

# Structure and stability of gaseous fluorine-bridged heterodimers and heteropolymers: $(AF)_n(MF_3)_m$ , $A'F_2MF_3$ ( $A = H, Li, Na, K$ ; $M = B, Al, Fe$ ; $A' = Be, Mg, Mn$ ; $n, m = 1, 2$ )

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## Abstract

Starting from an overview of experimentally identified and quantum chemically calculated gaseous fluoride heterodimers and oligomers, it is the intention of the authors to survey the present knowledge on structures and stabilities of these complexes and to draw some consequences for experimental chemistry.

General characteristics of gaseous halogen-bridged complexes are explained in Section 2. The present knowledge on experimentally identified and quantum chemically calculated fluorine-bridged heterocomplexes is summarized in Section 3. Finally, stabilities and structures of fluoroaluminate complexes in the vapour phase are discussed in Section 4. The discussion is focused on fluoroaluminate complexes containing mono-, di- and trivalent cations. © 1997 Elsevier Science S.A.

*Keywords:* Gaseous halogen-bridged complexes; Fluoroaluminate complexes; Equilibrium structures; Ab-initio quantum chemistry

## 1. Introduction

The formation of gaseous homo- and heterodimers and oligomers coexisting with solids or molten mixtures of metal halides is a well known phenomenon. Sparingly volatile halides can be transported through the vapour phase with the assistance of highly volatile halides. The ability to form complexes in the gaseous phase can be used in chemical synthesis including catalysis (see, for example, Refs. [1–8]) and to explore specific physical effects. Based on the interpretation of ligand field spectra, the first ideas concerning the structures of chloride complexes were published by Schäfer [9] 20 years ago. It was soon realized that the coexistence of several species in the vapour phase prevents a reliable determination of thermodynamic data of certain gaseous complexes.

In comparison to the field of chloride complexes, only a rather small number of examinations exists dealing with the composition of vapour phase and its interaction with mixtures of solid metal fluorides. Until now, the number of directly identified fluorine-bridged hetero-complexes is comparatively small. Relatively high melting points along with low vapour pressures of the fluoride solids are the reasons for this

situation. Furthermore, experiments with appropriate fluorides are challenging. Since the paper of Schäfer [9], published in 1976, remarkable progress has been made in the field of quantum chemistry [10]. Results of several quantum chemical calculations have been published on the equilibrium structures of gaseous fluoride complexes, which also can serve as model compounds for chloride complexes.

## 2. General characteristics of gaseous halogen-bridged complexes

The dimeric nature of gaseous aluminium and iron (III) chlorides was discovered as early as 1857. For a very long period this complex formation was considered as the exception in gas-phase chemistry. The development of special high-temperature techniques together with the mass spectrometric examination of gases, possible since about 1950, led to the conclusion that complex formation in the vapour phase is a general and chemically relevant reaction. It was established that vapours of metal halides partially associate at higher temperatures and form oligomeric gaseous molecules (homo-complexes). Similarly, the reaction with other gases or coexisting condensed phases can result in the formation of hetero-complexes [11]. The first examples of heterodimer com-

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plexes were  $\text{NaAlCl}_4$  ( $\text{NaCl}$  and  $\text{AlCl}_3$ ) and  $\text{KAlCl}_4$  ( $\text{KCl}$  and  $\text{AlCl}_3$ ) [9]. Today, homo- and heterocomplexes of more than 50 elements of the periodic table [9] are known.

Interest in homo- and heterocomplexes has considerably increased in the last 20 years. It was stimulated by various industrial applications, for example high-temperature processes, catalytic reactions, chemical syntheses or metal halide lamps. Other well known examples concern technical aluminium production [12] (formation of  $\text{NaAlF}_4$ ) and the segregation process in the extraction of copper from copper ores (formation of  $\text{Cu}_3\text{Cl}_3(\text{g})$ ). The use of vapour phase complexes in preparative chemistry ranges from the chemical transport of sparingly volatile halides interacting with highly volatile halides in a temperature gradient to the synthesis of intermetallic phases by chemical transport reactions [2,3]. Of special importance is the use of gaseous complexes for the preparation of both high-purity materials and doped solids. The techniques of vapour deposition and co-deposition are very well suited to form activated solids with peculiar chemical, optical or magnetic properties. Finally, halide complexes in excited states (e.g. excimers) are extensively used for operating excimer lasers in research and industrial applications.

Among gaseous fluorine-bridged complexes the fluoroaluminate complexes play an outstanding role as they are relevant (i) for the formation of fluoride glasses with unique optical properties [13], (ii) for the synthesis of  $\text{Cr}^{3+}$ -doped aluminium fluorides as potential laser materials, and (iii) for the electrolysis of molten mixtures of  $\text{AlF}_3/\text{MF}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) to produce aluminium.

The formation of 1:1 heterodimers can be understood in a simplified manner as proceeding according to Eq. (1).



The vapour-phase complexes are preferably formed during the superimposed physical and chemical processes of the evaporation of condensed phases. They can be observed coexisting both with the solid phases and with the melts of salts [14,15]. No general relations between the structures of the gaseous complexes and the corresponding subunits in the condensed phase can be drawn, and from the existence of a certain complex in the gas phase it is not necessarily possible to derive the existence of a similar subunit in the melt [16]. The formation of gaseous complexes has also to be discussed as result of gas-phase reactions.

Alkali metal and other halides of monovalent metals evaporate mainly as two-atomic molecules which coexist with dimeric and/or oligomeric species [17–20].

For the gas phase of  $\text{MX}_2$  compounds, a dominating dimer/monomer equilibrium is formulated. A trigonal coordination of  $\text{M}$  is assumed for the dimeric species  $(\text{MX}_2)_2$  (Fig. 1) [11]. Several equilibrium structures having  $\text{D}_{2h}$ ,  $\text{C}_{3v}$ , or  $\text{C}_{2v}$  symmetries with similar stabilities seem to be possible depending on the size of  $\text{M}$  [18,21–24]. Even the existence of molecular clusters formed by aggregation of up to four  $\text{MX}_2$  monomers was experimentally proven [25].

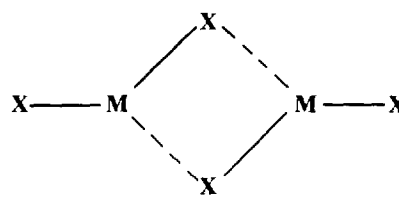


Fig. 1. Trigonal coordinated  $(\text{MX}_2)_2$  compounds in the gas phase.

In comparison, trivalent metal halides show a much stronger tendency to dimerize in the gas phase. The structures are usually built up of tetrahedral or tetrahedral-like units. A typical example is  $\text{Al}_2\text{Cl}_6$ , consisting of two edge-shared tetrahedra [26–30] and all gaseous  $\text{Al}_2\text{X}_6$  molecules ( $\text{X} = \text{F}, \text{Br}$ ) are similar [26,29,30]. Comparing the structures of  $\text{Al}(\text{III})$  halides determined for the solid, liquid and gaseous states, it seems that dimeric species only exist in the case of  $\text{Al}_2\text{Br}_6$  in solid and molten  $\text{AlBr}_3$  [30].  $\text{Al}_2\text{Cl}_6$  units are formed when solid  $\text{AlCl}_3$  is melted.  $\text{AlF}_3$  does not melt under normal conditions. Beside the low partial pressure of  $\text{AlF}_3$  in practice, a problem results connected with the aim of the paper: even with low levels of impurities such as  $\text{H}_2\text{O}$  and  $\text{OH}^-$ , the pressure above the solid is dramatically increased at higher temperatures. It is obvious that here chemical reactions effectively promote the evaporation process. In contrast to the other  $\text{Al}(\text{III})$  halides,  $\text{AlF}_3$  exhibits only a low dimerization tendency in the vapour phase [31].

The object of most papers published so far is the mass spectroscopic examination of new complexes as well as the thermodynamic aspects of their formation [11,32,33]. Experimental efforts to identify the most stable structures of these complexes [11,34,35] use in-situ Raman spectroscopy [36], IR and Raman matrix isolation techniques [11,37], electron excitation spectra [9], electron diffraction [38], photoelectron spectroscopy and rotation spectra [11,34]. However, the coexistence of several species in the vapour phase makes unambiguous experimental structure determinations difficult. The composition of the gas phase depends on the experimental conditions of temperature and pressure, the chemical properties of the metal halide and the geometry of the apparatus used. The formation and the properties of vapour phase complexes can be best understood on the basis of appropriate theoretical models and quantum chemical ab-initio calculations play an important role in determining the structures, stabilities and thermodynamic properties of gaseous complexes [21,22,39–43]. Very often they give the only access to an acceptable interpretation and structural characterization of the gaseous species.

20 years ago Schäfer [9] published a review of all known chlorine-bridged complexes. Both dimeric and oligomeric heterocomplexes exist, which are built up of submolecules with equal or mixed valency of the cations. In Schäfer's summary [9], hydrogen is one of the very few elements, the chloride of which was not considered to possess the ability to form complexes with other metal halides. However, the existence of  $\text{HAlCl}_4$  ( $\text{HCl}-\text{AlCl}_3$ ) in the vapour phase was indicated by mass spectrometry in 1967 [44] and 1973 [45].

