

Article

Electron Lone-Pairs Stereochemistry and Drastic van der Waals and Pressure Effects in AsF₃ from First Principles

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Abstract: AsF₃E as a representative of a molecular crystal has been chosen to find the precise localization of the lone pair (LP) E centroid 4s² of As³⁺ and to enlighten the behavior of lone pair triplets of fluorine atoms. Starting from stereochemistry rationale, Density Functional (DFT) electronic structure calculations yielding the electron localization (ELF) mapping led to precise large crystal structure evolutions from basic X-rays data ($V = 267.2 \text{ \AA}^3$ at 193K), to ($V = 230.5 \text{ \AA}^3$) and under Van der Waals forces (DEW) $V = 206.4 \text{ \AA}^3$, and then under pressure P, all illustrated with ELF maps and band structures. Calibrated pressures up to 100 GPa exhibit the remarkable shrinking of all inter-atomic distances including As-E from 0.94 Å down to 0.46 Å, while the major three bonds As-F1, As-F2 and As-F3 are continuously expanding. The resulting picture of the application of pressure on AsF₃ molecular structure leads to the progressive immersion of the 4s² doublet within the electronic cloud with an original new status of As with its 4s² E expressed as [AsE]³⁺. The expanded size becomes close to big LP-free K⁺, Ba²⁺ cations or LP characterized bismuth cation: [BiE]³⁺, which appear inserted in cubes or square anti-prisms with coordination number 8 (CN8) or in tricapped trigonal prisms with CN9.

Keywords: fluorides; stereochemistry; electron lone pair; bonding; DFT; ELF; DOS; COOP



Citation: Galy, J.; Matar, S.F. Electron Lone-Pairs Stereochemistry and Drastic van der Waals and Pressure Effects in AsF₃ from First Principles. *Condens. Matter* **2021**, *6*, 31. <https://doi.org/10.3390/condmat6030031>

Academic Editor:
Yoshikazu Mizuguchi

Received: 26 June 2021
Accepted: 6 August 2021
Published: 12 August 2021

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1. Introduction

Following our earlier research works on electron lone pair (LP) ns² elements [1,2], some particular features on fluoride compounds of group V_A trivalent elements prompted us to carefully settle their stereochemistry and to include the fluoride anions LP triplets. For this purpose, we focused on AsF₃E, where E designates As^{III} 4s² lone pair, to precisely address the features pertaining firstly to the stereoactivity of As^{III} lone pair E on one hand, and on the other hand to focus on the significant role of the LPs brought by the fluorine atoms of the three pending As-F bonds. Additionally, AsF₃ is a molecular solid state in its crystalline form [3], therefore it was a good candidate for highlighting and precisising the stereochemistry and metrics of the involved two natures of LPs and their implication in structural evolution such as with pressure. It needs to be mentioned here that a recent study dealing with Sn^{II} where the eminent role of the LP triplets in overlapping [SnF₄]_n layers was quantitatively shown [2].

Stressing further the original features above, the 4s² LP of As^{III} is not alone in influencing the atomic network. Indeed, in the present study, we show that the (2s²2p⁴) configuration of fluorine LP's triplets which are all non-bonding play a paramount role in the architecture of the molecule, and consequently on the shape of the three dimensional packing of the crystal.

For a complete picture of the stereochemistry of the title compounds, our investigations merge crystal chemistry rationale and electronic structure calculations. Specifically, the results allow extracting accurate information pertaining on one hand to the electron localization (cf. next Section 1), the stereochemistry and steric effects of LPs and to provide

quantitative LP metrics, and on the other hand to follow AsF_3 evolution at the atomic scale by accounting for van der Waals effects and under pressure (GPa) influence [4]. Let us note that during condensation of cell volume due to the effects of simulated pressure, there is a formation of original $[\text{As}_2\text{F}_6\text{E}_2]_n$ potential polymer chains along [100] and [001] around 10–15 GPa occurring through AsF_4E triangular bipyramids units sharing axial summits, and resulting in a three-dimensional crystal compound at 70–100 GPa closely related to β BiF_3E [5], characterized by a big bismuth cation.

Beside the LP metrics, further assessments of the electronic structure focusing on simulated van der Waals (vdW) and pressure (P) effects will be provided from the electronic band structures, mirrored by the site projected density of states and further illustrated through the qualitative assessment of the chemical bonding illustrating the interactions between pairs of atoms.

