

## NEW ALKALI METAL AND TETRAMETHYLAMMONIUM TETRAFLUOROARSENATES(III), THEIR VIBRATIONAL SPECTRA AND CRYSTAL STRUCTURE OF CESIUM TETRAFLUOROARSENATE(III)

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The title compounds were synthesised by the reaction of alkali metal and tetramethylammonium fluorides with liquid AsF<sub>3</sub>. Crystal structure of CsAsF<sub>4</sub> was determined. Raman and infrared spectra of the title compounds were analysed.

**Keywords:** Fluoroarsenates(III); Arsenates; Arsene fluoride; Crystal structure; Infrared spectroscopy; Raman spectroscopy; X-ray diffraction.

Out of the complex fluorides of the group-15 elements, fluoroantimonates(III) appear to be the most studied<sup>1</sup>. Fluoroarsenates(III) are rare<sup>2-6</sup>, known mostly as tetrafluoroarsenates(III) and heptafluorodiarsenates(III)<sup>2,3,6</sup>, very recently also as tridecafluorotetraarsenates(III)<sup>7</sup>. They lack the characterisation by vibrational spectroscopy. The first and the only published fluorophosphate(III)<sup>8</sup> was (CH<sub>3</sub>)<sub>4</sub>NPF<sub>4</sub> in 1994. In the present work the syntheses of two new fluoroarsenates(III), NaAsF<sub>4</sub> and (CH<sub>3</sub>)<sub>4</sub>NAsF<sub>4</sub>, are reported, the vibrational spectra of simple fluoroarsenates(III) of the general formula MAsF<sub>4</sub> (M = Na, Rb, Cs, (CH<sub>3</sub>)<sub>4</sub>N) are analysed and the crystal structure of CsAsF<sub>4</sub> is presented.

### EXPERIMENTAL

#### Materials

CsF (Aldrich; 99%) was melted, rapidly transferred into a drybox filled with dry argon and ground after cooling<sup>9</sup>. RbF was prepared by the reaction of Rb<sub>2</sub>CO<sub>3</sub> and 40% aqueous HF; after addition of NH<sub>4</sub>F, it was heated in a nitrogen flow at 570 K (ref.<sup>10</sup>). (CH<sub>3</sub>)<sub>4</sub>NF (Aldrich; 97%) was used as received. AsF<sub>3</sub> was prepared by the reaction of anhydrous HF and As<sub>2</sub>O<sub>3</sub> at

470 K in a 300-cm<sup>3</sup> stainless steel reactor and subsequently purified by bubbling through concentrated H<sub>2</sub>SO<sub>4</sub>. CsAsF<sub>4</sub> and RbAsF<sub>4</sub> were prepared from CsF and RbF in liquid AsF<sub>3</sub> at 353 K in a tube reactor made of the copolymer of tetrafluoroethylene with perfluoroalkyl vinyl ether (PFA)<sup>2,3</sup>.

### Syntheses

(CH<sub>3</sub>)<sub>4</sub>NaAsF<sub>4</sub> and NaAsF<sub>4</sub> were synthesised by the original procedure for the preparation of alkali metal fluoroarsenates(III), by dissolving (CH<sub>3</sub>)<sub>4</sub>NF and NaF, respectively, in liquid AsF<sub>3</sub> at 353 K in a PFA tube reactor<sup>2,3</sup>. The reaction mixtures were cooled to room temperature and excess AsF<sub>3</sub> was removed on a vacuum line while the reaction mixture was held at 295 K in the case of (CH<sub>3</sub>)<sub>4</sub>NaAsF<sub>4</sub> and at 273 K in the case of NaAsF<sub>4</sub>. Both (CH<sub>3</sub>)<sub>4</sub>NaAsF<sub>4</sub> and NaAsF<sub>4</sub> are white powders, sensitive to atmospheric moisture. (CH<sub>3</sub>)<sub>4</sub>NaAsF<sub>4</sub> is stable at room temperature. NaAsF<sub>4</sub> is stable at 258 K, while at room temperature it readily decomposes to give NaF and AsF<sub>3</sub>.