Table 1  
Experimentally observed gaseous fluorine-bridged heterocomplexes

System	T (K)	Method <sup>a</sup>	Dominating species in the gas phase
LiF–AlF <sub>3</sub>	946	MS	LiAlF <sub>4</sub> , Li <sub>2</sub> AlF <sub>5</sub> [46] (LiAlF <sub>4</sub> ) <sub>2</sub>
KF–AlF <sub>3</sub>		ED	KAlF <sub>4</sub> [70,71]
NaF–AlF <sub>3</sub>		ED	NaAlF <sub>4</sub> [71]
MF–AlF <sub>3</sub> (M = Li, Na, ...Cs)	800–1100	Matrix-IR	MAlF <sub>4</sub> (M = Li, ...Cs) [48,68,69]
MF–Me <sup>III</sup> F <sub>3</sub> (M = Li, Na, K; Me = Al, Ga)	> 950	MS, isothermal evaporation	MMeF <sub>4</sub> , M <sub>2</sub> MeF <sub>5</sub> (MMeF <sub>4</sub> ) <sub>2</sub> [47,99,106,107]
MF–Me <sup>III</sup> F <sub>3</sub> (M = Li, Na, K, Rb; Me = Sc, Y, La, V)	> 1100 evaporation	MS, isothermal	MMeF <sub>4</sub> [47]
LiF–BeF <sub>2</sub>	900	Matrix-IR	LiBeF <sub>3</sub> [108]
MF–Me <sup>II</sup> F <sub>2</sub> (M = Li, Na, K; Me = Be, Sn)	> 800	MS, isothermal evaporation	MBeF <sub>3</sub> (M = Li, Na, K) M <sub>2</sub> SnF <sub>3</sub> , (M = Na, K) (NaBeF <sub>3</sub> ) <sub>2</sub> , M <sub>2</sub> BeF <sub>4</sub> (M = Li, Na) [47,49,109,110]
MF–FeF <sub>2</sub> (M = Li, ...Cs)		MS	MFeF <sub>3</sub> [111] (M = Li, ...Cs)
MF–FeF <sub>3</sub> (M = Li, ...Cs)		MS	MFeF <sub>4</sub> [111] (M = Li, ...Cs)
MF–CuF <sub>2</sub> (M = K, Rb, Cs)	> 875	MS	MCuF <sub>3</sub> [112] (M = K, Rb, Cs)
KF–HfF <sub>4</sub>		MS	HfF <sub>5</sub> <sup>-</sup> , Hf <sub>2</sub> F <sub>9</sub> <sup>-</sup> [49]
MnF <sub>2</sub> –AlF <sub>3</sub>		coupled Thermo-analysis/MS	MnAlF <sub>5</sub> [98]
Me <sup>III</sup> F <sub>3</sub> –M <sup>III</sup> F <sub>3</sub> (M = Al, 3d-elements)	> 900	High temperature MS	negative ions [113] MF <sub>3</sub> <sup>-</sup> , MeF <sub>3</sub> <sup>-</sup> , MF <sub>3</sub> <sup>-</sup>
LiF–NaF		FTIR	LiNaF <sub>2</sub> [114]
CaF <sub>2</sub> –SrF <sub>2</sub>		FTIR	CaSrF <sub>4</sub> [114]
α-AlF <sub>3</sub> ·3H <sub>2</sub> O, α-AlF <sub>3</sub>	570–670	Thermograv./MS	HAIF <sub>4</sub> [80] HAIF <sub>3</sub> <sup>+</sup> , H <sub>2</sub> AlF <sub>4</sub> <sup>+</sup> HAIF <sub>3</sub> <sup>+</sup> , HAIF <sub>4</sub> <sup>+</sup> [80] {(HAIF <sub>4</sub> ) <sub>2</sub> }?
AlOHF <sub>2</sub> ·H <sub>2</sub> O	> 870	Thermograv./MS	
AlF <sub>3</sub> /FeF <sub>3</sub>	> 1070 > 1100	Thermograv./MS Thermograv./MS	H <sub>2</sub> AlF <sub>5</sub> [81] HFeF <sub>4</sub> , H <sub>2</sub> FeF <sub>5</sub> [82] <sup>b</sup>

<sup>a</sup> MS, mass spectroscopy; ED, electron diffraction.

<sup>b</sup> Water traces provide H atoms for the formation of HAIF<sub>4</sub> (HFeF<sub>4</sub>).

The ions HAICl<sup>+</sup>, HAICl<sub>2</sub><sup>+</sup>, HAICl<sub>3</sub><sup>+</sup> and HAICl<sub>4</sub><sup>+</sup> could also be detected, but the circumstance of their formation and the nature of their bonding was not known.

### 3. Fluorine-bridged heterocomplexes — experimental evidence and quantum chemical calculations

Whereas a variety of heterocomplexes of gaseous chlorides is known [9], the number of experimentally identified and well characterized fluoride complexes is small. In most cases spectroscopic evidence has been obtained by mass spectroscopy of the gaseous phase during isothermal evaporation of mixtures of the fluorides. For this purpose the high-temperature mass spectrometer was coupled with a Knudsen diffusion cell [46–49]. Further proofs have been obtained by electron diffraction [38], infrared spectroscopy of matrix isolated species and also by Raman spectroscopy of the gaseous phase. With the help of mass spectroscopy heterocomplexes with the stoichiometry 1:1, 2:1 and 2:2 have been identified, and the structures could be deduced from the fragmentation behaviour [46,47]. A compilation of the experi-

mentally detected heterocomplexes of gaseous fluorides is given in Table 1. As can be seen from this table the existence of both complexes with the same oxidation states of the metals (1/1, 2/2, 3/3) as well as those with mixed oxidation states (1/3, 1/2, 2/3) is established. The number of heterocomplexes with the combination 1/3 is greatest. There are also fluorometallate complexes where a M<sup>+</sup> cation is formally substituted by a proton. As in the case of HAICl<sub>4</sub>, the structure and bonding of these complexes are of interest. Thus, it had to be established whether halogen or hydrogen bridges are present. The latter could be a result of the strong Brønsted acidity of HF and HCl.

Results of quantum chemical ab-initio calculations have been published for 1:1, 1:2 and 2:1 complexes (see Table 2). These calculations also include results of the respective monomeric subunits. There are further theoretical publications dealing with the calculation of the structure and vibration frequencies of the anions, e.g. BeF<sub>4</sub><sup>2-</sup>, BeF<sub>3</sub><sup>-</sup>, MgF<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, AlF<sub>4</sub><sup>-</sup>, LiF<sub>2</sub><sup>-</sup>, NaF<sub>2</sub><sup>-</sup>, and of complex salts [18,50,51]. Additionally, a number of ab-initio calculations of gaseous metal hydride complexes of similar composition (Table 2) have been published [50,52–58]. It turns out that the optimized

Table 2  
Quantum chemical ab-initio calculations of high-temperature gas-phase metal fluoride complexes—heterocomplexes<sup>a</sup>

Complex	Method/basis set	Most stable structure	Reference
LiAlF <sub>4</sub>	HF/STO-3G HF/6-31G	C <sub>2v</sub> symmetry (3 models examined)	[73,74]
MAIF <sub>4</sub>	HF/DZHD <sup>b</sup>	C <sub>2v</sub> <sup>c</sup>	[18]
LiAlF <sub>4</sub> , NaAlF <sub>4</sub>	HF/Mini-1; Mini-1 + HF/6-31G* MP2/6-31G* <sup>d</sup> MP2/6-31 + G* <sup>d</sup> MP2(full)/6-31G(d) HF/6-31G* MPn(fc)/6-31G* <sup>d</sup>	C <sub>2v</sub> (LiAlF <sub>4</sub> ) C <sub>3v</sub> (C <sub>2v</sub> ) (NaAlF <sub>4</sub> )	[72,76]
NaAlF <sub>4</sub>	HF/6-31G* MP2/6-31G* <sup>d</sup> MP2/6-31 + G* <sup>d</sup> MP2(FC)/6-31G(2d)	C <sub>2v</sub> (LiAlF <sub>4</sub> ) C <sub>3v</sub> (C <sub>2v</sub> ) (NaAlF <sub>4</sub> ) C <sub>3v</sub> (C <sub>2v</sub> )	[59,60] [75]
BeAlF <sub>5</sub> , MgAlF <sub>5</sub>	HF/STO-3G; 6-31G	C <sub>2v</sub>	[74,100]
BeAl <sub>2</sub> F <sub>8</sub>	HF/STO-3G	D <sub>2d</sub> 7 models calculated	[101]
LiBeF <sub>3</sub>	HF/(7s3p)/[4s2p] <sup>c</sup>	C <sub>2v</sub>	[115]
MBeF <sub>3</sub> , MMgF <sub>3</sub> (M = Li, Na)	HF/DZHD <sup>b</sup>	C <sub>2v</sub> <sup>c</sup>	[18]
LiBeF <sub>3</sub> , Li <sub>2</sub> BeF <sub>4</sub>	HF/4-31 + G	C <sub>2v</sub> planar 6-membered cycle for Li <sub>2</sub> BeF <sub>4</sub>	[50 u, Zitate dort]
LiMgF <sub>3</sub>			[116]
LiNaF <sub>2</sub>			[116]
LiNaF <sub>2</sub>	HF/6-31G*	C <sub>2v</sub>	[21]
BeMgF <sub>4</sub>	HF/3-21G*, 6-31G*	C <sub>2v</sub> , C <sub>3v</sub>	[21]
Li <sub>2</sub> BeF <sub>4</sub>	HF/3-21G*	D <sub>2d</sub> , C <sub>2v</sub>	[21]
MnAlF <sub>5</sub>	HF/WDZP <sup>f</sup>	C <sub>2v</sub> , C <sub>3v</sub>	[98]
HF–AlF <sub>3</sub> (F-bridge)	HF/3-21G, 6-31G* HF/Mini-1, 6-31G** HF/6-31G*, 6-31 + G*, HF/dzp, tz2p MP2(full)/6-31G*, 6-31 + G* G2(MP2) energies HF/6-31G* MP2/6-31G* <sup>d</sup> MP3/6-31G** <sup>d</sup> MP4(SDTQ)/6-31G* <sup>d</sup>	C <sub>3v</sub> (3 models) C <sub>3v</sub> (3 models) C <sub>s</sub> (5 models calculated)	[117] [92] [84]
AlF <sub>3</sub> –HF (H-bridge)	HF/dzp	C <sub>2v</sub>	[79]
2HF–AlF <sub>3</sub>	HF/dzp, tz2p HF/Mini-1; NDDO	C <sub>1</sub> C <sub>1</sub>	[93] [92]
(HAlF <sub>4</sub> ) <sub>2</sub>	NDDO		[94]
HAl <sub>2</sub> F <sub>7</sub>	NDDO		[94]
H <sub>2</sub> Al <sub>2</sub> F <sub>6</sub>	NDDO		[94]
HF–FeF <sub>3</sub>	UHF/Mini-1, Wdzp <sup>f</sup> MP2/Wdzp <sup>f</sup>	C <sub>s</sub>	[88]

<sup>a</sup> The geometries of the molecules have been optimized with the method and basis set given, if not otherwise indicated.