The paper is organized as follows: After this contextual Introduction, the theory and computational frameworks are presented in Section 2. The stereochemistry of AsF_3 is described in details in Section 3, followed by the results of LP metrics together with the vdW and pressure (P) effects detailed in Section 4. Section 5 details the electronic band structures, the site projected DOS and properties of chemical bonding. The last section highlights the conclusions.

2. Theoretical and Computational Frameworks

The ab initio electronic structure calculations herein are based on the quantum density functional theory (DFT) [6,7], where the effects of exchange and correlation (XC) are equally taken into account, opposite to the Hartree–Fock method, which mainly treats exchange effects. In the founding papers, the first development of XC effects was operated thanks to local density approximation LDA [8] scheme based on the homogeneous electron gas. However, the need for introducing gradients to the electron density to correctly describe solid state chemical compounds rapidly led to the generalized gradient approximation GGA [9] used herein.

In the present work, we used two methods within DFT. The Vienna ab initio simulation package (VASP) code [10,11] with the projector augmented wave PAW method [11,12] for generating atomic potentials of As and F was used to obtain equilibrium crystal structures starting from experiment; those are usually found close to experimental findings. This method also allows accounting for van de Waals effects following Grimme scheme [4] within so-called DFT-D2 approach implemented in the MEDEA simulation package with VASP [13]. The main outcome of the calculations is to ‘build’ the electron localization around the chemical constituents, i.e., the atoms with their chemical trend to ionize either positively (decrease of localization) or negatively (increase of localization). Two different schemes are practiced for this purpose: the electron localization indicator (ELI-D) [14] and the electron localization function (ELF) [15]; the latter is used herein. ELF scheme is based on the kinetic energy in which the Pauli Exclusion Principle is included. ELF is a normalized function meaning, that its magnitude ranges from 0 to 1: 0 for no electron localization (blue zones) and 1 (red zones) for strong localization in the plane-slices the halfway value of $\frac{1}{2}$ corresponds to a free electron gas-like behavior (green zones), cf. Figures. These color codes identified in slices of planes crossing atomic zones of interest, are also accompanied by 3D iso-surfaces, which are relevant when analyzing electron lone pairs E stereo activity for the quantitative discussion of the LP metrics.

Detailed calculations of the electronic structure and the chemical bonding properties were carried out using the full-potential augmented spherical wave (ASW) method in its scalar-relativistic implementation [16], wherein the effects of exchange-correlation are treated with GGA [9]. In the ASW method, the wave function is expanded in atom-centered augmented spherical waves, which are Hankel functions and numerical solutions of Schrödinger’s equation, respectively, outside and inside the so-called augmentation spheres. In order to optimize the basis set, additional augmented spherical waves were placed at carefully selected interstitial sites. In the minimal ASW basis set, the outermost

shells were explicitly used to represent the valence states with partial waves up to $l_{\max} + 1$ for the different atomic species where l_{\max} is the maximum secondary quantum number; here, $l_{\max} = 2$ for As and $l_{\max} = 1$ for F. Filled As $3d^{10}$ states were not considered in the valence basis set. Self-consistency was achieved until the variation of the atomic charges was smaller than 10^{-8} electrons and the variation of the total energy was smaller than 10^{-7} eV. Further, the ASW method implements the chemical bonding for pair interactions provided as based on the overlap integral S_{ij} (i and j designating two chemical species) within the crystal orbital overlap population (COOP) by Hoffmann [17]. Here, we use the integrated COOP (iCOOP, unit less), whereby the larger the area underneath the curve, the larger the bonding is.

3. Stereochemical Considerations

3.1. Arsenic Trifluoride AsF₃E

In view of the Introduction section where fluorine LP (E) role is accounted for besides that of trivalent arsenic, we now express AsF₃ as As{E_{As}}F₃{E_F}₉.

An electron diffraction study of AsF₃ molecule was early reported [18], establishing an As-F bond length of 1.70 Å. In 1970, an electron diffraction study refining AsF₃ molecule parameters with As-F = 1.71 Å and F-As-F angle = 96.2° data was published [3]. Finally, in 1979, an X-ray structure determination on single crystal was reported [19] and discussed with Va element trihalides [20].