Due to the thermal decomposition of NaAsF<sub>4</sub> at room temperature, we could not perform a reliable chemical analysis of this compound or obtain its infrared spectrum. Therefore, evidence of the existence of NaAsF<sub>4</sub>, in addition to its Raman spectrum, was provided by following the weight loss of the reaction mixture (AsF<sub>3</sub> and NaAsF<sub>4</sub>) while removing the volatiles on a vacuum line at 258 K (Fig. 1). The weight loss vs time curve clearly shows a change in the slope at a 1:1 NaF:AsF<sub>3</sub> ratio. Raman spectra of the solid product of the reaction of NaF and AsF<sub>3</sub> were recorded in regular intervals while removing the volatiles from the tube reactor at 295 K, in the 1:5 to 5:1 range of molar ratios NaF:AsF<sub>3</sub>. No change in the Raman spectra was observed, except the diminishing intensity. This indicates that the Raman bands are attributable to a single compound, namely NaAsF<sub>4</sub>. The starting compound, NaF, under the same experimental conditions, did not provide sufficient signal to record a Raman spectrum.

In another experiment, NaAsF<sub>4</sub> was allowed to decompose at room temperature and the volatiles were removed. The white powder remaining in the reactor was identified by X-ray powder diffraction as NaF.

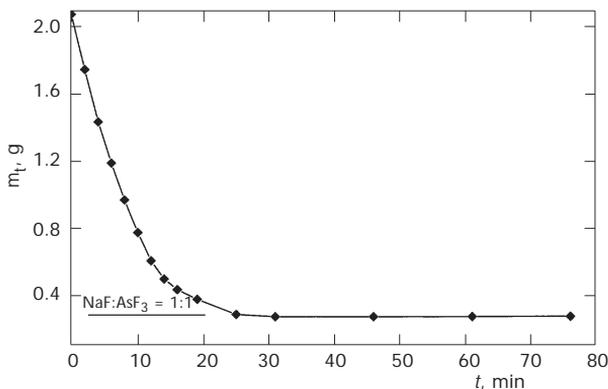


FIG. 1

The dependence of the total weight of the sample,  $m_t$ , on the time of pumping off volatiles in the course of the NaAsF<sub>4</sub> preparation at 258 K

## Chemical Analyses

The content of the free fluoride ions ( $F_f$ ) was determined, after reaction with water, using an ion-selective electrode<sup>11,12</sup>. The total amount of fluoride ions ( $F_t$ ) was determined by the same method, after decomposition of the sample.

The arsenic content was determined by the ICP-AES method<sup>13</sup>. For  $(CH_3)_4NASF_4$  (225.1) calculated: 33.29% As, 33.77% F; found: 35.2% As, 33.8%  $F_t$ , 33.6%  $F_f$ .

## Methods

X-Ray diffraction patterns of the powdered solid samples were obtained using a Debye-Scherrer camera with  $CuK\alpha$  radiation. Single-crystal X-ray diffraction data were collected on a Rigaku AFC7S diffractometer with graphite monochromatised  $MoK\alpha$  radiation at 293(1) K, using the  $\omega$ - $2\theta$  scan technique with a maximum  $2\theta$  value of  $65.0^\circ$ . The weak reflections ( $I < 10.0\sigma(I)$ ) were rescanned with a maximum of 6 scans and the counts were accumulated to ensure good counting statistics. Further details are given in Tables I and II.