<sup>b</sup> Double zeta basis set of Huzinaga and Dunning: (9s5p/4s2p) for atoms of the 2nd period, (12s9p/6s4p) for atoms of the 3rd period.

<sup>c</sup> No geometry optimization; Bond distances and angles have been extrapolated from calculations of the corresponding hydrides.

<sup>d</sup> MPn Moller–Plesset perturbation calculations to consider electron correlations have been performed with the given basis sets at HF/6-31G\* optimized geometry.

<sup>e</sup> Basis set of Roos and Siegbahn [118].

<sup>f</sup> WDZP corresponds to the [14s9p5d]/8s5p3d] basis set of Wachters [89] for Mn, [14s9p5d/9s3p2d] for Fe [90] and a DZP basis set [90] for Al and F.

geometries of these compounds are quite similar to those of the gaseous fluoride complexes. Very often they have been

used for extrapolations to get bond lengths and angles of the fluoride complexes.

Table 3  
Experimental dissociation enthalpies of alkali metal fluoroaluminate complexes ( $H_T$  in  $\text{kJ mol}^{-1}$ ) [47]

Alkaline metal	$T$ (K)	$\text{MAIF}_4^a$	$T$ (K)	$\text{M}_2\text{AlF}_5^b$	$T$ (K)	$(\text{MAIF}_4)_2^c$
Li	1000	305.4	1091	245.6	946	202.9
Na	910	336.8	1100	217.9	910	188.3
K	1020	353.5	1054	191.6	836	161.5

<sup>a</sup> According to the reaction:  $\text{MAIF}_4 \leftrightarrow \text{MF} + \text{AlF}_3$ .

<sup>b</sup>  $\text{M}_2\text{AlF}_5 \leftrightarrow \text{MF} + \text{MAIF}_4$ .

<sup>c</sup>  $(\text{MAIF}_4)_2 \leftrightarrow 2 \text{MAIF}_4$ .

All  $\text{MAF}_n$  complexes (M, metal atom) collected in Table 2 possess either  $C_{2v}$  or  $C_{3v}$  symmetry. In both cases the metal atoms are bridged by two or three fluorine atoms (edge-bridged or face-bridged). This, however, holds only for metal fluorometallate complexes. If the metal ion is formally substituted by a proton completely different energetic and structural situations arise (cf. Section 4). Since in Table 2 only fluorometallate complexes are given, it might be reasonable to cite here also some ab-initio calculations of tetrafluoroborate gas phase complexes  $\text{MBF}_4$  (M = Li, Na, K, Rb) [59–62] because their optimized structures bear a great resemblance to those of the fluoroaluminate complexes.

#### 4. Gaseous fluoroaluminate complexes: experimental results and quantum chemical calculations

At this point it is interesting to note that the anions of fluoroaluminate complexes are already detectable in melts consisting of aluminium fluoride and alkali metal fluorides as shown for  $\text{AlF}_4^-$ ,  $\text{AlF}_5^{2-}$  and  $\text{AlF}_6^{3-}$  [63–67] by IR and Raman measurements. While the formation of  $\text{AlF}_5^{2-}$  in melts has never been unambiguously proven [66], the  $\text{AlF}_6^{3-}$  anion mainly tends to dissociate into  $\text{AlF}_4^-$  and  $2\text{F}^-$  [67].

##### 4.1. $(\text{A}^I\text{F})_n(\text{M}^{III}\text{F}_3)_m$ complexes

###### 4.1.1. Alkaline metal fluoroaluminate complexes

Fluoroaluminate complexes with the title composition have been identified in the following cases as molecules in the gas phase:  $\text{MAIF}_4$  (M = Li, ... Cs),  $\text{M}_2\text{AlF}_5$  (M = Li, Na, K) and  $(\text{MAIF}_4)_2$  (M = Li, Na, K).

At high temperatures, the gas phase coexisting with a solid mixture of  $\text{LiF}$  with  $\text{AlF}_3$  has a very complex composition [46]. In addition to the molecules listed in Table 1,  $\text{LiF}$ ,  $\text{Li}_2\text{F}_2$ ,  $\text{Li}_3\text{F}_3$ ,  $\text{AlF}$  and  $\text{Al}_2\text{F}_6$  have been identified by mass spectroscopy [46]. Here, the detection of  $\text{LiAlF}_3^+$  has been taken as a proof for the existence of  $\text{LiAlF}_4$ . Similarly,  $\text{Li}_2\text{AlF}_4^+$  has been traced back to the formation of  $\text{Li}_2\text{AlF}_5$  and  $(\text{LiAlF}_4)_2$ . The composition of the starting mixture of fluorides, the temperature as well as the equilibrium partial pressures have a strong influence on the relative amount of the 2:1 and 2:2 complexes in the gas phase. A critical analysis of the mass spectra and the observed fragmentation behaviour

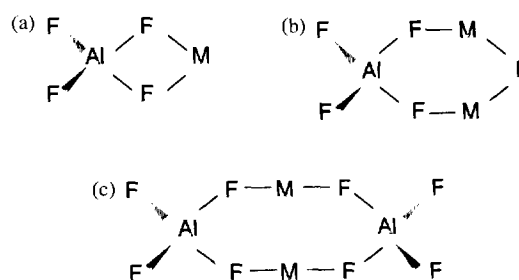


Fig. 2. Suggested structures of alkali metal fluoroaluminate complexes from mass spectroscopic fragmentation behaviour: (a)  $\text{MAIF}_4$ , (b)  $\text{M}_2\text{AlF}_5$ , (c)  $(\text{MAIF}_4)_2$ .

of the alkaline metal fluoroaluminate complexes has led to the proposal of the structures in Fig. 2.

The dissociation enthalpies derived from the mass spectra (Table 3) lead to the conclusion that all the observed alkali metal fluoroaluminate complexes are stable chemical compounds. Matrix IR [68,69] and electron diffraction studies [70,71] of  $\text{MAIF}_4$  complexes have been performed to determine the structure of these compounds. However, the interpretation of the observed vibrational frequencies is rather problematic. Theoretically, 12 normal modes can be expected for  $\text{MAIF}_4$  compounds according to the vibrational degrees of freedom ( $f = 3N - 6$ ;  $N$  = number of atoms). However, in all cases only seven normal vibrations have been assigned without doubt [69]. Based on the available vibrational and electron diffraction data, a  $C_{2v}$  symmetry has been proposed for all  $\text{MAIF}_4$  complexes. According to this, the alkali cation is formally bridged by two fluorine atoms at one edge of the  $\text{AlF}_4^-$  tetrahedron (so-called edge-bridged structure, see Fig. 1a). This  $C_{2v}$  structure served as a basis for thermodynamic calculations found in JANAF Thermochemical Tables [26]. Schäfer [9] also used this structure model as a basic assumption for the discussion of the chlorine-bridged heterodimers. However, the first quantum chemical calculations have raised some doubts about this structure, especially for complexes containing heavier alkali metal cations.

In the literature, three models have been considered for  $\text{MAIF}_4$  complexes (M = alkali metal atom) (Fig. 3): (i) a corner-bridged structure I ( $C_{3v}$ ), (ii) an edge-bridged structure II ( $C_{2v}$ ), and (iii) a face-bridged structure III ( $C_{3v}$ ).

Based on electron diffraction studies, both  $C_{2v}$  (Fig. 3, II) and  $C_{3v}$  (Fig. 3, III) structures have been excluded for  $\text{KAlF}_4$  [70]. A structure with  $C_s$  symmetry has been assumed for  $\text{KAlF}_4$  [70], which only deviates from structure II ( $C_{2v}$ ) by

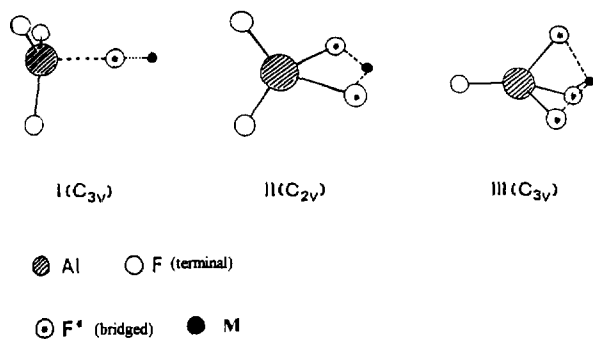


Fig. 3. Possible structures of  $MAIF_4$  complexes (I–III).

a non-planar ring {Al–F–K–F}. The determination of the position of the potassium atom has been difficult, which also prevented an unequivocal preference for one of the structure models given in Fig. 3.

At present, the controversial discussion on the structure of  $MAIF_4$  complexes is still not finished. Ab-initio Hartree–Fock and Møller–Plesset (MP2) calculations have contributed much to solve this problem. The determination of relative stabilities especially of the structures II and III is still a challenging task of quantum chemistry [21].