3.2. Crystal Formation and Structure

The crystal structure of AsF₃ was reported by Enjalbert and Galy [19] followed by crystal structure determination of other MF₃ compounds, where M is the Va element [20]. AsF₃ shows a typical molecular network with an AsF₃E triangular pyramidal model, arsenic sitting in a triangular pyramid with a base of three F and As 4s² lone pair E at the apex as shown in Figure 1 see upper left.

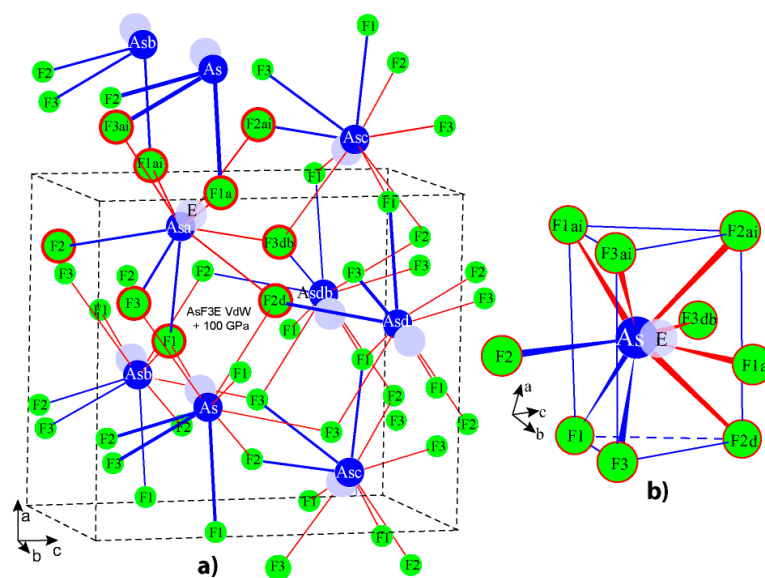


Figure 1. Perspective views of AsF₃E: (a) AsF₃E molecular network; (b) the distorted fluorine tricapped triangular prism (TTP) of nine fluorine atoms surrounding [AsE], i.e., [AsE]F₉.

Cell parameters determined by X-ray were used for basic features of the structure, the data involving E lone pair for As and the lone pair triplets {E_F} for fluorine atoms were issued from DFT–ELF analyses (DE) + Van der Waals (VdW); they complete the panel of AsF₃E data before applying increasing pressures from 3 up to 100 GPa (present work: *pw*). DE + VdW, designated by DEW, serve to create the CIF base (crystal information file) for

structural investigations under chosen pressures (GPa). As{EAs}F3{EF}3 crystallizes in the orthorhombic system with space group *Pna*21 as reported in Table 1.

Table 1. X-rays [19,20], DFT-ELF (DE), DE + VdW (DEW) and some DEW + GPa data of AsF3E{EF}3. Space group *Pna*21. Data: Bonds, interatomic distances (Å) and angles (°) from RX [19] and DEW + GPa [data pw]. (Ec centroid of As 4s² lone pair).

AsF3E/Cell (RX [21])	a (Å)	b (Å)	c (Å)	V (Å ³)	Z	rV (F/E) (Å ³)
RX [21] AsF3E	7.018	5.205	7.315	267.2	4	16.7
Atom coordinates of the molecule and E localization (Figure 1)	Atoms As F1 F2 F3 E	x 0.7862 0.5736 0.8077 0.6792 0.8885	y 0.5338 0.3995 0.3740 0.7956 0.5529	z 0.25 0.3065 0.0490 0.1493 0.3371	Wyckoff 4a 4a 4a 4a 4a	
AsF3E/Cells	a (Å)	b (Å)	c (Å)	V (Å ³)	Z	rV (F/E) (Å ³)
AsF3E (DE)	6.632	4.957	7.013	230.5	4	14.4
AsF3E (DEW)	6.346	4.780	6.806	206.4	4	12.9
DEW+ 3 GPa	6.174	4.681	6.691	193.4	4	12.1
DEW+ 30 GPa	5.701	4.353	6.339	157.3	4	9.8
DEW+ 100 GPa	5.319	3.910	5.954	123.8	4	7.7
Data (Å, °, GPa)	RX [21] (Å, °)	DEW + GPa (Å, °, 3 GPa)	DEW + GPa (Å, °, 30 GPa)	DEW + GPa (Å, °, 100 GPa)		
As-Ec	0.97	0.94	0.69	0.46		
As-F1	1.699	1.798	1.834	1.966		
As-F2	1.696	1.805	1.834	1.966		
As-F3	1.722	1.815	1.861	2.036		
F1-F2	2.503	2.593	2.535	2.380		
F2-F3	2.483	2.501	2.395	2.174		
F3-F1	2.474	2.543	2.491	2.381		
Asb-F1a	3.054	2.546	2.253	1.918		
As-F2c	2.890	2.422	2.218	2.032		
F-As-F angles (°)	95.0, 93.2, 92.7	89.5, 87.4, 92.1	87.4, 80.8, 84.8	74.5, 65.8, 73.0		

