetry. The left-to-right, horizontal, force constant trends are similar for each of these series, as the magnitudes are observed to increase to Group VIA and then decrease slightly for Group VIIA. The exception to this particular trend occurs in the lower series that increases continuously from left to right. There is a general decrease in the force constants in going from top to bottom for all groups in this table with the exception of VIIA that exhibits the reverse trend.

In the compilation of force constant data for the inorganic binary fluorides, it would be of interest to examine how bonding of additional atoms such as oxygen might affect the bond strengths of selected X—F bonds. Vibrational data have been compiled in Table IX for NF, ClF, NF_3, and ClF_3 along with various oxygenated forms of these compounds to illustrate this effect. The N—F and Cl—F stretching force constants are observed to be reduced to approximately one-half of their original values in going from NF to FNO and from ClF to FClO, respectively. Further addition of oxygen atoms in both series appears to have little effect on the corresponding X—F stretching force constants, except for an eventual slight increase over the value for the mono-oxygenated species. The N—F stretching force constant is essentially unaffected in going from NF_3 to NF_3O, whereas the Cl—F force constants are mildly reduced from ClF_3 to ClF_3O. The force constant for the unique bond of ClF_3O exhibits a much larger reduction than that for the axial bonds. On addition of a second oxygen atom to yield the molecule ClF_3O_2, both unique and axial force constants increase over the values for ClF_3O, with latter force constant having a value equal to that of ClF_3.

Of interest is also the effect that additional electrons have on the structures and stretching force constants for a given fluoride series

TABLE VIII

VIBRATIONAL DATA FOR VARIOUS ISOELECTRIC BINARY FLUORIDE SERIES OF FORMULA XF_6[a]

Parameter[b]	IIIA	IVA	VA	VIA	VIIA
	AlF_6^{3-} (*98*)	SiF_6^{2-} (*99*)	PF_6^- (*43*)	SF_6 (*40, 100, 101*)	ClF_6^+ (*40*)
Sym.	O_h	O_h	O_h	O_h	O_h
K_{F-X}	—	3.01	4.39	5.26	4.68
Obs. freq.	ν_1, 555 ν_5, 345 [MF—AlF_3 melts] ν_2, 390	ν_1, 663 ν_4, 483 [solid Na_2SiF_6] ν_2, 477 ν_5, 408 ν_3, 741	ν_1, 746 ν_4, 557 [PF_6^- salt] ν_2, 561 ν_5, 475 ν_3, 817	ν_1, 774 ν_4, 614 [gas] ν_2, 642 ν_5, 525 ν_3, 939	ν_1, 679 ν_4, 582 [solid $ClF_6^+PtF_6^-$] ν_2, 630 ν_5, 513 ν_3, 890
	—	GeF_6^{2-} (*99*)	AsF_6^- (*43*)	SeF_6 (*42, 100, 101*)	BrF_6^+ (*43, 102*)
Sym.	—	O_h	O_h	O_h	O_h
K_{F-X}	—	2.71	3.98	5.01	4.90
Obs. freq.	—	ν_1, 624 ν_4, 359, 339 ν_2, 471 ν_5, 335 [solid K_2GeF_6] ν_3, 603	ν_1, 682 ν_4, 385 [solid $BrF_6^+AsF_6^-$] ν_2, 568 ν_5, 369 ν_3, 696	ν_1, 707 ν_4, 437 [gas] ν_2, 659 ν_5, 405 ν_3, 780	ν_1, 658 ν_4, 430 [solid $BrF_6^+AsF_6^-$] ν_2, 668 ν_5, 405 ν_3, 775
	—	SnF_6^{2-} (*99*)	SbF_6^- (*43*)	TeF_6 (*43, 100, 101*)	IF_6^+ (*43, 103*)
Sym.	—	O_h	O_h	O_h	O_h
K_{F-X}	—	2.77	3.90	5.07	5.42
Obs. freq.	—	ν_1, 592 ν_4, 300 [solid Na_2SnF_6] ν_2, 477 ν_5, 252 ν_3, 559	ν_1, 653 ν_4, 280 [solid $BrF_6^+SbF_6^-$] ν_2, 561 ν_5, 273 ν_3, 667	ν_1, 697 ν_4, 325 [gas] ν_2, 670 ν_5, 314 ν_3, 752	ν_1, 708 ν_4, 343 [solid $IF_6^+AsF_6^-$] ν_2, 732 ν_5, 340 ν_3, 794

[a] References are given in parentheses; the state for which the frequencies were observed is denoted in brackets.

[b] Stretching force constant units are in millidynes per angström, and frequency is expressed per centimeter.