Our own calculations on  $LiAlF_4$  and  $NaAlF_4$  [72] as well as publications of other authors [59,60,73–75] agree in the result that both structures II and III (cf. Fig. 3) correspond to local minima at the HF/6-31G\* potential energy surface. Most optimizations of bond lengths and angles of the structure models I–III (Fig. 3) published so far have explored the Hartree–Fock (HF) approximation<sup>1</sup>. At the HF/6-31G\* level, structure II ( $C_{2v}$ ) is energetically favoured for both complexes. Whereas distinct energy differences have been obtained between structures II and III of  $LiAlF_4$  (27.2 kJ mol<sup>-1</sup>, HF/6-31G\*), only 5.2 kJ mol<sup>-1</sup> has been obtained for the corresponding energy difference of  $NaAlF_4$ . Optimizations using double-zeta or triple-zeta basis sets yield a similar energy sequence (see Table 4). As a result of MP2 calculations, including electron correlation effects, the energy difference between structures III and II is diminished for both  $LiAlF_4$  and  $NaAlF_4$ . In this approximation (MP2), even the face-bridged structure (three bridging fluorines) is favoured for  $NaAlF_4$  (Fig. 3, III).

First calculations of the  $KAlF_4$  molecule demonstrate that structure III is favoured even at the HF level depending on the basis set used (Table 4). Obviously, the stabilities of different model structures are essentially dependent on the size of the alkali cation<sup>2</sup>. With increasing size of the alkali cation a greater tendency to coordination via three bridging fluorines (face-bridged structure III, Fig. 3) can be estab-

Table 4

Relative energies (in kJ mol<sup>-1</sup>) of the edge (II)- and face (III)-bridged structures of  $MAIF_4$  molecules (M = Li, Na, K)

Molecule/basis set	Structure II	Structure III
$LiAlF_4$ <sup>a</sup>		
HF/6-31G*//HF/6-31G*	0.0	27.2
MP2/6-31G*//HF/6-31G*	0.0	20.1
MP2/6-31 + G*//HF/6-31G*	0.0	25.0
G2(MP2) <sup>b</sup>	0.0	20.9
$NaAlF_4$ <sup>a</sup>		
HF/dzp//HF/dzp <sup>c</sup>	0.0	2.1
HF/dz2p//HF/dz2p <sup>c</sup>	0.0	5.7
HF/tzp//HF/tzp <sup>c,d</sup>	0.0	5.4
HF/tz2p//HF/tz2p <sup>c</sup>	0.0	5.8
HF/6-31G*//HF/6-31G*	0.0	5.2
MP2/6-31G*//HF/6-31G* <sup>c</sup>	5.2	0.0
MP2/6-31 + G*//HF/6-31G*	3.4	0.0
G2(MP2) <sup>b</sup>	10.4	0.0
$KAlF_4$ <sup>c</sup>		
HF/dz//HF/dz	0.0	4.9
HF/tzp//HF/tzp <sup>d</sup>	2.1	0.0

<sup>a</sup> Present calculations [72].

<sup>b</sup> Energies calculated with the G2 method at MP2(full)/6-31G(d) optimized geometries [76].

<sup>c</sup> Present unpublished results.

<sup>d</sup> Tzp basis: tzp (Na,F), tzp hondo (Al).

<sup>e</sup> Møller–Plesset perturbation calculation of higher order Ordnung (MPn/6-31G\*//HF/6-31G\*, n = 2,3,4, [59]) are in the same range.

lished. These findings are in agreement with the results of Francisco and Williams [62] obtained for  $BF_4^-M^+$  complexes (M = Li, ...Rb) using also HF and MP2 methods combined with 6-31G\* and 6-31 + G basis sets.

The small energy differences between structures II and III obtained for  $NaAlF_4$  and  $KAlF_4$  lead to the conclusion that the formation of both structures should be possible in the vapour phase. As a consequence, the infrared spectra will become more complex and a superimposition of the vibrational frequencies of the  $C_{2v}$  and the  $C_{3v}$  isomers is expected. Quantum chemical calculations did not result in a  $C_s$  structure with a non-planar ring as a local minimum on the potential energy surface.

The structure with  $C_{2v}$  symmetry described in Ref. [77] (Fig. 3, II) is obviously only valid for  $LiAlF_4$ . MP2 optimizations of  $NaAlF_4$  have shown [75,76] that this complex has a face-bridged structure with  $C_{3v}$  symmetry (Fig. 3, III). Similar results have been obtained for chloride complexes [75]. HF/6-31G\* calculations resulted in structure III as the most stable for  $NaAlCl_4$  [75].

For  $LiAlF_4$  a good agreement has been obtained between experimental and calculated complex formation energies (see Table 3) at the MP2/6-31 + G\*//HF/6-31G\* level if zero point vibrational energies are taken into account ( $LiAlF_4$ , structure II:  $\Delta E = -295.3$  kJ mol<sup>-1</sup>). HF/6-31G\* calculations led to  $-292.9$  kJ mol<sup>-1</sup> for the complex formation of  $NaAlF_4$  (structure III) [75]. Bock et al. [75] demonstrated that this value can be enormously improved by MP2(FC)/

<sup>1</sup> Exceptions are MP2(FC)/6-31G(2d) optimizations of  $NaAlF_4$ , NaF and  $AlF_3$  for the calculation of dissociation energies [75] and the MP2(full)/6-31G(d) optimization of  $LiAlF_4$  and  $NaAlF_4$  of Curtiss [76].

<sup>2</sup> The optimized geometries of  $LiAlF_4$  and  $NaAlF_4$  are collected in Ref. [72]. Here a distinct deviation from an  $AlF_4^-$  tetrahedron can be established. The angle between the bridging fluorines is smaller and the Al–F\* bond length (cf. Fig. 2) is larger than the corresponding parameters in the tetrahedron.

6-31G(2d)//MP2/6-31G(2d) calculations ( $\Delta E = -357.3$  kJ mol<sup>-1</sup>).

So far, there is no report in the literature on ab-initio calculations of fluoroaluminate complexes MAIF<sub>4</sub> with larger alkali cations (M = K, Rb, Cs) or the larger complexes M<sub>2</sub>AlF<sub>5</sub> and (MAIF<sub>4</sub>)<sub>2</sub>. They demand a large computational effort if electron correlation and relativistic effects are taken into account.

#### 4.1.2. Substitution of the alkali metal cation by a proton: complexes with the composition HAIF<sub>4</sub> and H<sub>2</sub>AlF<sub>5</sub>

The existence of HAIF<sub>4</sub> has already been mentioned in Section 1. The first quantum chemical calculations on HAIF<sub>4</sub> were published by Wilson et al. (1992) [78] and Scholz (1994) [79].

In addition to the stable alkali metal fluoroaluminate complexes, Table 1 also lists such complexes which can be considered as having been formed by substitution of the alkali metal cation by a proton, e.g. HAIF<sub>4</sub>, H<sub>2</sub>AlF<sub>5</sub>, HFeF<sub>4</sub>, (HAIF<sub>4</sub>)<sub>2</sub>. The existence of these complexes was only proven by coupled thermoanalytical and mass spectroscopic experiments. Under these conditions they are formed in the course of solid-state chemical reorganization processes [80–82]. This makes them especially interesting for a comparison of equilibrium geometries and stabilities with those of the alkali metal fluoroaluminate complexes discussed before.

Until now, experimental information on hydrogen containing structures has only been available for HCl–BF<sub>3</sub>. For this purpose, molecular beam examinations coupled with electric resonance spectroscopy [83] were performed.

Two different possibilities arise from the formation of complexes between molecules having Lewis acidity (like BF<sub>3</sub>, BCl<sub>3</sub>, AlF<sub>3</sub>, AlCl<sub>3</sub>) and molecules having both Lewis basicity and Brønsted acidity (HF, HCl): (i) formation of a hydrogen bond between the HX molecule and one halogen atom of the MX<sub>3</sub> molecule, and (ii) formation of an intermolecular M–X bond, leading to a halogen-bridged heterodimer complex. Furthermore, the formation of ion-pair complexes like H<sup>+</sup>MX<sub>4</sub><sup>-</sup> could also be possible.

As in the case of the alkali metal fluoroaluminate complexes, the structure models given in Fig. 3 have been used for HAIF<sub>4</sub> calculations. Geometry optimizations at the HF/6-31G\*\* level showed that structure I (C<sub>3v</sub>) was the most stable among the three structures considered. However, struc-

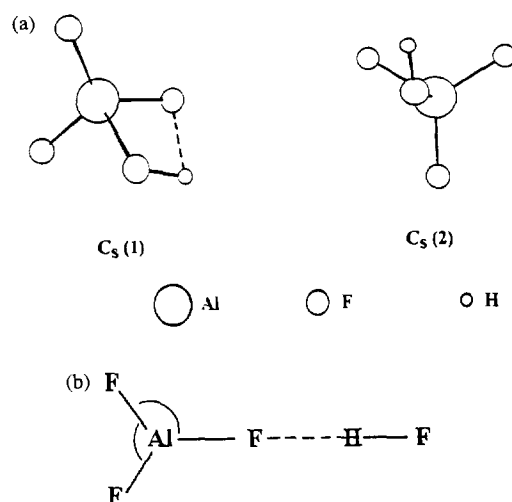


Fig. 4. (a) C<sub>s</sub> structures of the HF–AlF<sub>3</sub> (HX–MX<sub>3</sub>) complexes equilibrium structure: C<sub>s</sub> (I). (b) structure I (C<sub>3v</sub>) for the formation of a hydrogen bridge between AlF<sub>3</sub> and HF.

ture I (C<sub>3v</sub>) appears not as a minimum at the potential energy surface but represents a second-order saddle point. In addition, the two C<sub>s</sub> structures illustrated in Fig. 4(a) were optimized. The relative energies of all five structures are listed in Table 5. The equilibrium structure of HAIF<sub>4</sub> (C<sub>s</sub>(1), Fig. 4(a)) consists of a slightly pyramidal AlF<sub>3</sub> and a nearly undistorted HF molecule. HF is bonded to AlF<sub>3</sub> by a long fluorine bridge and a hydrogen bridge in a cyclic arrangement. The subunits are connected via a long F<sub>a</sub>–Al bridge (199 pm) and an H···Al<sub>b</sub> bridge of 223 pm (MP2(full)/6-31+G\* results). There is no indication for the existence of the ion-pair complex H<sup>+</sup>AlF<sub>4</sub><sup>-</sup>. The dissociation energies, optimized bond distances and angles, harmonic vibrational frequencies and thermodynamic functions of complex formation have been published by Curtiss and Scholz [84] at the HF and MP2 level. It is remarkable that the dissociation energy of 67.1 kJ mol<sup>-1</sup>, obtained with the G2(MP2) method, is in good agreement with the HF/DZP value of 67.0 kJ mol<sup>-1</sup>, which includes corrections for the basis set superposition error. A dissociation energy of ~67 kJ mol<sup>-1</sup> suggest the bonding of HAIF<sub>4</sub>, (better HF–AlF<sub>3</sub>) as between a van der Waals and stable complex.