3.3. Description and Crystal Chemistry Rationale

The molecular network shows largely separated AsF3E molecules exhibiting with cationic As^{III} and its lone pair E the classical AsF3E triangular pyramidal (TP) coordination shape (Figure 1a). The molecules coil around 21 screw axes (along [001]), and they are packed in planes parallel to (100) and (010). However, the packing reveals a remarkable organization of five molecules around the molecule model AsF1F2F3Ec and more precisely around its lone pair Ec giving six fluorine atoms to complete a tricapped triangular prism around [AsE]. The two bases, F1F2F3 and F1a2a3a, of the prism, completed by F2c, F3b and F1b capping the three rectangular faces, are shown in Figure 1b. The Ec-F1,F2,F3 average distance amounts to 2.38Å, while the six other fluorine atoms enclosing [AsE] show Ec-F distances ranging between 2.58Å and 3.15Å (average 2.74Å). In Figure 1b, these fluorine atoms surrounding [AsF3E] molecule make a closed polyhedron, a distorted tricapped triangular prism (TTP), which merges [AsE].

4. Results for Stereochemical Assessments

4.1. Electron Localization Function ELF

From the calculation results, selective ELF sections allow us to enter in a precise location and description of lone pairs. Coordination details of AsF3 are summarized in Figure 2.