TABLE IX

VIBRATIONAL DATA FOR SELECTED NITROGEN AND CHLORINE FLUORIDES CONTAINING OXYGEN[a]

Compound	Symmetry	Observed frequencies (cm^{-1})	F—X stretching force constant (mdyn/Å)
1. NF			
NF* *(55, 56)*[b]	$C_{\infty v}$	—	5.90
FNO *(104)*	C_s	ν_1, 1877 ν_2, 775 [gas] ν_3, 521	2.26
FNO$_2$ *(105)*	C_{2v}	ν_1, 1310 ν_4, 1792 ν_2, 822 ν_5, 560 [gas] ν_3, 569 ν_6, 742	2.66
NF$_3$* *(72, 73)*[c]	C_{3v}	—	4.16
NF$_3$O *(106, 107)*	C_{3v}	ν_1, 1689 ν_4, 880 ν_2, 740 ν_5, 522 [gas] ν_3, 534 ν_6, 398	4.25
2. ClF			
ClF* *(6, 47)*[b]	$C_{\infty v}$	—	4.24
FClO* *(108)*	C_s	ν_1, 1038 ν_2, 594 [Ar matrix] ν_3, 315	2.59
FClO$_2$ *(109)*	C_s	ν_1, 1106 ν_4, 402 ν_2, 630 ν_5, 1271 [gas] ν_3, 547 ν_6, 351	2.53
FClO$_3$ *(110, 111)*	C_{3v}	ν_1, 1061 ν_4, 1315 ν_2, 715 ν_5, 589 [gas] ν_3, 549 ν_6, 405	2.79
ClF$_3$* *(77)*[c]	C_{2v}	—	4.19,[e] 2.70
ClF$_3$O* *(112)*	C_s	ν_1, 1223 ν_4, 478 ν_7, 652 ν_2, 686 ν_5, 323 ν_8, 499 [N$_2$ matrix] ν_3, 484 ν_6, 224[d] ν_9,414	3.16,[e] 2.34
ClF$_3$O$_2$* *(113)*	C_{2v}	ν_1, 1093 ν_5, 287 ν_9, 372 ν_2, 683 ν_6, 417 ν_{10}, 1331 [N$_2$ ν_3, 519 ν_7, 686 ν_{11}, 531 matrix] ν_4, 487 ν_8, 591 ν_{12}, 222[d]	3.35,[e] 2.70

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[a] Asterisk (*) indicates that matrix data are available; references are given in parentheses; the state for which the frequencies were observed is denoted in brackets.

[b] Observed frequencies are given in Table II.

[c] Observed frequencies are given in Table IV.

[d] Gas-phase frequency.

[e] Unique fluorine atom.

TABLE X

VIBRATIONAL AND STRUCTURAL DATA FOR ClF_2^n ($n = +1, 0, -1$) SERIES[a]

ClF_2 species	Symmetry	Observed frequencies (cm^{-1})		Bond angle	F—Cl stretching force constant (mdyn/Å)
ClF_2^+ (*6, 114, 115*)	C_{2v}	ν_1, 807 ν_2, 387 ν_3, 830	[solid $ClF_2^+SbF_6^-$]	100°	4.74
ClF_2 (*6, 20*)[b]	C_{2v}	—		~150°	2.48
ClF_2^- (*116*)	$D_{\infty h}$	ν_3, 476 ν_3, 635	[solid $Na^+ClF_2^-$ $Rb^+ClF_2^-$]	180°	2.35

[a] References are given in parentheses; the state for which the frequencies were observed is denoted in brackets.

[b] Observed frequencies given in Table III.

having the same molecular formula. This effect is illustrated in Table X for the ClF_2^+, ClF_2, and ClF_2^- series. The structures range from bent (C_{2v}) for ClF_2^+ and ClF_2 with bond angles of 100° and ~150°, respectively, to linear ($D_{\infty h}$) for ClF_2^-. The stretching force constants for ClF_2 and ClF_2^- are 2.48 and 2.35 mdyn/Å, respectively, which is approximately half the value for that of ClF_2^+ and indicates that the additional electrons for ClF_2 and ClF_2^- are largely antibonding. A more complete discussion of ClF_2 will be made in the next section.

In concluding this section, a list of other main group binary fluorides for which there are either complete or partial vibrational data available is presented in Table XI.

III. Matrix Isolation Studies of Transient, Inorganic, Binary Fluoride Species

The area in which matrix isolation is perhaps of greatest value is the stabilization of transient species such as free radicals and high-temperature vapors. Until quite recently, infrared spectroscopy was utilized almost exclusively for the vibrational studies of matrix-isolated species. With the introduction of laser sources and the development of more sensitive, electronic, light detection systems, Raman matrix-isolation studies are now feasible and have recently been applied to a limited number of unstable inorganic fluoride species including the molecules OF (*5*) and ClF_2 (*6*). Both of these species were formed for Raman study by a novel technique that utilizes the

TABLE XI

List of Other Binary Fluorides for Which Vibrational Data are Available[a]