No experimental data on the structure of HF–AlF<sub>3</sub> are available so far. However, the observed mass spectroscopy fragmentation pattern gives information concerning the struc-

Table 5  
Relative energies <sup>a</sup> of the optimized geometries of HF–AlF<sub>3</sub> <sup>b</sup>

Model	HF/6-31G*	HF/DZP	MP2(full)/6-31G*	MP2(full)/6-31+G*
I (C <sub>3v</sub> )	27.0 (2)	17.8	39.2 (2)	43.4 (2)
II (C <sub>2v</sub> )	41.5 (1)	19.1	13.0 (1)	25.0 (1)
III (C <sub>3v</sub> )	274.1 (2)	–	–	–
C <sub>s</sub> (2)	6.7 (1)	4.1	12.9 (1)	5.3 (1)
C <sub>s</sub> (1)	0.0 (0)	0.0 (0)	0.0 (0)	0.0 (0)

<sup>a</sup> In kJ mol<sup>-1</sup>.

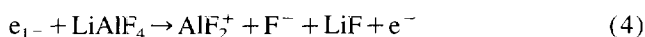
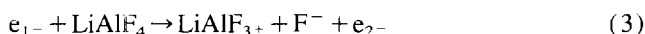
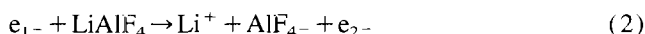
<sup>b</sup> Values in parentheses indicate the nature of the stationary points; 0, local minimum, 1, first-order saddle point, 2, second-order saddle point.

Table 6  
Total energies  $E^{\text{tot}}$  and complex interaction energies  $\Delta E$ ,  $\Delta E^{\text{c}}$  of the equilibrium structures of  $\text{HAlF}_4$  (HF/DZP results)

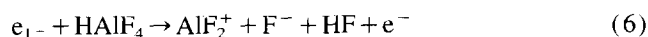
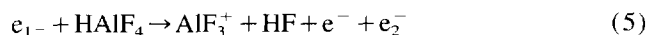
Molecule	$E^{\text{tot}}$ (au)	$\Delta E$ (kJ mol $^{-1}$ )	$\Delta E^{\text{c}}$ (kJ mol $^{-1}$ )	$\Delta \epsilon$ (kJ mol $^{-1}$ )
$\text{HF-AlF}_3$ , $C_s(1)$ fluorine bridge	-640.43072	-88.9	-67.0	21.9
$\text{AlF}_3\text{-HF}$ , $C_2v$ hydrogen bridge	-640.40660	-25.6	-19.36.3	

<sup>a</sup> Including corrections for the basis set superposition error.

ture of the complex. As generally accepted, the fragmentation probability of a molecule depends among other factors on the dissociation energy of the bond to be split. It is interesting that the observed fragmentation behaviour of the  $\text{HAlF}_4$  complex [80] differs from that of analogous alkali metal fluoroaluminate complexes  $\text{MAlF}_4$ . The fragmentation of  $\text{LiAlF}_4$  can be simplified as follows [46,47]:



The relative intensities of the fragments according to Eqs. (2)–(4) were determined as:  $\text{Li}^+:\text{LiAlF}_3^+:\text{AlF}_2^+ \equiv 100:14.3:18.3$  [46]. Obviously, the breaking of the Li–F and Al–F bonds take place with comparable efficiency which reflects the complex stability (see Table 3). In contrast, a completely changed fragmentation behaviour resulted for  $\text{HAlF}_4$ . The reaction according to Eq. (3), which implies the formation of a  $\text{HAlF}_3^+$  fragment, was not observed. The weakest bond in the complex should be predestinated for splitting. In the case of  $\text{HF-AlF}_3$  it appears to be the intermolecular Al–F<sub>a</sub> bridge (cf. Fig. 4,  $C_s(1)$  structure). Consequently, the experimentally observed fragmentation behaviour relates in an acceptable manner to the quantum chemically calculated equilibrium structure and stability of this species. Reactions (5) and (6) describe the fragments occurring [80]:



Until now, it has been assumed that the formation of a bond between HF and a centre with Lewis-acid properties like aluminium will be through an electron donor, in that case the fluorine atom of the HF group. However, it has been shown that a linear hydrogen bond to one of the fluorine atoms of  $\text{AlF}_3$  (structure I ( $C_{2v}$ ), Fig. 4b) is also a minimum at the potential energy surface [79]. For comparison, the total energies and the energies of complex formation of both equilibrium structures  $\text{HF-AlF}_3$  and  $\text{AlF}_3\text{-HF}$  are given in Table 6. The calculated interaction energy of the hydrogen-bridged complex amounts to  $-19.3 \text{ kJ mol}^{-1}$  after correction for the basis set superposition error (HF/DZP level) [79]. This is a usual value for hydrogen-bridged systems [85]<sup>3</sup>. The flu-

orine-bridged heterodimer complex is about three times more stable than the hydrogen bridged. Therefore, it can be assumed that the experimentally determined mass of 104 [80] corresponds to the more stable complex.

Starting from the  $\text{HF-AlF}_3$  (structure  $C_s(1)$ , Fig. 4(a)) it has been shown [79] that all other  $\text{HX-MX}_3$  complexes ( $X = \text{F, Cl}; M = \text{B, Al}$ ) have similar structures and properties. The intermolecular distance of 315.9 pm, calculated for  $\text{HCl-BF}_3$  including electron correlation effects (MP2/D95\*\*), is in good agreement with the experimental value of 317.1 pm [79]. All  $\text{HX-MX}_3$  complexes consist of nearly undistorted  $\text{MX}_3$  and  $\text{HX}$  subunits which are connected by long and weak intermolecular halogen bridges [79]. Hence, these complexes can be described as weak electron pair donor–acceptor adducts. The cyclic structure (Fig. 4(a),  $C_s(1)$ ) is characterized by the additional formation of a hydrogen bridge. Calculated shared electron numbers (SEN) [86,87] and net charges reveal that the bonding character is mainly covalent in the  $\text{BX}_3$  species. In the  $\text{AlX}_3$  subunits ionic bond character dominates [79]. After corrections for the basis set superposition errors, the interaction energies cover the range between  $-1.4 \text{ kJ mol}^{-1}$  ( $\text{HCl-BF}_3$ ) up to  $-67.0 \text{ kJ mol}^{-1}$  ( $\text{HF-AlF}_3$ ). The HF adducts are more stable than the HCl adducts. The complexes  $\text{HF-AlF}_3$  and  $\text{HF-AlCl}_3$  possess binding energies between values for chemical and van der Waals bonds. Bearing in mind that the structure of the  $\text{HCl-BF}_3$  complex, which has one of the lowest stabilities, has been examined experimentally, the energetic stabilities of the other complexes promise successful experimental structure determinations under suitable conditions.

Finally, calculations of the open shell complex  $\text{HF-FeF}_3$  (Wachters/DZP basis set [88–90]) also established in this case the  $C_s(1)$  structure (Fig. 4(a)) as the only minimum at the potential energy surface. Only marginal differences exist between the equilibrium structures of the open-shell  $\text{HF-FeF}_3$  and the closed-shell  $\text{HF-AlF}_3$  complex. However, the intermolecular distance depends remarkably on the basis set used for the iron atom. Distinct changes are caused not only by the inclusion of a third Fe d-function, but also by using additional s- and p-functions [91]. Until now, however, an unambiguous experimental proof of the  $\text{HF-FeF}_3$  complex has not been presented.

Bond distances, bond angles and dissociation energies of  $\text{LiAlF}_4$ ,  $\text{HF-AlF}_3$  and  $\text{HF-FeF}_3$  are summarized in Table 7. This table reveals essential differences between alkali metal and hydrogen containing  $\text{MAlF}_4$  complexes.

<sup>3</sup> The calculated corrected interaction energies (HF/6-31G\* level) are, for example: for  $(\text{HF})_2$ ,  $-18.6 \text{ kJ mol}^{-1}$ ; for  $(\text{H}_2\text{O})_2$ ,  $-19.6 \text{ kJ mol}^{-1}$ ; and for  $\text{CO}_2\text{-HF}$ ,  $-10.7 \text{ kJ mol}^{-1}$  [85].