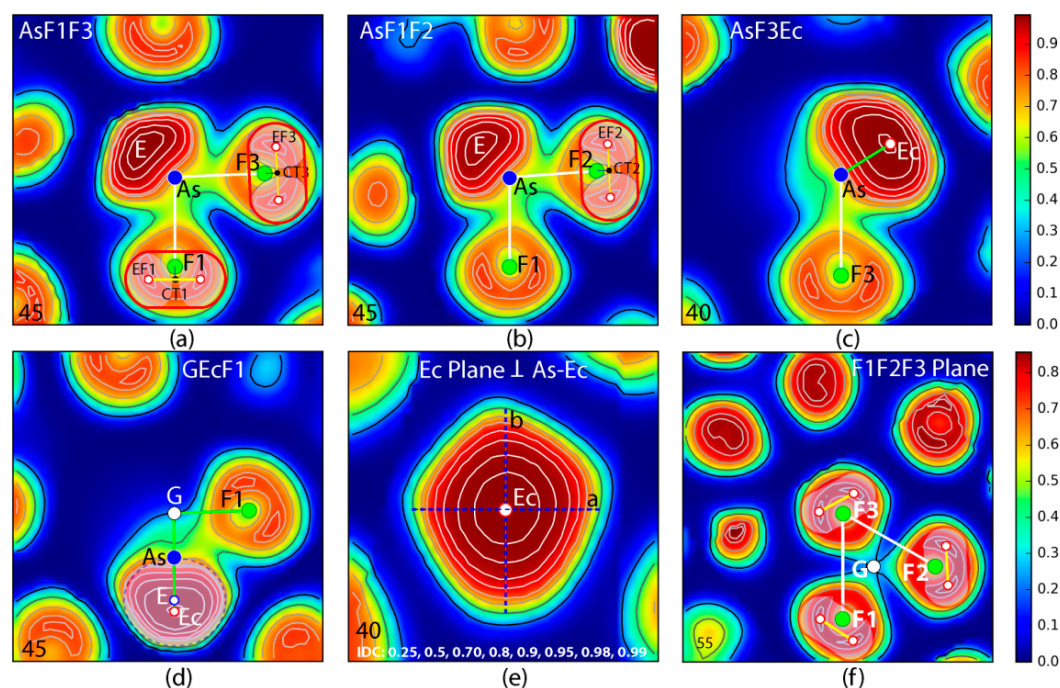


Figure 2. Arsenic trifluoride ELF. (a,b) Sections based on As, F1, F2, and F3 atoms showing the presence of As lone pair Ec. The (c,d) sections allow us to find some precise metrics of the lone pair Ec of the couple [AsE]; (e) this Ec section is directly obtained by calculating a plane perpendicular to As-Ec in Ec, allowing us to refine a and b parameters of Ec ellipsoid. (d) Ec centroid is marked by a little red-white circle and pale blue ellipse circling also the center (blue-white circle) of electronic cloud ellipsoid. (e) Plane of Ec perpendicular to As-Ec. (f) Section based on the three fluorine atoms F1, F2, F3 (G their gravity centre) slicing also densities due to fluorine lone pairs $2s^2 2p^4$.

In Figure 2a,b, the sections by AsF1F3 and AsF1F2 reveal an important electronic density (this term being used indifferently from localization herein) on the top of As with the slice of As lone pair $4s^2$ of volume E. By using special software (cf. ref. [2]), the coordinates of its maximum density were determined and refined. This clear Ec centroid location allowed us to calculate the section illustrated in Figure 2c determined by AsF3Ec plane.

Subsequently, the coordinates of the center of gravity G of F1, F2 and F3 was calculated allowing us to precisely find a better symmetric section of Ec in GEcF1 plane. A precise volume of Ec and of its associated electronic cloud completed by a section perpendicular to As-Ec in Ec (Figure 2e) allowed us to determine the parameters of an Ec ellipsoid corresponding to a sphere of influence (Ec) in the packing with a radius $r_{Ec} = 0.94 \text{ \AA}$. This is detailed in forthcoming figures. Therefore, it is worth noting the particular shape of the figure when we focus on fluorine atoms: They show two maxima around F1, F2 and F3 immersed in a density rounded rectangle (Figure 2f).

To set up these tori searches of density, maxima were systematically performed in the vicinity of the fluorine atoms. Figure 3a illustrates this search by several points with marked density shown with blue-green circles. After the precise localization of their coordinates in the network, they show that they were at the same distance from F with $F-\{EF\} = 0.56 \text{ \AA}$ and characterized with a center of gravity CT ($CT-\{EF\} = 0.53 \text{ \AA}$) (Table 2).

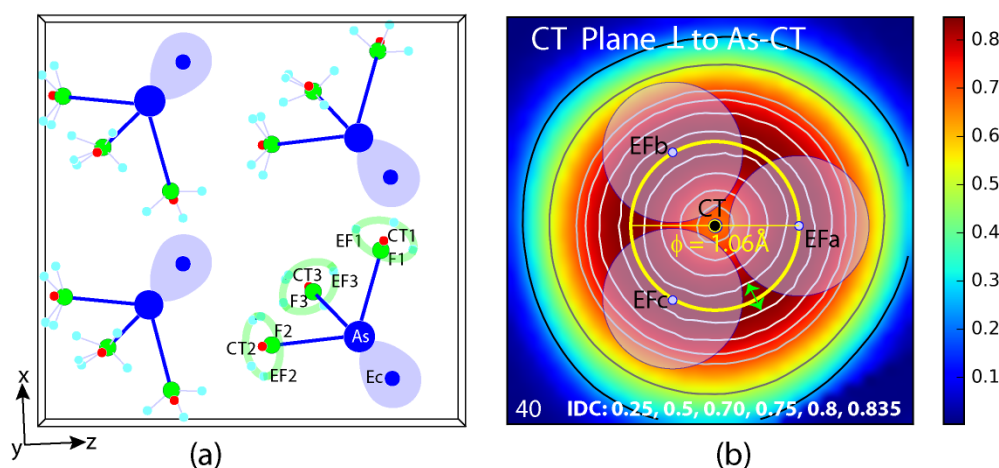


Figure 3. (a) Projection onto (010) of the complex $\text{AsEF}_3\{\text{EF}_3\}_3$ molecules. The three LPs of each F atom, $\{\text{EF}_3\}$, have been localized (blue little circles). These points are located in a circle, the center (CT red circle) of which is moved away by 0.2Å . Section plane in CT perpendicular to As-F direction shows the generation by the three LPs $\{\text{EF}_{a,b,c}\}$ of the electronic torus (green circle) around each fluorine. (b) The ring with maximum intensity ($\text{IDC} = 0.835$) and thickness (green arrow) is the locus of gyration circle indicated by yellow ring, the diameter of which amounts 1.06Å .