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
$(\mathrm{LiF})_2^*$ (*24, 117*)	$\mathrm{BeF_4}^{2-}$ (*120*)	$\mathrm{B_2F_4}^*$ (*121*)	$\mathrm{C_2F_4}^*$ (*33, 123*)	$\mathrm{N_2F}^+$ (*126*)	$\mathrm{O_2F_2}^*$ (*134, 135*)	$\mathrm{F_3}^{-*}$ (*10*)	—
$(\mathrm{LiF})_3^*$ (*118*)		$(\mathrm{BF_3})_2^*$ (*29*)	$\mathrm{C_2F_6}^*$ (*33, 124*)	$\mathrm{N_2F_2}^*$ (*56, 127, 128*)	$\mathrm{O_4F_2}^*$ (*136*)	—	—
				$\mathrm{N_2F_3}^+$ (*129*)	—	—	—
				$\mathrm{N_2F_4}^*$ (*65, 130, 131*)	—	—	—
				$\mathrm{N_3F}^*$	—	—	—
$(\mathrm{NaF})_2^*$ (*9, 119*)	$(\mathrm{MgF_2})_2^*$ (*8, 28*)	$(\mathrm{AlF})_2^*$ (*31, 49*)	$\mathrm{Si_2F_6}$ (*125*)	$\mathrm{P_2F_4}^*$ (*36, 132, 133*)	$\mathrm{S_2F_{10}}^*$ (*11, 137, 138*)	$\mathrm{ClF_4}^-$ (*142*)	—
		$(\mathrm{AlF_3})_2^*$ (*31, 122*)	—	$\mathrm{PF_3{=}PF}^*$ (*36*)	$\mathrm{S_2F_2}$ (*139*)	$\mathrm{Cl_2F}^+$ (*143, 144*)	—
					$(\mathrm{SF_4})_2^*$ (*77*)	$\mathrm{Cl_2F}^*$ (*21, 145*)	—
					$\mathrm{S_2F_4}$ (*140*)	$\mathrm{Cl_2F_2}^*$ (*21, 145*)	—
					$\mathrm{SF_5}^-$ (*141*)	$\mathrm{Cl_2F_3}^*$ (*21, 145*)	—
						$(\mathrm{ClF_3})_2^*$ (*145*)	—
$(\mathrm{KF})_2^*$ (*9*)	—	$(\mathrm{GaF})_2^*$ (*49*)	$(\mathrm{GeF_2})_2^*$ (*7, 37*)	—	$(\mathrm{SeF_4})_2^*$ (*85*)	$\mathrm{BrF_2}^+$ (*115*)	KrF^* (*147*)
		$(\mathrm{GaF_3})_2^*$ (*49*)	—	—	$\mathrm{SeF_5}^-$ (*141*)	$\mathrm{BrF_4}^-$ (*142*)	KrF^+ (*148, 149*)
						$\mathrm{Br_2F}^*$ (*21*)	$\mathrm{Kr_2F_3}^+$ (*149*)
						$\mathrm{Br_2F_2}^*$ (*21*)	—
						$(\mathrm{BrF_3})_2^*$ (*77*)	—
$(\mathrm{RbF})_2^*$ (*9*)	—	—	—	$\mathrm{SbF_5}^{2-}$ (*76*)	$\mathrm{TeF_5}^-$ (*76, 141*)	$\mathrm{IF_4}^-$ (*142*)	XeF^* (*147*)
				$\mathrm{Sb_2F_{11}}^-$ (*102*)	$\mathrm{Te_2F_{10}}$ (*137*)	$\mathrm{IF_6}^-$ (*146*)	XeF^+ (*150*)
					$(\mathrm{TeF_4})_2^*$ (*85*)	$\mathrm{IF_6}^{3-}$ (*142*)	$\mathrm{Xe_2F_3}^+$ (*150*)
						$\mathrm{I_2F}^*$ (*21*)	$\mathrm{XeF_6}^*$ (*151*)
$(\mathrm{CsF})_2^*$ (*9*)	—	$(\mathrm{TlF})_2^*$ (*52*)	—	—	—	$\mathrm{I_2F_2}^*$ (*21*)	—

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[a] Asterisk (*) indicates that matrix data are available; references numbers are given in parentheses.

4880-Å output from an Ar ion laser as both the photolysis source and the Raman excitation source. The examples of ClF_2 (*6*), GeF_2 (*7*), and MgF_2 (*8*) illustrate the complementary data that Raman matrix-isolation spectroscopy can provide. Other binary fluoride molecules for which Raman matrix data are available include OF_2 (*5*), MF_2 and MF_3 (M = alkali metals) (*9, 10*), S_2F_{10} (*11*), KrF_2 and XeF_2 (*5*), with the latter two molecules having been formed by the same laser photolysis method as previously mentioned. Raman matrix-isolation spectroscopy has recently been reviewed by Ozin (*12*), and, although merely in the early stages of development, it is anticipated that this area will continue to grow and become a valuable counterpart to the infrared technique.