Table 7

Comparison of the calculated bond distances and angles <sup>a</sup> of LiAlF<sub>4</sub>, HF–AlF<sub>3</sub> and HF–FeF<sub>3</sub>

Molecule/structure	Method/basis set	R(MF <sup>*</sup> )	R(Al(Fe)F <sup>*</sup> )	R(Al(Fe)F)	∠FAl(Fe)F	∠F <sup>*</sup> AlF <sup>*</sup>	∠Al(Fe)F <sup>*</sup> H
LiAlF <sub>4</sub> II(C <sub>2v</sub> ) <sup>b</sup>	HF/6-31G <sup>*</sup>	177.0	173.7	163.9	118.2	88.4	–
HF–AlF <sub>3</sub> C <sub>s</sub> (1) <sup>c</sup>	HF/dzp	91.8	197.9	163.7	119.8	–	109.0
	MP2/ 6-31 + G <sup>*</sup>	96.0	198.7	166.5	119.9	–	103.0
HF–FeF <sub>3</sub> C <sub>s</sub> (1) <sup>c</sup>	HF/Wdzp	91.9	209.8	173.0	–	–	103.1
	MP2/Wdzp	95.4	208.3	176.1	–	–	–
				171.4			
				177.9		–	85.3

<sup>a</sup> Dissociation energies: LiAlF<sub>4</sub>, 348.5 kJ mol<sup>-1</sup> (HF/6-31G<sup>\*</sup>); HF–AlF<sub>3</sub>, 67.0 kJ mol<sup>-1</sup> (HF/dzp); HF–FeF<sub>3</sub>, 59.9 kJ mol<sup>-1</sup> (HF/Wdzp) [72,84,88]; bond lengths in pm, angles in degrees; accuracies: ± 2 pm (distances), ± 1° (angles).

<sup>b</sup> Fig. 2.

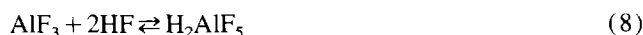
<sup>c</sup> Fig. 3.

#### 4.1.3. H<sub>2</sub>AlF<sub>5</sub>

The formation of the 1:2 (AlF<sub>3</sub>:HF) vapour-phase complex with the formula H<sub>2</sub>AlF<sub>5</sub> has been proven by mass spectroscopy above 850°C. Several mechanisms can be discussed for its formation. A reaction following the formation of HAlF<sub>4</sub> according to Eq. (7)



or direct reactions between AlF<sub>3</sub> and HF (or (HF)<sub>2</sub>) molecules would yield the desired species:



Both semiempirical NDDO formalism [92] and ab-initio calculations [93] have been used to determine the equilibrium geometry and bonding situation of this complex. Eight structure models have been taken into account, considering a four-fold as well as a five-fold coordination of the aluminium atom [92,93]. The resulting global minimum (cf. Fig. 5) corresponds to a cyclic arrangement of only slightly distorted AlF<sub>3</sub> and HF molecules. The intermolecular Al–F distance of 190.7 pm is substantially longer than a Al–F bond in the AlF<sub>3</sub> molecule. The strength of the intermolecular Al–F interaction is only about 30% of a typical Al–F single bond. As for HF–AlF<sub>3</sub>, there is also in this case no evidence for the existence

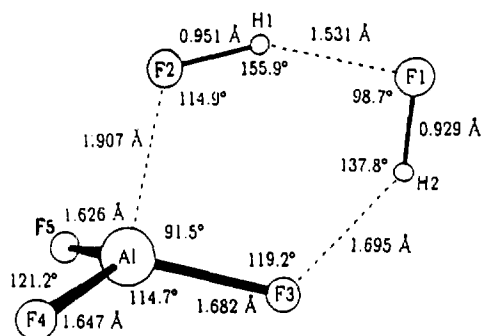


Fig. 5. Equilibrium structure of the 2HF–AlF<sub>3</sub> complex (C<sub>1</sub>). Distances in Å, angles in degrees.

of an AlF<sub>4</sub><sup>-</sup> anion. All available data such as deformation energies, binding energies, two-body and three-body interaction energies, harmonic vibrational frequencies as well as thermodynamic properties of complex formation calculated for the reaction according to Eq. (8) have been summarized [93]. The stability of larger vapour phase complexes of HF and AlF<sub>3</sub> molecules has been estimated only at a semiempirical level [94]. Thirteen structure models have been considered for the complexes HAl<sub>2</sub>F<sub>7</sub>, H<sub>2</sub>Al<sub>2</sub>F<sub>8</sub> and H<sub>2</sub>Al<sub>2</sub>F<sub>6</sub>. It turns out that the most stable structures are those which contain either Al<sub>2</sub>F<sub>6</sub> units or, similar to H<sub>2</sub>AlF<sub>5</sub>, a cyclic arrangement of the H–Al–F atoms [94].

The calculated structures in the gas phase can be compared with crystalline HF compounds like KF·2.5HF, KF·3HF [95], or (CH<sub>3</sub>)<sub>4</sub>NF·2HF, (CH<sub>3</sub>)<sub>4</sub>NF·3HF, (CH<sub>3</sub>)<sub>4</sub>NF·5HF [96]. Structure determinations of the crystalline compounds have been performed by Mootz and Boenigk [95,96]. Polyhydrogenfluoride anions [H<sub>n</sub>F<sub>n+1</sub>]<sup>-</sup> are found in these solids. They have a cyclic arrangement in those compounds with low HF content (2HF, 2.5HF). Examples are the formation of [H<sub>2</sub>F<sub>3</sub>]<sup>-</sup> in KF·2.5HF [95] and (CH<sub>3</sub>)<sub>4</sub>NF·2HF [96], and [H<sub>3</sub>F<sub>4</sub>]<sup>-</sup> in KF·2.5HF [95]. It is interesting to note that the cyclic structures observed in the solids show similarities to the calculated equilibrium structures of the vapour phase complexes HF–AlF<sub>3</sub>, 2HF–AlF<sub>3</sub> etc. The H–F–Al cycle in HF–AlF<sub>3</sub> might be formally interpreted as [HF<sub>2</sub>]<sup>-</sup>[AlF<sub>2</sub>]<sup>+</sup> (Fig. 4), in 2HF–AlF<sub>3</sub> as [H<sub>2</sub>F<sub>3</sub>]<sup>-</sup>[AlF<sub>2</sub>]<sup>+</sup> (Fig. 5), and in the cyclic structure of (HAlF<sub>4</sub>)<sub>2</sub> as [H<sub>2</sub>F<sub>3</sub>]<sup>-</sup>[Al<sub>2</sub>F<sub>5</sub>]<sup>+</sup>. Furthermore, the calculated fluorine–fluorine distances in the vapour-phase complexes are in the same range as in the solids with poly-HF anions.

It could be important to examine experimentally gas phases coexisting with the crystalline HF compounds. It is not known whether the cyclic poly-HF structures of the solids are preserved in the vapour phase <sup>4</sup>.

<sup>4</sup> Results of first semiempirical and ab initio calculations of [H<sub>n</sub>F<sub>n+1</sub>]<sup>-</sup>, [H<sub>n+1</sub>F<sub>n</sub>]<sup>+</sup> and (HF)<sub>n</sub> have been published [97].

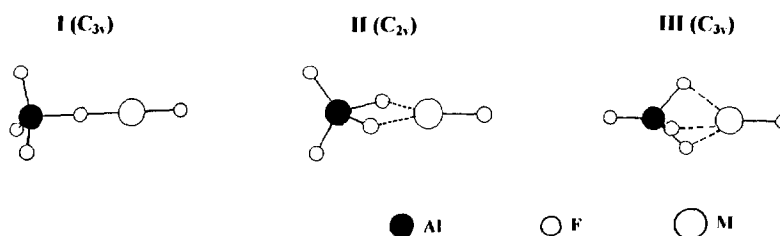


Fig. 6. Three possible structure models for  $MAIF_5$  complexes.

#### 4.2. $A''F_2-M''F_3$ complexes

There is no report in the literature on fluoroaluminate complexes of the type  $A'AlF_5$  ( $A'F_2:AlF_3 = 1:1$ ) except for  $MnAlF_5$  [98]. However, difficulties with the separation of Mg and Ca impurities during the sublimation of  $AlF_3$  indicate the existence of  $MgAlF_5$  and  $CaAlF_5$  [82]. On the other hand, the corresponding chlorine and bromine complexes are well known [36,99].

Curtiss and Heinricher [74,100] performed ab-initio Hartree–Fock calculations on  $BeAlF_5$  and  $MgAlF_5$  to obtain information about structures, bonding and energies. Bond angles and lengths of three structure models (cf. Fig. 6) have been optimized at the HF/STO-3G and HF/6-31G levels. A complete optimization without structural limitations has not been performed for  $MgAlF_5$ . HF/6-31G calculations yield the result that structure II ( $C_{2v}$ ) (cf. Fig. 6) is favoured as the most stable structure both for  $BeAlF_5$  and for  $MgAlF_5$ . However, the nature of the stationary point (saddle point or local minimum) was not examined [74,100]. Whereas structure II is energetically favoured by  $79.9 \text{ kJ mol}^{-1}$  for  $BeAlF_5$  in comparison with structure III, this value is lowered to  $22.2 \text{ kJ mol}^{-1}$  for  $MgAlF_5$ . Bearing in mind that there neither complete geometry optimizations nor larger basis sets or electron correlations were included [74,100], the question what is the most stable structure of these complexes cannot be unambiguously answered.

Open-shell UHF calculations on  $MnAlF_5$  [98] using the combined Wachters/DZP basis set [89,90] demonstrated that both structure II as well as structure III (cf. Fig. 6) are local minima on the potential energy surface. Structure II is energetically preferred by about  $13 \text{ kJ mol}^{-1}$ . However, the inclusion of electron correlation effects should decrease the energy difference between the two structure models or can even reverse the energy sequence.

Summarizing the published results [74,98,100], it can be stated that they are in good agreement with the ideas developed by Schäfer [9] for the structure of  $BeAlCl_5$ . The assumption of two face-bridged tetrahedra for  $BeAlCl_5$  corresponds formally to structure III (Fig. 6).

