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NDDO studies of large vapour-phase complexes consisting of HF and AlF_3 molecules

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Abstract

NDDO calculations have been performed on several hypothetical model structures of the vapour-phase complexes HAl_2F_7, $H_2Al_2F_8$ and $H_2Al_2F_6$ formed by gas–gas interactions between HF and AlF_3. The number of relevant structure models which are interesting for further *ab initio* geometry optimizations could be remarkably diminished.

Introduction

During the vaporization of AlF_3, aluminium hydroxyfluoride $AlOHF_2 \cdot H_2O$, or, for example, $(H_3O)_3AlF_6 \cdot 3H_2O$, several new vapour-phase complexes of AlF_3 molecules with HF molecules ar formed. Experimental information about the existence of these complexes has been obtained by mass spectrometry coupled with dynamic thermal gas analysis [1, 2]. $HAlF_4$ (AlF_3:HF = 1:1) [1] and H_2AlF_5 (1:2) [2] complexes were identified in temperature regions between 300–400 °C and above 850 °C, respectively.

Whereas the formation of H_2AlF_5 can be discussed in terms of a direct reaction between the gas-phase molecules, the occurrence of the $HAlF_4$ complex may be explained as the result of adsorption/desorption processes at the solid surface of AlF_3. Due to the extremely low stability of these complexes, an experimental structural determination using methods such as electron diffraction, microwave or FT-IR spectroscopy has not been possible to date. For this reason, *ab initio* [3, 4] and semi-empirical NDDO [5] calculations have been performed to determine the most stable structures and relative stabilities of various structure models of $HAlF_4$ and H_2AlF_5.

It was shown recently [5] that the application of a modified version of the NDDO method [6] is justified for a semi-quantitative estimation of the relative stabilities and for rough structure determinations of such complexes. A large number of interaction possibilities between fragments and molecules exist which might be responsible for the formation of the new vapour-phase complexes. As in the case of other studies [3, 4], only possible gas–gas

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interactions between HF and AlF_3 molecules have been considered in the present work.

Because of the fragments $HAlF_3^+$ and $HAlF_4^+$ simultaneously observed in the mass spectra and their different ion currents at various temperatures, the existence of further complexes containing $HAlF_3$ and $HAlF_4$ as subunits has also to be considered. Experimental results give insufficient information to decide whether the formation of complexes such as $(HAlF_4)_2$, HAl_2F_7 or $H_2Al_2F_6$ is possible or not. Hence, the purpose of the present work is to study the relative stabilities of various structural models of $(HAlF_4)_2$, $H_2Al_2F_6$ and HAl_2F_7 using the modified NDDO version [6].

Method

The calculation of structures and stabilities of such large complexes using *ab initio* methods at a qualified basis set level still poses a severe problem. Hence, only a modified NDDO method [6] was used for the first estimation of the relative stabilities of the various structural models. The number of probable complexes should be reduced with the help of such NDDO calculations. Through the use of the NDDO method, it is possible to calculate even larger complexes than those which are discussed in this paper.

Results

Three complexes, i.e., HAl_2F_7, $H_2Al_2F_8$ and $H_2Al_2F_6$, have been considered. The structural models of these complexes were selected from both a consideration of direct gas–gas interactions and the formation of $HAlF_3^+$ and $HAlF_4^+$ fragments in the mass spectrometer.

The formation of HAl_2F_7 (2:1) and $H_2Al_2F_8$ (2:2) can be discussed in terms of a direct reaction between AlF_3 and HF.

$$2AlF_3 + HF \rightleftharpoons HAl_2F_7 \qquad (1)$$

$$2AlF_3 + 2HF \rightleftharpoons H_2Al_2F_8 \qquad (2)$$

Various interactions between HF, AlF_3 and reactive species which are formed in the ion source of the spectrometer can be considered for the formation of the $H_2Al_2F_6$ molecule which is also observed

$$AlF_3 + 2HF + AlF \rightleftharpoons H_2Al_2F_6 \qquad (3)$$

HAl_2F_7 (2:1)

For this complex, the three structure depicted in Fig. 1 were taken into account. The geometries were optimized within the given symmetry limitations. The bond distances and special angles calculated via the NDDO method are included in Fig. 1.