This section represents a brief review of matrix-isolation studies of the main group, binary fluoride free radicals and high-temperature vapor species. A discussion of the halogen fluoride molecules will be stressed since this is an area of considerable interest to our laboratory. A list of main group binary fluorides that have been characterized by matrix isolation appears in Table XII. It is apparent from Table XII that there are large gaps in the existing data for species such as the halogen fluoride radicals, which must be filled in order to gain a better understanding of the structural properties and bonding characteristics of these systems. Presently, ClF_2 and Cl_2F are the only halogen fluoride radicals for which vibrational data have been published. The ClF_4 (*13, 14*), ClF_6 (*14, 15*), BrF_6 (*15, 16*), and IF_6 (*15*) radicals have recently been prepared by γ-radiolysis and characterized by ESR, although no vibrational spectroscopic data are available. Other interhalogen radicals, Cl_3 and Br_3, which were reportedly formed by microwave discharge (*17, 18*) may in fact be the ionic X_3^- species (*19*).

The ClF_2 radical is of sufficient chemical significance to merit a brief discussion. This particular radical is an interesting species because it possesses 21 valence electrons and appears to have an intermediate bond angle of $\sim 150°$. Such a bond angle is apparently unique for interhalogen species since the bond angles for most of these molecules are very near 90° or 180°. The ClF_2 radical was first prepared in our laboratory through the matrix reaction $ClF + F \rightarrow ClF_2$ (*20*). This reaction was initiated by production of F atoms through *in situ* UV photolysis of molecular fluorine. From the infrared data, the three vibrational fundamentals were assigned. On this basis and on the basis of ^{35}Cl, ^{37}Cl isotopic shift data for ν_3, compound ClF_2 was assigned a bent (C_{2v}) structure with a bond angle of $\sim 135°$. Very recently, however, Andrews' group (*6*) has repeated the infrared work and, in addition, has successfully prepared ClF_2 by the laser photolysis technique for Raman study. Based on the new Raman data, the ν_1 mode

TABLE XII

INORGANIC BINARY FLUORIDE FREE RADICALS, INTERMEDIATES, AND HIGH-TEMPERATURE VAPOR SPECIES CHARACTERIZED BY MATRIX ISOLATION[a]

IA	IIA	IIIA	IVA	VA	VIA	VIIA
LiF (*23, 24*)	BeF_2 (*26*)	—	CF (*53*)	NF (*56*)	OF (*5, 25, 59*)	—
			CF_2 (*33*)	NF_2 (*33, 65*)	O_2F (*134, 136*)	—
			CF_3 (*33*)	—	—	—
NaF (*9, 119*)	MgF (*48*)	AlF (*31*)	SiF_2 (*37, 62*)	PF_2 (*36*)	SF_2 (*67*)	ClF_2 (*6, 20*)
	MgF_2 (*8, 27, 28*)	AlF_3 (*31, 32*)	SiF_3 (*71*)	—	SF_3 (*67*)	Cl_2F (*21, 145*)
					SF_5 (*89*)	—
KF (*9*)	CaF_2 (*27*)	GaF (*49, 50*)	GeF_2 (*7, 37*)	—	—	BrF_2 (*21*)
		GaF_3 (*49*)	—	—	—	Br_2F (*21*)
—	SrF_2 (*27*)	—	SnF_2 (*63, 64*)	SbF_3 (*76*)	—	—
			SnF_4 (*64*)	—	—	—
—	BaF_2 (*27*)	TlF (*52*)	PbF_2 (*63, 64*)	—	—	I_2F (*21*)
			PbF_4 (*64*)	—	—	—

[a] There are no listings for Group VIIIA. References are given in parentheses.

was reassigned from a value of 536 cm^{-1} to that of 500 cm^{-1}. It appears that the principle of mutual exclusion holds for the ClF_2 radical, which is indicative of a linear triatomic species, but, as Andrews points out, mutual exclusion is valid only within the limits of detectability, which may be a problem for weakly active modes in dilute matrices. In a reassessment of the data, Andrews favors a slightly bent structure with a bond angle of $\sim 150°$.

Recently we have completed (in collaboration with E. S. Prochaska and L. Andrews of the University of Virginia) a matrix-isolation study of the halogen fluorine systems (*21*). Evidence for the formation of BrF_2, Br_2F, Br_2F_2, I_2F and I_2F_2 as well as more definitive data for Cl_2F and Cl_2F_2 were obtained. These experiments involved UV photolysis of matrix mixtures and microwave discharge experiments. The microwave experiments were stimulated by a recent mass spectrometric kinetic study (*22*) that appeared to present a method producing BrF in a much purer form. The data for BrF_2 are of considerable interest for the purposes of comparison with ClF_2. A doublet near 569 cm^{-1} with a 2.2 cm^{-1} isotopic splitting was attributed to BrF_2, and a calculation of 152° ± 8° for the lower limit of the F—Br—F valence angle strongly indicates that, like ClF_2, compound BrF_2 is also obtusely bent. Bands observed at 555 and 507 cm^{-1} were attributed to Br_2F_2 and Br_2F, respectively, based on photolysis behavior similar to their chlorine analogs.