TABLE I  
Data for the crystal structure determination of  $CsAsF_4$

Formula	$CsAsF_4$
Formula weight	283.83
Crystal system	monoclinic
Crystal size, mm	$0.15 \times 0.15 \times 0.1$
Space group	$P2_1$ (No. 4)
$a$ , pm	659.7(1)
$b$ , pm	487.2(1)
$c$ , pm	849.22(8)
$\beta$ , $^\circ$	111.92
$V$ , $nm^3$	0.25321(8)
$Z$	2
$T$ , K	293(2)
$\mu(MoK\alpha)$ , $mm^{-1}$	13.748
$D_c$ , $g\ cm^{-3}$	3.723
$F(000)$	248
$\Theta_{max}$ , $^\circ$	32.50
No. of diffractions measured	2149
No. of diffractions unique, $R_{int}$	1829
No. of diffractions observed [ $I > 2\sigma(I)$ ]	1148
$R1$ (all); $R1$	0.0742; 0.0286
$WR$ (all); $wR$	0.0813; 0.0684
$\rho$ , $e\ nm^{-3}$	660 and -694
Programs used	SHELXL97 <sup>14</sup> , SIR92 <sup>15</sup>

The structure of CsAsF<sub>4</sub> was solved using direct methods<sup>15</sup>. An empirical  $\psi$ -absorption correction based on azimuthal scans of several reflections was used, which resulted in transmission factors ranging from 0.225 to 0.249. During the full-matrix least-squares refinement<sup>14</sup> on  $F^2$ , racemic twinning was observed, resulting in the Flack parameter of 0.44(8). CCDC 413041 contains the supplementary crystallographic data for CsAsF<sub>4</sub>. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

### Vibrational Spectroscopy

A Renishaw Raman microscope 1000 with a He-Ne (632.8 nm) laser excitation source was employed to record Raman spectra of solid samples. Infrared spectra were recorded as Nujol or Fluorolube mulls on a Perkin Elmer FTIR 1710 infrared spectrometer.

### Theoretical Characterisation of AsF<sub>4</sub><sup>-</sup> Anion

The electronic molecular orbital calculations were carried out using Gaussian 98 program<sup>16</sup>. The equilibrium structure of AsF<sub>4</sub><sup>-</sup> was fully optimised by the second-order Møller-Plesset (MP2) method<sup>17</sup>, and the Becke three-parameter nonlocal exchange functional<sup>18</sup> with the nonlocal correlation of Lee, Yang and Parr (B3LYP)<sup>19,20</sup>. The large 6-311+G(3df) basis set, as implemented in the program, was employed in the calculations. The harmonic frequencies were computed from numerical and analytical derivatives at the MP2 and B3LYP levels, respectively, using geometries calculated at the same levels of theory.

## RESULTS AND DISCUSSION

(CH<sub>3</sub>)<sub>4</sub>NF and NaF were reacted with liquid AsF<sub>3</sub> at 358 K. From the reaction mixtures, (CH<sub>3</sub>)<sub>4</sub>NAsF<sub>4</sub> and NaAsF<sub>4</sub> were isolated at 295 and 273 K, respectively. The synthesis of LiAsF<sub>4</sub> was attempted at 358 K (using LiF and a large excess of AsF<sub>3</sub>) but no hint of its existence was detected even upon cooling the reaction mixture to 253 K.

TABLE II  
Fractional atomic coordinates and displacement parameters for CsAsF<sub>4</sub>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup> , pm <sup>2</sup>
Cs1	0.09711(6)	-0.2066	0.78213(5)	0.03621(13)
As1	0.54168(10)	0.2912(6)	0.68915(7)	0.03432(15)
F1	0.2339(7)	0.283(3)	0.5867(6)	0.0648(18)
F2	0.4940(8)	0.3642(14)	0.8738(6)	0.057(2)
F3	0.5457(11)	-0.0440(11)	0.7040(9)	0.0635(17)
F4	0.8398(7)	0.315(3)	0.8337(6)	0.0454(16)

<sup>a</sup> One third of the trace of orthogonalised  $U_{ij}$  tensor.