Structure I is a cyclic compound consisting of two AlF_3 and one HF molecule, whereas the dominating subunit of structures II and III is Al_2F_6.

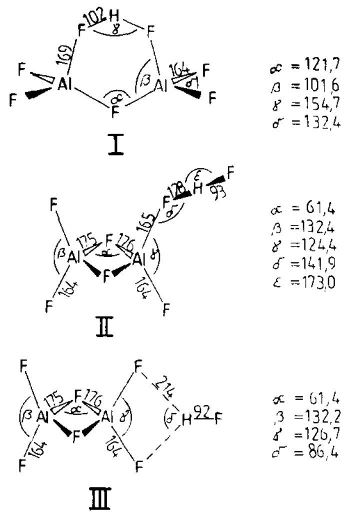

Fig. 1. Optimized geometries of the HAl_2F_7 vapour-phase complex (structure I–III).

TABLE 1

Relative energies for the optimized geometries of HAl_2F_7, $H_2Al_2F_8$ and $H_2Al_2F_6$ molecules

Molecule	Structure	Symmetry	E (kJ mol^{-1})
HAl_2F_7	I	C_{2v}	271.5
	II	C_1	68.0
	III	C_{2v}	0
$H_2Al_2F_8$	I	D_{3h}	1223.7
	II	D_{2h}	438.1
	III	D_{2d}	446.9
	IV	C_1	212.2
	V	D_{2h}	0
	VI	C_i	34.3
$H_2Al_2F_6$	I	D_{2h}	1217.4
	II	D_{2h}	0
	III	C_1	343.3
	IV	C_i	1246.5

Only for structure I do the resulting values of bond distances indicate stable bonds in a chemical sense. Nevertheless, Table 1 shows that structure III is the most stable of models I–III, whereas structure I is energetically disfavoured.

$H_2Al_2F_8$ (2:2)

Figure 2 depicts the six structures considered in this work. In the structures I–III, two tetrahedral AlF_4 subunits are combined in different ways via hydrogen bridges.

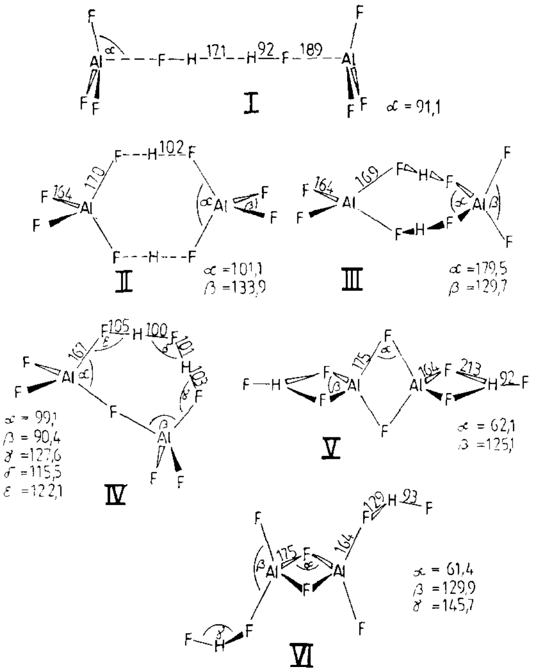

Fig. 2. Optimized geometries of the $H_2Al_2F_8$ vapour-phase complex (structures I–VI).