Finally, good agreement has been achieved between the mean value of the calculated complex dissociation enthalpies of structures II and III of the  $MnAlF_5$  complex ( $\sim 190 \text{ kJ mol}^{-1}$  (1008 K)) and the experimentally determined value of  $197 \text{ kJ mol}^{-1}$ .

HF/STO-3G calculations of Curtiss and Heinricher [101] on  $BeAl_2F_8$  served as model calculations for possible  $MA_2X_8$

complexes ( $X = Cl, Br$ ). In this case, based on HF/STO-3G calculations, the most stable structure is a  $D_{2d}$  chain structure with four-fold coordinated Be in a tetrahedral environment. Again this result is in qualitative agreement with the ideas developed by Schäfer [9]. The structures preferred energetically among seven examined structure models [101] are those which possess the higher fluorine coordination at the Be atoms ( $\geq 4$ ). Also one further structure containing a planar ring and Be in trigonal configuration is relatively stable.

Quantum chemical ab-initio calculations of the  $A'F_2-AlF_3$  complexes ( $A' = Be, Mg, Mn$ ) are presently the only way to obtain structural information on these compounds. The large value of the calculated complex formation energies shows that these vapour-phase complexes are energetically stable compounds.

Contrary to fluorine-bridged complexes between HF and  $AlF_3$  molecules, oxygen-bridged species like  $AlX_3-OH^-$  or  $AlX_3-H_2O$  ( $X = F, Cl$ ) are energetically stable complexes, as has been shown in ab-initio calculations using HF and MP2 approximations. The complex binding energies are 1.6 to 8 times larger than those of the most stable experimentally studied fluorine-bridged complex  $HF-AlF_3$  [102]. Although lacking direct experimental evidence of their existence, the energetics of the oxygen-bridged complexes make their existence probable. Perhaps they play a crucial role during reorganization processes in fluoride solids. The latter was observed for example in ESR spectroscopically in situ by the fluorination of paramagnetic centers during thermally induced dehydration processes [103,104,119]. Results of HF, MP2 and DFT calculations on  $AlF_3-2H_2O$  and  $AlF_3-3H_2O$  underline their energetic stability [105]. The binding energy per water molecule decreases with increasing number of water molecules in the complex. The smallest complex,  $AlF_3-H_2O$  is therefore the most stable. The different ab-initio methods used (HF, MP2, DFT) did not result in qualitative differences in the binding energies, provided that all necessary energy contributions (basis set superposition errors, zero-point vibrational energies) were considered [105].

## 5. Conclusions

Whereas a large number of gaseous heterocomplexes consisting of chlorine and bromine molecules have been experimentally proven, the experimental evidence of corresponding fluorine complexes is mainly restricted to fluorides of the first three main groups of the periodic table. Checking

the available material critically results in the finding that knowledge of their structures and stabilities is still at the beginning. A derivation of structural information from experimental IR, Raman and electron diffraction measurements is difficult, mostly caused by equilibria of coexisting vapour phase species. Therefore, quantum chemical ab-initio calculations play an important role for the determination of equilibrium structures, stabilities, binding energies and harmonic vibrational frequencies of the vapour phase complexes.

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## References

- [1] S. Gerighausen, M. Binnewies, *Z. Anorg. Allg. Chem.* 621 (1995) 936.
- [2] R. Neddermann, M. Binnewies, *Z. Anorg. Allg. Chem.* 622 (1996) 17.
- [3] R. Neddermann, S. Gerighausen, M. Binnewies, *Z. Anorg. Allg. Chem.* 622 (1996) 21.
- [4] T. Dahmen, R. Gruhn, *Z. Anorg. Allg. Chem.* 621 (1995) 417.
- [5] W. Reichelt, H. Oppermann, *Z. Anorg. Allg. Chem.* 620 (1994) 1463.
- [6] S. Fechter, S. Kruger, H. Oppermann, *Z. Anorg. Allg. Chem.* 619 (1993) 424.
- [7] F.T. Lange, H. Barnighausen, *Z. Anorg. Allg. Chem.* 619 (1993) 1747.
- [8] H. Oppermann, D.Q. Huong, *Z. Anorg. Allg. Chem.* 621 (1995) 659.
- [9] H. Schäfer, *Angew. Chem.* 23 (1976) 775.
- [10] R. Janoschek, *Chem. Unserer Zeit.* 29 (1995) 122.
- [11] G.N. Papatheodorou, *Current Top. Mater. Sci.* 10 (1982) 249.
- [12] K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky, J. Thonstad, *Aluminium Electrolysis*, Aluminium-Verlag, Düsseldorf, 1982.
- [13] A.E. Comyns (Ed.), *Fluoride Glasses*, Wiley, New York, 1989.
- [14] J.W. Hastie, in: J. Braunstein, G. Mamantov, G.P. Smith (Eds.), *Advances in Molten Salt Chemistry*, Vol. 1, Plenum Press, New York, 1971.
- [15] G. Mamantov (Ed.), *Advances in Molten Salt Chemistry* 5, Elsevier, Amsterdam, 1983.
- [16] M.H. Brooker, G.N. Papatheodorou, *Vibrational spectroscopy of molten salts and related glasses and vapors*, Ref. [15], p. 26.
- [17] P. Davidovits, D.L. McFadden (Eds.), *Alkali Halide Vapors*, Academic Press, New York, 1979.
- [18] N.M. Klimenko, V.G. Zakshevskii, O.P. Charkin, *Koord. Chim.* 8(7) (1982) 903.
- [19] C.P. Baskin, C.F. Bender, P.A. Kollmann, *J. Am. Chem. Soc.* 95 (1973) 5868.
- [20] M. Rupp, R. Ahlrichs, *Theor. Chim. Acta* 46 (1977) 117.
- [21] F. Ramondo, L. Bencivenni, M. Spoliti, *J. Mol. Strukt. (Theochem.)* 277 (1992) 171.
- [22] M. Spoliti, L. Bencivenni, F. Ramondo, V. Rossi, *J. Mol. Strukt. (Theochem.)* 315 (1994) 19.
- [23] M. Kaupp, H.G.v. Schnering, *Inorg. Chem.* 33 (1994) 2555.
- [24] E.D. Simandiras, C.A. Nicolaidis, *Chem. Phys. Lett.* 223 (1994) 233.
- [25] B. Saha, K. Hilpert, L. Bencivenni, *Adv. Mass Spectrom. B* (1985) 1001.
- [26] D.R. Stull, H. Prophet (Eds.), *JANAF Thermochemical Tables*, NSRDS-NBS, 1971, p. 37.
- [27] L.A. Curtiss, *Int. J. Quant. Chem. XIV* (1978) 709.
- [28] P.A. Akishin, N.G. Rambidi, E.J. Zazorin, *Kristallografiya* 4 (1959) 186.
- [29] M.W. Chase, C.A. Davies Jr., J.R. Downey, D.J. Frurip Jr., R.A. McDonald, A.N. Syverud, *J. Phys. Chem. Ref. Data* 14 (1985) Suppl. No. 1.
- [30] A.D. Alvarenga, M.-L. Saboungi, L.A. Curtiss, M. Grimsditch, *Molec. Phys.* 81(2) (1994) 409.
- [31] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, UK, 1984.
- [32] J.W. Hastie, *High Temperature Vapors*, Academic Press, New York, 1975.
- [33] Proc. of the Symposium on High Temperature Metal Halide Chemistry, in D.L. Hildebrand, D.D. Cubiciti (Eds.), *The Electrochem. Soc. Inc. Proc. 78-1*, Princeton, NJ, 1978.
- [34] I.R. Beattie, D.A. Greenhalgh, *Proc. 10th Mat. Res. Symp. on Characterization of High-Temp. Vapors and Gases*, NBS, Gaithersburg, MD, 1978, p. 597.
- [35] W. Horlbeck, H.H. Emons, *Abh. Sächs. Akad. Wiss. Leipzig, Math. Nat. Kl.* 56 (1985) 42.
- [36] G.N. Papatheodorou, *Proc. 10th Mat. Res. Symp. on Characterization of High-Temp. Vapors and Gases*, NBS, Gaithersburg, MD, 1978, p. 647.
- [37] G.N. Papatheodorou, *Vibrational spectroscopy of high temperature metal halide vapor complexes*, in J.L. Jole, W.C. Stwalley (Eds.), *Metal Bonding and Interactions in High Temperature Systems*, ACS Symposium Series 179, Washington, DC, 1982, p. 309.
- [38] M. Hargittai, I. Hargittai, *Molecular Geometries of Coordination Compounds in the Vapor Phase*, Elsevier, Amsterdam, 1977.
- [39] R.P. Dickey, D. Maurice, R.J. Cave, R. Mawhorter, *J. Chem. Phys.* 98(3) (1993) 2182.
- [40] P.N. Swepston, H.L. Sellers, L. Schäfer, *J. Chem. Phys.* 74 (1981) 2372.
- [41] K.K. Sunil, K.D. Jordan, *J. Phys. Chem.* 91 (1987) 1710.
- [42] C. Ochsenfeld, R. Ahlrichs, *J. Chem. Phys.* 97 (1992) 3487.
- [43] C. Ochsenfeld, R. Ahlrichs, *Ber. Bunsenges.* 98 (1994) 34.
- [44] T. Imanaka, *Bull. Chem. Soc. Jpn.* 40 (1967) 2182.
- [45] H. Rabeneck, H. Schäfer, *Z. Anorg. Allg. Chem.* 395 (1973) 69.
- [46] E.N. Kolosov, V.B. Sholtz, L.N. Sidorov, *Vestn. Moskovsk. Univ.* 1 (1972) 49.
- [47] V.B. Sholtz, L.N. Sidorov, *Vestn. Moskovsk. Univ.* 4 (1972) 371.
- [48] L.N. Sidorov, M.I. Nikitin, E.V. Shokan, I.D. Sorokin, *Adv. Mass Spectr.* 8A (1980) 462.
- [49] M.I. Nikitin, I.D. Sorokin, E.V. Shokan, L.N. Sidorov, *Zh. Fiz. Khim.* 54(5) (1980) 1337.
- [50] E.-U. Würthwein, M. Krogh-Jespersen, P.v.R. Schleyer, *Inorg. Chem.* 20 (1981) 3663.
- [51] L.A. Curtiss, R. Nichols, *Proc. of the 5th Int. Symp. on Molten Salts*, The Electrochem. Soc., Pennington, New Jersey, 1986, p. 289.
- [52] A.I. Boldyrev, L.P. Sukhanov, V.G. Zakshevskii, O.P. Charkin, *Chem. Phys. Lett.* 79 (1981) 421.
- [53] R. Cimraglia, M. Persico, J. Tomasi, O.P. Charkin, *J. Comput. Chem.* 5 (1984) 263.
- [54] V. Kello, M. Urban, A. Boldyrev, *Chem. Phys. Lett.* 106 (1984) 455.
- [55] Y.B. Kirillov, A.I. Boldyrev, N.M. Klimenko, O.P. Charkin, *Chem. Phys. Lett.* 84 (1981) 604.
- [56] V.M. Ozerova, S.P. Konowalov, V.G. Solomonik, *Koord. Khim.* 14 (1988) 1341.