### Crystal Structure of CsAsF<sub>4</sub>

CsAsF<sub>4</sub> crystallises in the *P2*<sub>1</sub> (No. 4) space group, with *a* = 659.7(1), *b* = 487.2(1) and *c* = 849.22(8) pm, β = 111.92°, *V* = 0.25321(8) nm<sup>3</sup>, and containing two formula units in the cell. The structure of CsAsF<sub>4</sub> is composed of Cs<sup>+</sup> cations and AsF<sub>4</sub><sup>-</sup> anions. As1 in CsAsF<sub>4</sub> is linked to four fluorine atoms (Fig. 2, Table III). AsF<sub>4</sub><sup>-</sup> anion adopts a bisphenoidal shape, found in SF<sub>4</sub> (ref.<sup>21</sup>) and SeF<sub>4</sub> (ref.<sup>22</sup>), with two long axial and two short equatorial bonds. The angle F1–As1–F4 in CsAsF<sub>4</sub> is 168.1(3)° (Table III) close to the corres-

TABLE III

Selected bond lengths (in pm) and angles (in °) in CsAsF<sub>4</sub>, N<sub>2</sub>H<sub>6</sub>AsF<sub>4</sub>F (ref.<sup>8</sup>) and 1,1,3,3,5,5-hexamethylpiperidinium fluoroarsenate(III) (pip<sup>+</sup>AsF<sub>4</sub><sup>-</sup>)<sup>4</sup>, and comparison with data calculated for the AsF<sub>4</sub><sup>-</sup> anion

Atoms	CsAsF <sub>4</sub>	N <sub>2</sub> H <sub>6</sub> AsF <sub>4</sub> F	pip <sup>+</sup> AsF <sub>4</sub> <sup>-</sup>	Method	
				MP2/ 6-311+G(3df)	B3LYP/ 6-311+G(3df)
As1–F1	188.7(4)	173.9(3)	187.8(2)	188.1	190.8
As1–F2	174.7(5)	173.2(3)	172.4(2)	175.8	177.3
As1–F3	163.8(7)	174.4(3)	172.7(2)	175.8	177.3
As1–F4	189.3(4)	259.2(4)	186.2(3)	188.1	190.8
F1–As1–F4	168.1(3)	164.1(1)	165.7(1)	168.3	170.8
F1–As1–F3	89.9(6)	90.9(1)	85.2(1)	86.2	87.0
F1–As1–F2	84.0(3)	91.1(1)	84.4(1)	86.2	87.0
F2–As1–F3	97.9(3)	93.5(1)	97.5(1)	98.3	98.1

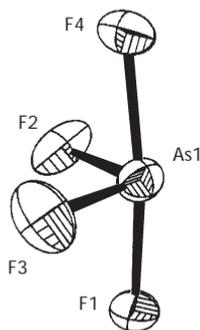


FIG. 2

ORTEP drawing<sup>36</sup> of AsF<sub>4</sub><sup>-</sup> anion in CsAsF<sub>4</sub> (Table III), with thermal ellipsoids representing 50% probability

ponding angle in  $\text{KAs}_2\text{F}_7$  ( $167.3(5)^\circ$ )<sup>6</sup> and in 1,1,3,3,5,5-hexamethylpiperidinium fluoroarsenate(III) ( $165.7(1)^\circ$ )<sup>4</sup>. The corresponding angle in  $\text{AsF}_4$  units of  $\text{CsAs}_4\text{F}_{13}$  is  $164.3(1)^\circ$  (ref.<sup>7</sup>).

Further close contacts of As1 to fluorine atoms in  $\text{CsAsF}_4$  are those to  $\text{F3}^g$  (324.1(7) pm) and  $\text{F3}^h$  (326.8(8) pm), almost at the van der Waals distance (335 pm)<sup>23</sup>. Cesium atom adopts decacoordination (Fig. 3). The distances between Cs1 and fluorine atoms range from 301.0(12) pm (Cs1–F4) to 353.6(8) pm (Cs1–F3<sup>b</sup>). The environment of Cs1 is better described in terms of distorted octahedra of six  $\text{AsF}_4$  units. Four  $\text{AsF}_4$  units are linked to Cs1 with two fluorine atoms, and two  $\text{AsF}_4$  units are linked to Cs1 with one fluorine atom (Fig. 3).