Vibrational data for the majority of the molecules in Table XII were presented in Section I, and these species will not be discussed further.

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REFERENCES

1. Reynolds, D. J., *Adv. Fluorine Chem.* **7**, 1 (1973).

2. Andrews, L. *in* "Vibrational Spectroscopy of Trapped Species" (H. E. Hallam, ed.), p. 197. Wiley, New York, 1973.

3. Alexander, L. E., and Beattie, I. R., *J. Chem. Phys.* **56**, 5829 (1972).

4. Aljibury, A. L. K., and Redington, R. L., *J. Chem. Phys.* **52**, 453 (1970).

5. Andrews, L., *Appl. Spectrosc. Rev.* **11**, 125 (1976).

6. Prochaska, E. S., and Andrews, L., *Inorg. Chem.* **16**, 339 (1977).

7. Huber, H., Künig, E. P., Ozin, G. A., and Vander Voet, A., *Can. J. Chem.* **52**, 95 (1974).

8. Lesiecki, M. L., and Nibler, J. W., *J. Chem. Phys.* **64**, 871 (1976).

9. Howard, W. F., Jr., and Andrews, L., *Inorg. Chem.* **14**, 409 (1975).

10. Ault, B. S., and Andrews, L., *J. Am. Chem. Soc.* **95**, 1591 (1976).

11. Smardzewski, R. R., Noftle, R. E., and Fox, W. B., *J. Mol. Spectrosc.* **62**, 449 (1976).

12. Ozin, G. A., *in* "Vibrational Spectroscopy of Trapped Species" (H. E. Hallam, ed.), p. 373. Wiley, 1973.

13. Morton, J. R., and Preston, K. F., *J. Chem. Phys.* **58**, 3112 (1973).

14. Nishikida, K., Williams, F., Mamantov, G., and Smyrl, N., *J. Am. Chem. Soc.* **97**, 3526 (1975).

15. Boate, A. R., Morton, J. R., and Preston, K. F., *Inorg. Chem.* **12**, 3127 (1975).

16. Nishikida, K., Williams, F., Mamantov, G., and Smyrl, N., *J. Chem. Phys.* **63**, 1693 (1975).

17. Nelson, L., and Pimentel, G. C., *J. Chem. Phys.* **47**, 3671 (1967).

18. Boal, D. H., and Ozin, G. A., *J. Chem. Phys.* **55**, 3598 (1971).

19. Wight, C. A., Ault, B. S., and Andrews, L., *J. Chem. Phys.* **65**, 1244 (1976).

20. Mamantov, G., Vasini, E. J., Moulton, M. C., Vickroy, D. G., and Maekawa, T., *J. Chem. Phys.* **54**, 3419 (1971).

21. Prochaska, E. S., Andrews, L., Smyrl, N. R., and Mamantov, G., *Inorg. Chem.* (in press).

22. Appleman, E. H., and Clyne, M. A. A., *Trans. Faraday Soc.* **71**, 2072 (1975).

23. Schlick, S., and Schnepp, O., *J. Chem. Phys.* **41**, 463 (1964).

24. Linevsky, M. J., *J. Chem. Phys.* **38**, 658 (1963).

25. Andrews, L., and Raymond, J. I., *J. Chem. Phys.* **55**, 3078 (1971).

26. Snelson, A., *J. Phys. Chem.* **70**, 3208 (1966).

27. Calder, V., Mann, D. E., Seshadri, K. S., Allavena, M., and White, D., *J. Chem. Phys.* **51**, 2093 (1969).

28. Hauge, R. H., Margrave, J. L., and Kana'an, A. S., *Trans. Faraday Soc.* **71**, 1082 (1975).

29. Bassler, J. M., Timms, P. L., and Margrave, J. L., *J. Chem. Phys.* **45**, 2704 (1966).

30. Duncan, J. L., *J. Mol. Spectrosc.* **13**, 338 (1964).

31. Snelson, A., *J. Phys. Chem.* **71**, 3302 (1967).

32. Yang, Y. S., and Shirk, J. S., *J. Mol. Spectrosc.* **54**, 39 (1975).

33. Milligan, D. E., and Jacox, M. E., *J. Chem. Phys.* **48**, 2265 (1968).

34. Krebs, B., Müller, A., and Fadini, A., *J. Mol. Spectrosc.* **24**, 198 (1967).

35. Beattie, I. R., Livingston, K. M. S., and Reynolds, D. J., *J. Chem. Phys.* **51**, 4269 (1969).

36. Burdett, J. K., Hodges, L., Dunning, V., and Current, J. H., *J. Phys. Chem.* **74**, 4053 (1970).

37. Hastie, J. W., Hauge, R., and Margrave, J. L., *J. Phys. Chem.* **72**, 4492 (1968).

38. Müller, A., and Krebs, B., *J. Mol. Spectrosc.* **24**, 180 (1967).

39. Wendling, E. J. L., Mahmoudi, S., and MacCordick, H. J., *J. Chem. Soc. A* p. 1747 1971.

40. Christe, K. O., *Inorg. Chem.* **12**, 1580 (1973).

41. Shirk, J. S., and Claassen, H. H., *J. Chem. Phys.* **54**, 3237 (1971).

42. Abramowitz, S., and Levin, I. W., *Inorg. Chem.* **6**, 538 (1967).

43. Christe, K. O., and Wilson, R. D., *Inorg. Chem.* **14**, 694 (1975).

44. Khanna, R. K., *J. Mol. Spectrosc.* **8**, 134 (1972).

45. Lord, R. C., Lynch, M. A., Schumb, W. C., and Slowinski, E. J., *J. Am. Chem. Soc.* **72**, 522 (1950).

46. Eyseland, H. H., and Seppelt, K., *J. Chem. Phys.* **56**, 5081 (1972).

47. Jones, L. H., "Inorganic Vibrational Spectroscopy," pp. 183–187. Dekker, New York, 1971.

48. Mann, D. E., Calder, G. V., Seshadri, K. S., White, D., and Linevsky, M. J., *J. Chem. Phys.* **46**, 1138 (1967).

49. Hastie, J. W., Hauge, R. H., and Margrave, J. L., *J. Fluorine Chem.* **3**, 285 (1973).

50. Hastie, J. W., Hauge, R. H., and Margrave, J. L. *in* "Spectroscopy in Inorganic Chemistry" (Rao, C. N. R., and Ferraro, J. R. eds.), Vol. 1, p. 69. Academic Press, New York, 1970.

51. Barrow, R. F., Glaser, D. V., and Zeeman, P. B., *Proc. Phys. Soc., London, Sect. A* **68**, 962 (1955).

52. Brom J. M., and Franzen, H. F., *J. Chem. Phys.* **54**, 2874 (1971).

53. Jacox, M. E., and Milligan, D. E., *J. Chem. Phys.* **50**, 3252 (1969).

54. Appelbald, O., Barrow, R. F., and Verma, R. D., *J. Phys. B* **1**, 274 (1968).

55. Jones, A. E., and Jones, W. E., *Can. J. Phys.* **44**, 2251 (1966).

56. Milligan, D. E., and Jacox, M. E., *J. Chem. Phys.* **40**, 2461 (1964).

57. Douglas, A. E., and Frackowiak, M., *Can. J. Phys.* **40**, 832 (1962).

58. Liu, D. S., and Jones, W. E., *Can. J. Phys.* **50**, 1230 (1972).

59. Arkell, A., Reinhard, R. R., and Larson, L. P., *J. Am. Chem. Soc.* **87**, 1016 (1965).

60. Mamantov, G., and Smyrl, N., unpublished results.

61. Stein, L., *in* "Halogen Chemistry" (V. Gutman, ed.), Vol. 1, p.176. Academic Press, New York, 1967.

62. Milligan, D. E., and Jacox, M. E., *J. Chem. Phys.* **49**, 4269 (1968).

63. Margrave, J. L., Hastie, J. W., and Hauge, R. H., *Am. Chem. Soc., Div. Petroleum Chem., Preprint.* **14**, E11–E13, (1969).