- [57] A.S. Zjubin, G.M. Chaban, O.P. Charkin, H. Kaneti, *Zh. Neorg. Khim.* 31 (1986) 2105.
- [58] V.G. Zakshevskii, O.P. Charkin, *Koord. Khim.* 8 (1982) 759.
- [59] F. Ramondo, L. Bencivenni, V. Di Martino, *Chem. Phys. Lett.* 158 (1991) 41.
- [60] M. Spoliti, N. Sanna, V. Di Martino, *J. Mol. Struct. (Theochem)* 258 (1992) 83.
- [61] V.G. Zakshevskii, A.I. Boldyrev, O.P. Charkin, *Chem. Phys. Lett.* 73 (1980) 54.
- [62] J.S. Francisco, I.H. Williams, *J. Phys. Chem.* 94 (1990) 8522.
- [63] E. Tikhon, E. Robert, B. Gilbert, *Appl. Spectroscopy* 48 (1994) 1477.
- [64] H. Zhou, O. Herstad, T. Østvold, in E.R. Cutshall (Ed.), *Light Metals*, 1992, p. 511.
- [65] B. Gilbert, T. Materne, *Appl. Spectroscopy* 44 (1990) 299.
- [66] S.K. Ratkje, S.J. Cyvin, B. Hafskjold, *Appl. Spectroscopy* 47 (1993) 375.
- [67] B. Gilbert, G. Mamantov, G.M. Begun, *J. Chem. Phys.* 62 (1975) 950.
- [68] S.J. Cyvin, B.N. Cyvin, A. Snelson, *J. Phys. Chem.* 75 (1971) 2609.
- [69] R. Huglen, S.J. Cyvin, H.A. Oye, *Z. Naturforsch.* 349 (1979) 1118.
- [70] E. Vajda, I. Hargittai, J. Tremmel, *Inorg. Chim. Acta* 25 (1977) L143.
- [71] V.P. Spiridonov, E.V. Erokhin, *Russ. J. Inorg. Chem.* 14 (1969) 332.
- [72] G. Scholz, L.A. Curtiss, *J. Mol. Struct. (Theochem.)* 258 (1992) 251.
- [73] L.A. Curtiss, *Chem. Phys. Lett.* 68(1) (1979) 225.
- [74] L.A. Curtiss, *Inorg. Chem.* 21 (1982) 4100.
- [75] C.W. Bock, M. Trachtman, G.J. Mains, *J. Phys. Chem.* 98 (1994) 478.
- [76] L.A. Curtiss, *Proc. Int. Symp. on Molten Salts Chemistry, Technology* 93-9 (1993) 31.
- [77] R.J. Mawhorter, M. Fink, J.G. Hartley, *J. Chem. Phys.* 83 (1985) 4418.
- [78] M. Wilson, M.B. Coolidge, G.J. Mains, *J. Phys. Chem.* 96 (1992) 4851.
- [79] G. Scholz, *J. Molec. Struct. (Theochem.)* 309 (1994) 227.
- [80] D.-H. Menz, L. Kolditz, K. Heide, C. Schmidt, Ch. Kunert, Ch. Mensing, H.G.v. Schnering, W. Hönle, *Z. Anorg. Allg. Chem.* 551 (1987) 231.
- [81] D.-H. Menz, Ch. Mensing, W. Hönle, H.G.v. Schnering, *Z. Anorg. Allg. Chem.* 611 (1992) 107.
- [82] D.-H. Menz, 1995, personal communication.
- [83] J.M. LoBue, J.K. Rice, Th.A. Blake, S.E. Novick, *J. Chem. Phys.* 85 (1986) 4261.
- [84] L.A. Curtiss, G. Scholz, *Chem. Phys. Lett.* 205 (1993) 550.
- [85] P. Hobza, R. Zahradnik, *Intermolecular Complexes*, Academia, Prague, 1988.
- [86] K.R. Roby, *Molec. Phys.* 27 (1974) 81.
- [87] C. Ehrhardt, R. Ahlrichs, *Theor. Chim. Acta* 68 (1985) 231.
- [88] G. Scholz, *Chem. Phys. Lett.* 206 (1993) 555.
- [89] A.J.H. Wachters, *J. Chem. Phys.* 52 (1970) 1033.
- [90] T.H. Dunning, Jr., *J. Chem. Phys.* 53 (1970) 2823.
- [91] G. Scholz, *Habilitation*, Humboldt-Universität zu Berlin, 1996, submitted.
- [92] G. Scholz, C. Nieke, D.-H. Menz, L. Kolditz, *J. Molec. Struct. (Theochem.)* 231 (1991) 95.
- [93] A. Burkhardt, U. Wedig, G. Scholz, D.-H. Menz, *Chem. Phys. Lett.* 182 (1991) 556.
- [94] C. Nieke, G. Scholz, D.-H. Menz, *J. Fluorine Chem.* 59 (1992) 41.
- [95] D. Mootz, D. Boenigk, *J. Am. Chem. Soc.* 108 (1986) 6634.
- [96] D. Mootz, D. Boenigk, *Z. Anorg. Allg. Chem.* 544 (1987) 159.
- [97] W.D. Chandler, K.E. Johnson, J.L.E. Campbell, *Inorg. Chem.* 34 (1995) 4943.
- [98] D.-H. Menz, G. Scholz, D. Becker, M. Binnewies, *Z. Anorg. Allg. Chem.* 620 (1994) 1976.
- [99] G.N. Papatheodorou, M.A. Capote, *J. Chem. Phys.* 69 (1978) 2067.
- [100] L.A. Curtiss, A. Heinricher, *Chem. Phys. Lett.* 86 (1982) 467.
- [101] L.A. Curtiss, A. Heinricher, *Int. J. Quant. Chem. Symp.* 16 (1982) 285.
- [102] G. Scholz, R. Stößer, J. Bartoll, *J. Phys. Chem.* 100 (1996) 6518.
- [103] G. Scholz, R. Stößer, S. Sebastian, E. Kemnitz, J. Bartoll, *J. Phys. Chem. Sol.* (1996), submitted.
- [104] R. Stößer, G. Scholz, M. Päch, *J. Solid State Chem.* 116 (1995) 249.
- [105] M. Krossner, G. Scholz, R. Stößer, *J. Phys. Chem.* 101 (1997) 1555.
- [106] E.N. Kolosov, T.N. Turavaeva, L.N. Sidorov, *Russ. J. Phys. Chem.* 49 (1975) 476.
- [107] L.N. Sidorov, N.A. Zhegulskaya, *Int. J. Mass Spectrom. Ion Phys.* 17 (1975) 111.
- [108] A. Snelson, B.N. Cyvin, S.J. Cyvin, *J. Mol. Struct.* 24 (1975) 165.
- [109] Y. Berkowitz, W.A. Chupka, *Ann. N.Y. Acad. Sci.* 79 (1960) 1073.
- [110] L.N. Sidorov, V.I. Belousov, P.A. Akishin, *Russ. J. Phys. Chem.* 43 (1969) 39; 45 (1971) 14.
- [111] I.D. Sorokin, L.N. Sidorov, M.I. Nikitin, E.V. Shokan, *Int. J. Mass Spectrom. and Ion Physics* 41 (1981) 45.
- [112] I.V. Morozov, Yu.M. Korenev, *Zh. Neorg. Khim.* 38(4) (1993) 659.
- [113] O.V. Boltalina, A.Ja. Borshevskii, L.N. Sidorov, *Zh. Fiz. Khim.* 66(9) (1992) 2289.
- [114] F. Ramondo, L. Bencivenni, V. Rossi, *Chem. Phys. Lett.* 124 (1988) 291.
- [115] V.G. Zakzhevskii, A.I. Boldyrev, O.P. Charkin, *Chem. Phys. Lett.* 70 (1980) 147.
- [116] V.V. Sliznev, V.G. Solomonik, *Koord. Khim.* 14(1) (1988) 13.
- [117] G. Scholz, J. Sauer, D.-H. Menz, *Chem. Phys. Lett.* 156 (1989) 125.
- [118] B. Roos, P. Siegbahn, *Theoret. Chim. Acta* 17 (1970) 209.
- [119] R. Stösser, G. Scholz, *Appl. Magnet. Res.* (1997) in press.