### Vibrational Spectra of Fluoroarsenates(III), $\text{MASF}_4$ ( $M = \text{Na}, \text{Rb}, \text{Cs}, (\text{CH}_3)_4\text{N}$ )

Vibrational spectra of  $\text{MASF}_4$  ( $M = \text{Na}, \text{Rb}, \text{Cs}, (\text{CH}_3)_4\text{N}$ ) in the 200–800  $\text{cm}^{-1}$  region (Raman) and in the 250–800  $\text{cm}^{-1}$  region (IR) are shown in Figs 4, 5 and Tables IV, V. Bands in the vibrational spectra of  $(\text{CH}_3)_4\text{NAsF}_4$  were assigned to vibrations of the  $(\text{CH}_3)_4\text{N}^+$  cation and the  $\text{AsF}_4^-$  anion, and those in the vibrational spectra of  $\text{NaAsF}_4$ ,  $\text{RbAsF}_4$  and  $\text{CsAsF}_4$  only to vibrations of the  $\text{AsF}_4^-$  anion.

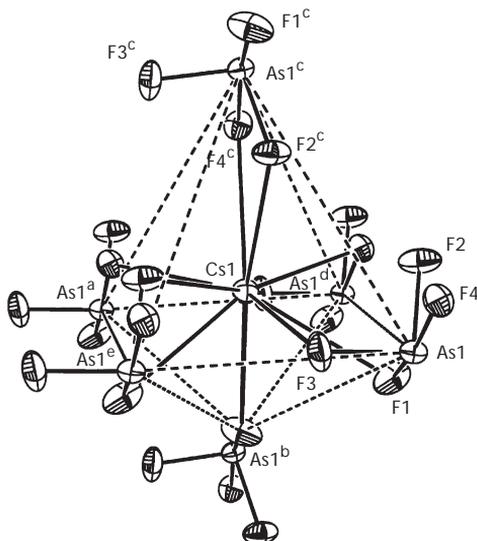


FIG. 3  
ORTEP drawing<sup>36</sup> of the  $\text{Cs}^+$  cation environment in  $\text{CsAsF}_4$ , with thermal ellipsoids representing 50% probability

The vibrational spectrum of  $(\text{CH}_3)_4\text{NAsF}_4$  in the 200–4000  $\text{cm}^{-1}$  region was compared with those of  $(\text{CH}_3)_4\text{NF}$  (ref.<sup>24</sup>)  $(\text{CH}_3)_4\text{NCl}$ ,  $(\text{CH}_3)_4\text{NBr}$ ,  $(\text{CH}_3)_4\text{NI}$  (refs.<sup>25,26</sup>) and  $(\text{CH}_3)_4\text{NPF}_4$  (ref.<sup>8</sup>). The following bands were assigned to vibrations of the  $(\text{CH}_3)_4\text{N}^+$  cation. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3126 w, 3042 s, 2973 w, 2589 w, 2523 w, 2484 w, 2365 w, 1787 w, 1711 w, 1495 vs, 1415 m, 1209 w, 1176 w, 1030 w, 953 vs, 922 sh, 447 sh. Raman ( $\nu$ ,  $\text{cm}^{-1}$ ): 3364 (0.1), 3039 (10), 2987 sh, 2964 (8.0), 2923 (2.8), 2890 sh, 2812 (1.7), 2239 (0.1), 1653 (0.1), 1641 sh, 1537 (0.1), 1470 (3.9), 1410 (0.5), 1372 (0.1), 1288 (0.3), 1176 (0.5), 947 (5.4), 914 sh, 831 (0.2), 751 (6.9), 447 sh.