64. Hauge, R. H., Hastie, J. W., and Margrave, J. L., *J. Mol. Spectrosc.* **45**, 420 (1973).

65. Harmony M. D., and Myers, R. J., *J. Chem. Phys.* **37**, 636 (1962).

66. Selig, H., and Holloway, J. H., *J. Inorg. Nucl. Chem.* **33**, 3169 (1971).

67. Smardzewski, R. R., and Fox, W. B., *J. Fluorine Chem.* **7**, 353 (1976).

68. Claassen, H. H., Goodman, G. L., Malm, J. G., and Schreiner, F., *J. Chem. Phys.* **42**, 1229 (1965).

69. Hallam, H. E. ed., *in* "Vibrational Spectroscopy of Trapped Species," p. 107. Wiley, New York, 1973.

70. Brown, C. W., and Overend, J., *Spectrochim. Acta*, Part A **25**, 1535 (1969).

71. Milligan, D. E., and Jacox, M. E., *J. Chem. Phys.* **49**, 5330 (1968).

72. Jacox, M. E., and Milligan, D. E., *J. Mol. Spectrosc.* **52**, 322 (1974).

73. Allan, A., Duncan, J. L., Holloway, J. H., and McKean D. C., *J. Mol. Spectrosc.* **31**, 368 (1969).

74. Mirri, A. M., Scappini, F., and Favero, P. G., *Spectrochim. Acta* **21**, 965 (1965).

75. Brieux De Mandirola, O., *J. Mol. Struct.* **1**, 203 (1967).

76. Adams, C. J., and Downs, A. J., *J. Chem. Soc. A* p. 1534 (1971).

77. Frey, R. A., Redington, R. L., and Aljibury, A. L. K., *J. Chem. Phys.* **54**, 344 (1971).

78. Christe, K. O., Curtis, E. C., and Pilipovich, D., *Spectrochim. Acta, Part A* **27**, 931 (1971).

79. Schmeisser, M., Naumann, D., and Lehmann, E., *J. Fluorine Chem.* **3**, 441 (1973).

80. Monostori, B., and Weber, A., *J. Chem. Phys.* **33**, 1867 (1960).

81. Jones, E. A., Kirby-Smith, J. S., Woltz, P. J. H., and Nielsen, A. H., *J. Chem. Phys.* **19**, 242 (1951).

82. Woltz, P. J. H., and Nielsen, A. H., *J. Chem. Phys.* **20**, 307 (1952).

83. Christe, K. O., and Sawodny, W., *J. Chem. Phys.* **52**, 6320 (1970).

84. Christe, K. O., Curtis, E. C., Schack, C. J., Cyvin, S. J., Brunvoll, J., and Sawodny, W., *Spectrochim. Acta, Part A* **32**, 1141 (1976).

85. Adams, C. J., and Downs, A. J., *Spectrochim. Acta*, **28***A*, 1841 (1972).

86. Claassen, H. H., Chernick, C. L., and Malm, J. G., *J. Am. Chem. Soc.* **85**, 1927 (1963).

87. Tsao, P., Cobb, C. C., and Claassen, H. H., *J. Chem. Phys.* **54**, 5247 (1971).

88. Selig, H., Holloway, J. H., Tyson, J., and Claassen, H. H., *J. Chem. Phys.* **53**, 2559 (1970).

89. Smardzewski, R. R., and Fox, W. B., *J. Fluorine Chem.* **7**, 456 (1976).
90. Christe, K. O., *Spectrochim. Acta, Part A* **27**, 631 (1971).
91. Begun, G. M., Fletcher, W. H., and Smith, D. F., *J. Chem. Phys.* **42**, 2236 (1965).
92. Goubeau, J., and Bues, W., *Z. Anorg. Allg. Chem.* **268**, 221 (1952).
93. Bonadeo, H., and Silberman, E., *J. Mol. Spectrosc.* **32**, 214 (1969).
94. Gilbert, B., Mamantov, G., and Begun, G. M., *Inorg. Nucl. Chem. Lett.* **10**, 1123 (1974).
95. Goetschel, C. T., Campanile, V. A., Curtis, R. M., Loos, K. R., Wagner, C. D., and Wilson, J. N., *Inorg. Chem.* **7**, 1696 (1972).