Table 2. $\text{AsEcF}_3\{\text{EF}_3\}$. Data involving E or $\{\text{EF}\}$ lone pairs as issued from DFT–ELF analyses.

As-Ec	0.97	Ec-F1,2,3	2.38	∠FAsF *	93.6 *
F-{EF} (1,2,3)	0.57	F-CT (1,2,3)	0.20	Ec a/b/c ellipsoid	0.94/1.03/0.85
CT-{EF}(1,2,3)	0.53	As-CT (1,2,3)	1.91	{EF}a/b/c ellipsoid	0.41/0.41/0.55
T. Rd. rect. {EF}	1.98/1.10/0.75	ϕT.ext.{EF3}	1.98	T. gyr. ϕ yellow stick or ϕ circle	1.06
(Figure 2a,b) L/H/R		blue dotted circle			
rEc	0.94			r{EF}	0.45

Ec coordinates: Wyckoff $4a$ site x,y,z : 0.112, 0.447, 0.837. [pw]: present work. Ec: Oblate ellipsoid a/b/c: $0.94/1.03/0.85\text{Å}$. * average. $\{\text{EF}\}$ density maxima found around each F_{1,2,3} atoms. T. rd.rect. $\{\text{EF}\}$ L/H/R: Rounded rectangle embedding $\{\text{EF}\}$ (red line) lone pair triplet which generates a fluorine electronic torus by LP $\{\text{EF}_3\}$ rotation around As-F bonds capping F atoms. CT_{1,2,3} tori centers of $\{\text{EF}_{1,2,3}\}$ triplets. T gyr. ϕ $\{\text{EF}_3\}$: torus gyration diameter = 1.06Å .

Figure 3a shows, for example, an ELF section based on these points $\{\text{EF}\}$ around As-F axes. It has been possible to link these points by a circle (green) with a radius CT- $\{\text{EF}\}$ representing the torus gyration circle of $\{\text{EF}\}$, LP's triplet locus of F. Figure 3b is of paramount importance, looking at the highest ring designed by the two $\text{IDC} = 0.835$ density curves (the size of the ring is indicated by green arrow). A constant ring density is shown, establishing that it results from the $\{\text{EF}_3\}$ triplet rotating around the As-CT axis. The triplets $\{\text{EF}_1\}$ and $\{\text{EF}_2\}$ show identical sizes.

The gyration diameter is drawn in the middle of a ring of stable IDC designated by a yellow circle, with a diameter estimated at $r = 1.06\text{Å}$. The three $\{\text{EF}_{a,b,c}\}$ LPs are represented by pale blue transparent circles, their center (little clear blue circles) being settled on the yellow gyration circle. Their radii determined in Figures 2 and 3, $r\{\text{EF}\} = 0.45\text{Å}$, suggest they are separated by 120° . Figure 3a shows the coherent dynamic crowns formed by these tori capping F atoms with their centers aligned on yellow gyration circle perpendicular in CT to As-F direction (angles: As-F₁-CT₁ = 179.5° , As-F₂-CT₂ = 179.9° and As-F₃-CT₃ = 179.9°) and distant by F-CT = 0.20Å .

The particular “dynamic” surface generated by the fluorine triplets lets us suppose that they participate in the high reactivity of this fluoride, especially through its extreme hygroscopicity.

4.2. Calculations Accounting for van der Waals Forces and Simulation of Various Pressures

From the above developments, the AsF₃E structure, perfectly organized, lets us strongly suggest that subtle molecular interactions, at short and long ranges, were likely to cause a phase transition accompanied by network reorganizations after being exposed to pressures with increasing magnitudes. It was decided to apply pressures up to 100 GPa.

Parameters relevant to the cell volume V and cell dimensions (a, b, c) are reported in Table 1 and depicted in Figure 4a–d. A first approach was accomplished with the simulation of structure network already treated by DFT-ELF (DE) as previously done by adding up van der Waals forces (vdW). Such a DFT + D2 interaction is treated via a pair-wise force field optimized for DFT functional according to Grimme's development in the MEDEA package [4].