In  $\text{MAsF}_4$  ( $\text{M} = \text{Rb}$ ,  $\text{Cs}$ ,  $(\text{CH}_3)_4\text{N}$ ), the cations are large and do not allow significant distortion of the  $\text{AsF}_4^-$  anion, while in  $\text{NaAsF}_4$  and  $\text{N}_2\text{H}_6\text{AsF}_4\text{F}$  (ref.<sup>8</sup>) the cations interact strongly with the fluorine atoms of the  $\text{AsF}_4^-$  anion, which results in its deformation. The assignment of bands attributed to vi-

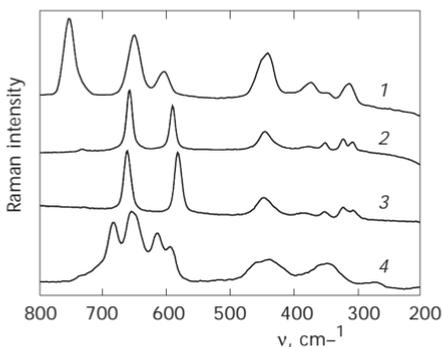


FIG. 4

Raman spectra of  $\text{MAsF}_4$  ( $\text{M} = (\text{CH}_3)_4\text{N}$  (1),  $\text{Cs}$  (2),  $\text{Rb}$  (3),  $\text{Na}$  (4))

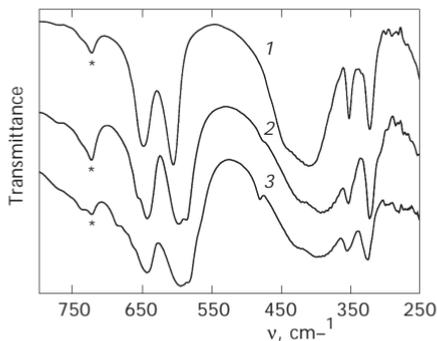


FIG. 5

Infrared spectra (Nujol) of  $\text{MAsF}_4$  ( $\text{M} = (\text{CH}_3)_4\text{N}$  (1),  $\text{Cs}$  (2),  $\text{Rb}$  (3)). Bands marked with asterisks are due to Nujol

brations of the  $\text{AsF}_4^-$  anion ( $C_{2v}$ ) in the vibrational spectra of  $(\text{CH}_3)_4\text{NAsF}_4$ ,  $\text{CsAsF}_4$  and  $\text{RbAsF}_4$  was made by comparison with the vibrational spectra of isoelectronic  $\text{SeF}_4$  (ref.<sup>22</sup>) and fluoroantimonates(III)<sup>27-29</sup>, taking into account the mass differences. The vibrational representation for the  $\text{AsF}_4^-$  unit ( $C_{2v}$ ) contains the species  $4a_1 + a_2 + 2b_1 + 2b_2$ . Nine of them generate

TABLE IV

Infrared and Raman spectra ( $\nu$ ,  $\text{cm}^{-1}$ ) of fluoroarsenates(III),  $\text{MAsF}_4$  ( $M = (\text{CH}_3)_4\text{N}$ , Cs, Rb)<sup>a</sup>, in the range 250–800  $\text{cm}^{-1}$ , and their assignment

$(\text{CH}_3)_4\text{NAsF}_4$		$\text{CsAsF}_4$		$\text{RbAsF}_4$		Assignment
Raman <sup>b</sup>	IR	Raman <sup>b</sup>	IR	Raman <sup>b</sup>	IR	
650(7.8)	648 vs	659(10)	654 sh 642 vs	662(10)	685 w 643 vs	$(A_1)v_1$
603(3.0)	606 vs	592(7.4)	596 vs 585 s	582(10)	594 vs 583 sh	$(B_2)v_8$
447 sh 441(5.5)	444 sh	447(3.2)	422 sh	447(2.7)	480 m	$(A_1)v_2$
	411 vs	397(0.2)	394 vs	385(0.5)	424 m	$(B_1)v_6$
373(1.7)	378 w	377(0.7)	454 m	353(0.8)	400 vs	$(B_1)v_7$
347(0.7)	352 s	354(1.3)			356 s	
317 sh	322 s	325(1.9)	322 s	323(1.7)	326 vs	$(A_1)v_3$
313(8.3)	299 w 291 w 280 w 271 w	311(1.4)	305 sh 296 sh 285 w	309(1.4)	302 w 282 w 275	$(A_2)v_5$

<sup>a</sup> s, strong; m, medium; w, weak; v, very; sh, shoulder. <sup>b</sup> Raman intensities are given in parentheses.