96. Christe, K. O., Guertin, J. P., Pavlath, A. E., and Sawodny, W., *Inorg. Chem.* **6**, 533 (1967).
97. Christe, K. O., and Sawodny, W., *Inorg. Chem.* **12**, 2879 (1973).
98. Gilbert, B., Mamantov, G., and Begun, G. M., *J. Chem. Phys.* **62**, 950 (1975).
99. Begun, G. M., and Rutenberg, A. C., *Inorg. Chem.* **6**, 2212 (1967).
100. Claassen, H. H., Goodman, G. L., Holloway, J. H., and Selig, H., *J. Chem. Phys.* **53**, 341 (1970).
101. Weinstock, B., and Goodman, G., *Adv. Chem. Phys.* **9**, 169 (1965).
102. Gillespie, R. J., and Schrobilgen, G. J., *Inorg. Chem.* **13**, 1230 (1974).
103. Christe, K. O., and Sawodny, W., *Inorg. Chem.* **6**, 1783 (1967).
104. Ryan, R. R., and Jones, L. H., *J. Chem. Phys.* **50**, 1492 (1969).
105. Bernitt, D. L., Miller, R. H., and Hisatsune, I. C., *Spectrochim. Acta, Part A* **23**, 237 (1967).
106. Hirschmann, R. P., Harnish, D. F., Holmes, J. R., MacKenzie, J. S., and Fox, W. B., *Appl. Spectrosc.* **23**, 333 (1969).
107. Abramowitz, S., and Levin, I. W., *J. Chem. Phys.* **51**, 463 (1969).
108. Andrews, L., Chi, F. K., and Arkell, A., *J. Am. Chem. Soc.* **96**, 1997 (1974).
109. Smith, D. F., Begun, G. M., and Fletcher, W. H., *Spectrochim. Acta*, **20**, 1763 (1964).
110. Lide, D. R., and Mann, D. E., *J. Chem. Phys.* **25**, 1128 (1956).
111. Sawodny, W., Fadini, A., and Ballein, K., *Spectrochim. Acta* 21, 995 (1965).
112. Christe, K. O., and Curtis, E. C., *Inorg. Chem.* **11**, 2196 (1972).
113. Christe, K. O., and Curtis, E. C., *Inorg. Chem.* **12**, 2245 (1973).
114. Gillespie, R. J., and Morton, M. J., *Inorg. Chem.* **9**, 616 (1970).
115. Christe, K. O., and Schack, C. J., *Inorg. Chem.* **9**, 2296 (1970).
116. Christe, K. O., Sawodny, W., and Guertin, J. P., *Inorg. Chem.* **6**, 1159 (1967).
117. Abramowitz, S., Acquista, N., and Levin, I. W., *J. Res. Nat. Bur. Stand.* **72*A*** 487 (1968).
118. Snelson, A., *J. Chem. Phys.* **46**, 3652 (1967).
119. Cyvin, S. J., Cyvin, B. N., and Snelson, A., *J. Phys. Chem.* **74**, 4338 (1970).
120. Quist, A. S., Bates, J. B., and Boyd, G. E., *J. Phys. Chem.* **76**, 78 (1972).
121. Nimon, L. A., Sheshadri, K. S., Taylor, R. C., and White, D., *J. Chem. Phys.* **53**, 2416 (1970).
122. Cyvin, S. J., *Spectrosc. Lett.* **7**, 255 (1974).
123. Nielsen, J. R., Claassen, H. H., and Smith, D. C., *J. Chem. Phys.* **18**, 812 (1950).
124. Nielsen, J. R., Richards, C. M., and McMurry, H. L., *J. Chem. Phys.* **16**, 67 (1948).
125. Timms, P. L., Kent, R. A., Ehlert, T. C., and Margrave, J. L., *J. Am. Chem. Soc.* **87**, 2824 (1965).
126. Moy, D., and Young, A. R., II, *J. Am. Chem. Soc.* **87**, 1889 (1965).
127. King, S., and Overend, J., *Spectrochim. Acta* **22**, 689 (1966).
128. King, S., and Overend, J., *Spectrochim. Acta, Part A* **23**, 61 (1967).
129. Young, A. R., II, and Moy, D., *Inorg. Chem.* **6**, 178 (1967).
130. Durig, J. R., and Clark, J. W., *J. Chem. Phys.* **48**, 3216 (1968).