TABLE 2

Optimized and experimental geometries of Al_2F_6, AlF_3 and HF (bond lengths in pm, angles in degrees)

Molecule	Method	$R(\mathrm{AlF_{br}})$	$R(\mathrm{AlF})$	∢$\mathrm{AlF_{br}Al}$	∢FAlF	$R(\mathrm{HF})$
Al_2F_6	NDDO	176	164	66	123	–
	Expt. [7]	180	163	90	120	–
	Expt. [8]	180	163	82	116	–
AlF	NDDO	–	163.4	–	120	–
	Expt. [10]	–	163	–	120	–
HF	NDDO	–	–	–	–	91.8
	Expt. [9]	–	–	–	–	91.7

The optimized bond distances in the linear structure I (D_{2h}) show that the complex consists of slightly distorted HF and AlF_3 subunits (Table 2). The structures II (D_{2h}) and III (D_{2d}) differ in the relative positions of the two AlF_4 tetrahedra. In structure II they share a common edge, and in structure III the tetrahedra edges are rectangular crossed. Structure IV is again a ring structure having C_1 symmetry. The most stable structures amongst models I–VI are structures V (D_{2h}) and VI (C_i) which again have the Al_2F_6 fragment as dominating subunit. A comparison of the geometry optimization

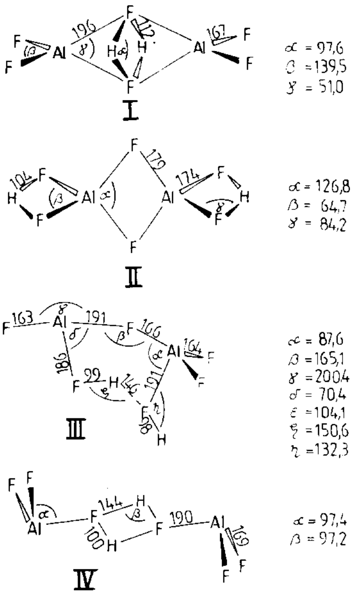

Fig. 3. Optimized geometries of the $H_2Al_2F_6$ vapour-phase complex (structure I–IV).

of V and VI with that of the free molecule Al_2F_6 (Table 2) shows that there is only a slight influence on the Al_2F_6 framework geometry.

$H_2Al_2F_6$ (1:2+AlF)

Figure 3 shows the four structures considered in the present calculations. The main feature of the D_{2h} models I and II is the Al_2F_6 subunit. However, whilst the two central F atoms are additionally bridged by two H atoms in structure I, the hydrogen is bonded to terminal fluorine atoms in structure II. Structure III (C_1) is a ring structure and the main feature of model IV (C_i) is a $(HF)_2$ ring. A comparison of the values summarized in Table 1 shows that models I and IV are very unfavourable while model II, having D_{2h} symmetry, is the most stable of all four. In model II the geometry of the Al_2F_6 subunit is almost the same as that of the free Al_2F_6 molecule.

Discussion and conclusions

Using the quantum chemical NDDO method, 13 structural models of the complexes HAl_2F_7, $H_2Al_2F_8$ and $H_2Al_2F_6$ have been calculated. It turns out that the common feature of the most stable structural models (III of HAl_2F_7, V of $H_2Al_2F_8$, II of $H_2Al_2F_6$) is the existence of the Al_2F_6 subunit in each case. Thus the number of relevant models which should be considered for further *ab initio* geometry optimizations can be reduced to eight (cf. Table 1). All these structures contain the Al_2F_6 subunit or are cyclic.

The following structural models should be examined using further *ab initio* calculations: structure I–III of HAl_2F_7, structures IV–VI of $H_2Al_2F_8$, and structures II and III of $H_2Al_2F_6$. The calculated geometric parameters should be suitable starting values for *ab initio* geometry optimizations. As for H_2AlF_5 [4], the formation of the assumed complexes HAl_2F_7, $H_2Al_2F_8$ and $H_2Al_2F_6$ should be discussed as a consequence of the intermolecular interactions between HF and AlF_3/Al_2F_6 molecules as well as AlF.

It is interesting to note that despite missing chemical bonds between the Al_2F_6 and HF units (cf. Fig. 1, structure III; Fig. 2, structure V) these structures are the most stable. In agreement with experiment, the stabilities of such complexes are mainly caused by many-body effects.

The cyclic structures should be examined carefully bearing in mind that even these vapour-phase complexes could be possible sources for the formation of the fragments $HAlF_3^+$ and $HAlF_4^+$.

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