TABLE V

Raman spectrum<sup>a</sup> of  $\text{NaAsF}_4$  in the range 200–800  $\text{cm}^{-1}$ , and its assignment

$\nu^b$ , $\text{cm}^{-1}$	Assignment
683(8.4); 653(10); 648 sh; 614(6.9); 593(5.1)	$\text{AsF}_{\text{eq}}^s$
459 sh; 438(2.9)	$(\text{AsF}_{\text{ax}})_s$
358 sh; 349(2.9); 273(0.8)	$(\text{AsF})_d$

<sup>a</sup> sh, shoulder. <sup>b</sup> Raman intensities are given in parentheses.

Raman-active fundamentals ( $4a_1 + a_2 + 2b_1 + 2b_2$ ); eight of them are allowed in the infrared spectrum ( $4a_1 + 2b_1 + 2b_2$ )<sup>22</sup>.

The symmetry of the distorted  $\text{AsF}_4^-$  anion in  $\text{N}_2\text{H}_6\text{AsF}_4\text{F}$  (ref.<sup>8</sup>) is  $C_s$ . Due to the presence of the small  $\text{Na}^+$  cation of high polarising power, the  $\text{AsF}_4^-$  anion in  $\text{NaAsF}_4$  is expected to be distorted in the same manner. However, based on the experimental data (Table V) for the  $\text{AsF}_4^-$  anion in  $\text{NaAsF}_4$ , it was not possible to distinguish between  $C_s$  and  $C_i$  symmetries.

### *Theoretical Characterisation of the $\text{AsF}_4^-$ Anion Geometry*

The optimised  $C_{2v}$  geometric parameters of the  $^1A_1$  ground state of  $\text{AsF}_4^-$  are given in Table III. The differences in the As–F bond lengths and F–As–F bond angles between the two theoretical methods are less than 2 pm and  $1^\circ$ , respectively. We believe that the geometry predictions are of good quality. Note that both methods, using the same basis set, were tested on the  $\text{AsF}_3$  molecule, which is well characterised. The calculated structural parameters as well as vibrational frequencies were found to satisfactorily reproduce the experimental data.

### *Harmonic Vibrational Frequencies*

The equilibrium structure of the  $\text{AsF}_4^-$  anion has been confirmed to be represented by minima, by evaluation of its vibrational frequencies. These data are provided in Table VI, together with the IR intensities. A comparison of the MP2 and B3LYP frequencies and intensities shows that there is a reasonably good agreement between the two approaches.

The B3LYP calculations predict the As– $F_{2,\text{eq}}$  symmetric and asymmetric stretching frequencies of 627 and 590  $\text{cm}^{-1}$ , respectively, with relatively high IR intensities. These two vibrations reasonably match the bands around 642 and 585  $\text{cm}^{-1}$  observed in the IR spectra of  $\text{CsAsF}_4$  and  $\text{RbAsF}_4$ . The As– $F_{2,\text{ax}}$  asymmetric stretching vibration at 431  $\text{cm}^{-1}$  resulted from the calculations as the most intense in IR. It may correspond to the very strong infrared bands observed at 394  $\text{cm}^{-1}$  for  $\text{CsAsF}_4$  and 424  $\text{cm}^{-1}$  for  $\text{RbAsF}_4$ . Among the other calculated frequencies, that of 296  $\text{cm}^{-1}$  has a noticeable IR intensity, which likely corresponds to the weak band detected around 280  $\text{cm}^{-1}$ . The relatively good agreement between the calculated frequencies and the observed values supports the conclusions that the geometry of free  $\text{AsF}_4^-$  is preserved in the studied solid  $\text{MAsF}_4$  ( $M = \text{Rb}, \text{Cs}, (\text{CH}_3)_4\text{N}$ ) compounds.