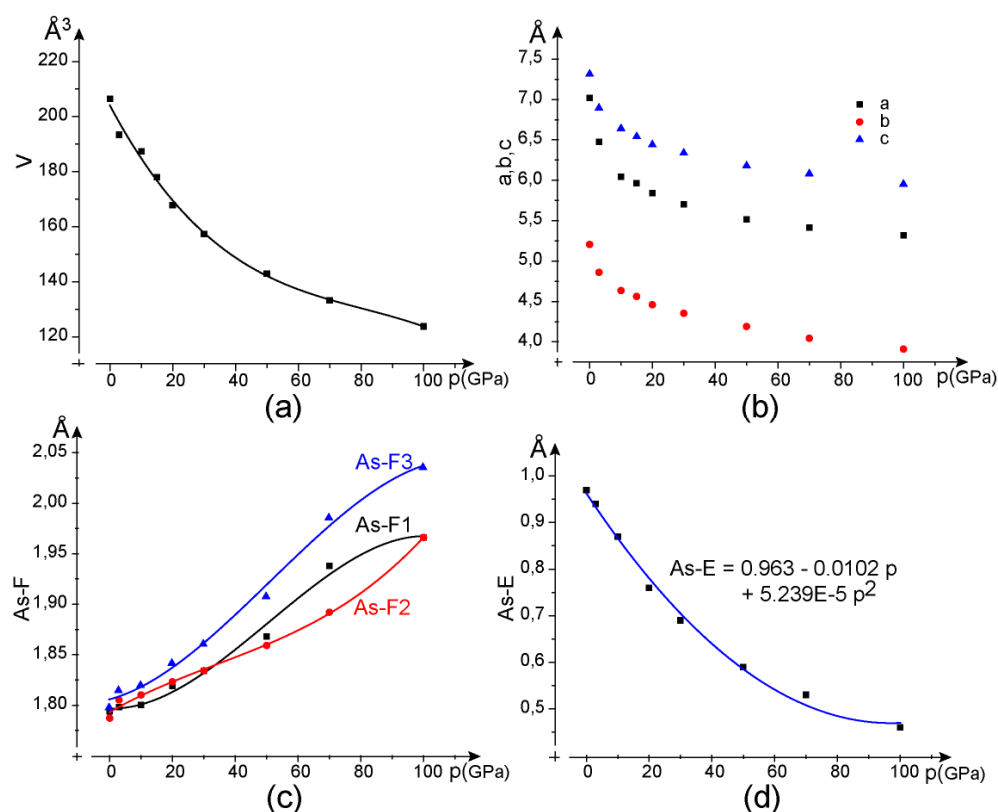


Figure 4. (a) Volume (V) of the AsF₃E cell versus pressure p (GPa) decreasing up to 100 GPa; (b) cell parameters a, b, c vs. p ; (c) As-F bonds of initial molecule AsF₃E increasing with pressure, and (d) the drastic negative evolution of As-E spacing.

Coming to these high pressures a first test at isotropic pressure of only 3 GPa V (DEW + 3 GPa) shows again an extra cell condensation, its volume decreasing from 206.4 Å³ to 193.4 Å³. Two examples at 20 GPa and 70 GPa are given (Figure 5c,d), cell volume decreasing down to 133 Å³. Some large interaction in [100] and [001] directions, sensitive to high pressure, are marked by dotted red sticks, and their lengths are indicated (Figure 5).

The cell shape indicates its exponential decreasing evolution up to 100 GPa. Concomitantly, at the level of AsF₃E molecule, the pressure shows atom by atom that the AsF₃E atomic network evolves to a progressive phase transition, via its condensation, largely engaged around 70 GPa (Figure 4a–d). Some molecular data evolution, As-E, and As-F1,2,3, are directly illustrated by diagrams versus pressure steps (Figure 4c,d). A remarkable impact is revealed through the fundamental bonds As-F1,2,3 which, astonishingly, are all increasing up to $P = 100$ GPa. Therefore, another fact of paramount importance concerns the lone pair E, which starts to coil the As atom following a large diminution of As-E distance from 0.97 to 0.46 Å. This highlights that the lone electronic centroid pair Ec and its

associate electronic cloud E are very sensitive to the pressure, which pushes As^{3+} to the creation of a new cation: As^{3+} with its lone pair, i.e., $[\text{AsE}]^{3+}$.