131. Koster, D. F., and Miller, F. A., *Spectrochim. Acta, Part A* **24**, 1487 (1968).

132. Rudolph, R. W., Taylor, R. C., and Parry, R. W., *J. Am. Chem. Soc.* **88**, 3728 (1966).

133. Rhee, K. H., Snider, A. M., and Miller, F. A., *Spectrochim. Acta, Part A* **29**, 1029 (1973).

134. Spratley, R. D., Turner, J. J., and Pimentel, G. C., *J. Chem. Phys.* **44**, 2063 (1966).

135. Loos, K. R., Goetschel, G. T., and Campanile, V. A., *J. Chem. Phys.* **52**, 4418 (1970).

136. Arkell, A., *J. Am. Chem. Soc.* **87**, 4057 (1965).

137. Dodd, R. E., Woodward, L. A., and Roberts, L. H., *Trans. Faraday Soc.* **53**, 1545 (1957).

138. Wilmhurst, J. K., and Bernstein, H. J., *Can. J. Chem.* **35**, 191 (1957).

139. Brown, R. D., and Pez, G. P., *Spectrochim. Acta, Part A* **26**, 1375 (1970).

140. Seel, F., and Budenz, R., *J. Fluorine Chem.* **1**, 117 (1971).

141. Christe, K. O., Curtis, E. C., Schack, C. J., and Pilipovich, D., *Inorg. Chem.* **11**, 1679 (1972).

142. Christe, K. O., and Naumann, D., *Inorg. Chem.* **12**, 59 (1973).

143. Gillespie, R. J., and Morton, M. J., *Inorg. Chem.* **9**, 811 (1970).

144. Christe, K. O., and Sawodny, W., *Inorg. Chem.* **8**, 212 (1969).

145. Clarke, M. R., Fletcher, W. H., Mamantov, G., Vasini, E. J., and Vickroy, D. G., *Inorg. Nucl. Chem. Lett.* **8**, 611 (1972).

146. Christe, K. O., *Inorg. Chem.* **11**, 1215 (1972).

147. Ault, B. S., and Andrews, L., *J. Chem. Phys.* **64**, 3075 (1976).

148. Selig, H., and Peacock, R. D., *J. Am. Chem. Soc.* **86**, 3895 (1964).

149. Gillespie, R. J., and Schrobilgen, G. J., *J. Chem. Soc., Chem. Commun.* 90 (1974).

150. Sladky, F., Bulliner, P. A., and Bartlett, N., *J. Chem. Soc. A* p. 2179 (1969).

151. Claassen, H. H., Goodman, G. L., and Kim, H., *J. Chem. Phys.* **56**, 5042 (1972).

152. Beattie, I., Crocombe, R., German, A., Jones, P., Marsden, C., Van Schelkwyk, G., and Bukovszky, A., *J. Chem. Soc. Dalton*, p. 1380 (1976).