### Coordination of Arsenic Atom in CsAsF<sub>4</sub>

Arsenic atom As1 in CsAsF<sub>4</sub> is coordinated by four fluorine atoms, two axial and two equatorial. The axial bonds in AsF<sub>4</sub><sup>-</sup> are weaker than the equatorial ones. The increase in the ratio of As–F axial-to-equatorial bonding distances,  $r_{\text{ax}}/r_{\text{eq}}$ , from 1.02 to 1.11 was found for the isoelectronic series<sup>8,29</sup> IF<sub>4</sub><sup>+</sup>, TeF<sub>4</sub>, SbF<sub>4</sub><sup>-</sup>. Similar values were obtained for the isoelectronic series BrF<sub>4</sub><sup>+</sup>, SeF<sub>4</sub>, AsF<sub>4</sub><sup>-</sup>, where the ratio increases from 1.048 to 1.088 going from BrF<sub>4</sub><sup>+</sup> to AsF<sub>4</sub><sup>-</sup> (refs<sup>8,29,30</sup>).

For the coordination in alkaline fluoroantimonates(III), Ducourant and Fourcade<sup>28</sup> observed three different types (E = electron lone pair): AX<sub>6</sub>E (monocapped octahedron), AX<sub>5</sub>E (octahedron) and AX<sub>4</sub>E (trigonal bipyramid), with individual intermediate cases. The AsF<sub>4</sub><sup>-</sup> anion in CsAsF<sub>4</sub> belongs to trigonal bipyramid. In terms of the VSEPR theory<sup>31–35</sup> the trigonal bipyramid in AsF<sub>4</sub><sup>-</sup> is defined by the four fluorine atoms and the lone pair. There are two additional fluorine atoms F3<sup>g</sup> and F3<sup>h</sup> at the distances close to the van der Waals distance, defining a distorted octahedron.

TABLE VI

Calculated harmonic vibrational frequencies (in cm<sup>-1</sup>) and IR intensities (in km mol<sup>-1</sup>) for the AsF<sub>4</sub><sup>-</sup> anion

Assignment	MP2/6-311+G(3df)		B3LYP/6-311+G(3df)		Dominant normal mode <sup>a</sup>
	frequency	IR intensity	frequency	IR intensity	
(A <sub>1</sub> )ν <sub>1</sub>	662	111	627	107	As–F <sub>2,eq</sub> symm. stretching
(A <sub>1</sub> )ν <sub>2</sub>	463	434	431	420	As–F <sub>2,ax</sub> asymm. stretching
(A <sub>1</sub> )ν <sub>3</sub>	325	26	296	20	As–F <sub>4</sub> umbrella
(A <sub>1</sub> )ν <sub>4</sub>	159	2	145	2	F <sub>eq</sub> –As–F <sub>ax</sub> bending
(A <sub>2</sub> )ν <sub>5</sub>	307	0	282	0	F <sub>eq</sub> –As–F <sub>eq</sub> bending
(B <sub>1</sub> )ν <sub>6</sub>	448	0.1	424	0.1	As–F <sub>2,ax</sub> symm. stretching
(B <sub>1</sub> )ν <sub>7</sub>	344	5	315	0.1	As–F <sub>4</sub> wagging
(B <sub>2</sub> )ν <sub>8</sub>	632	145	590	143	As–F <sub>2,eq</sub> asymm. stretching
(A <sub>1</sub> )ν <sub>9</sub>	202	10	184	10	F <sub>ax</sub> –As–F <sub>ax</sub> bending

<sup>a</sup> Based on inspection of normal mode animation.

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