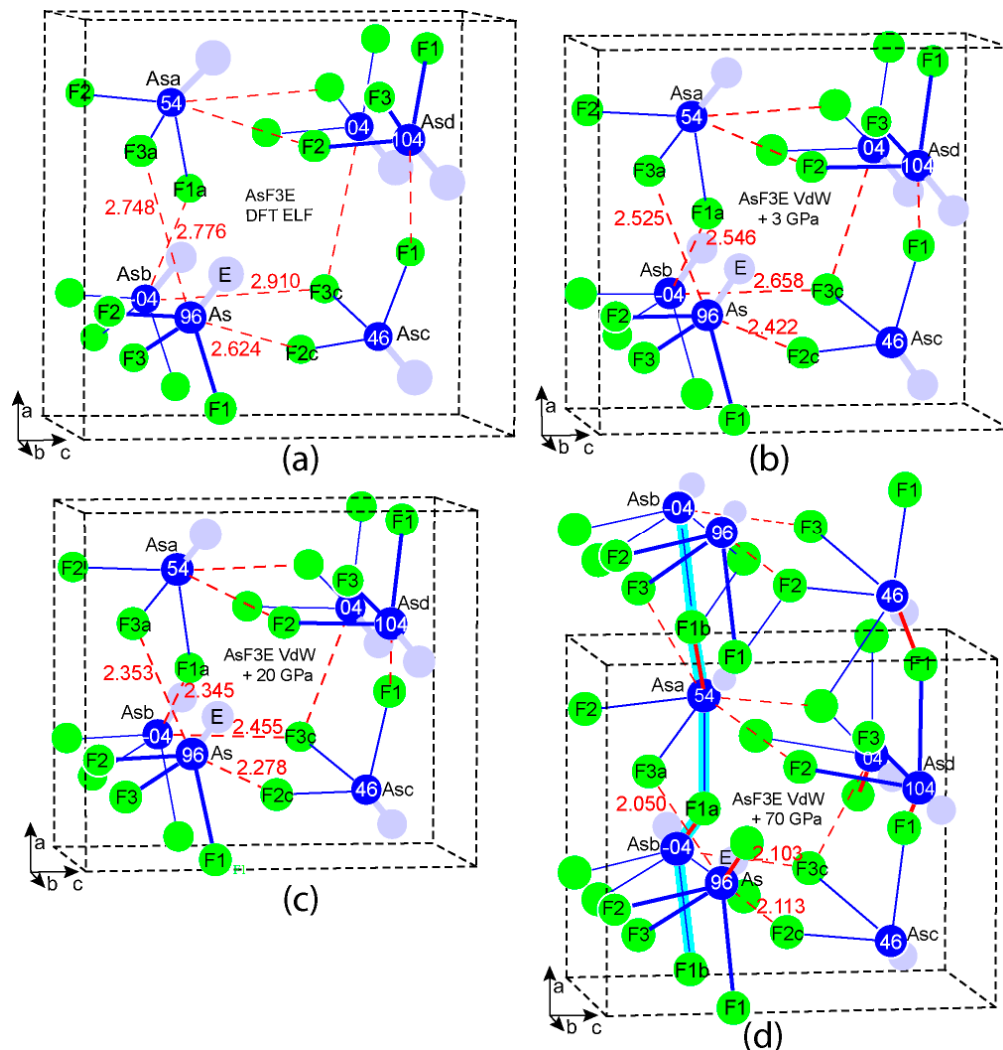


Figure 5. AsF_3E . (a) DFT-ELF (DE) situation where large As–F interactions are marked by dotted red sticks, (b) vdW and 3 GPa applied drastic contraction of As–F interactions was noted; (c) situation onto 20 GPa and (d) under 70 GPa pressure where contraction of these As–F interactions perpetuate a polymeric chain can be outlined (highlighted by a thick pale blue stick (4d)). All intermolecular interactions are drastically reduced (some indicated by dotted red sticks and their values in red numbers) but, concomitantly, As–F1,2,3 original bonds increase.

In a perspective cell view, some large As–F interactions are designed in Figure 5 by dotted red sticks roughly oriented to the three directions $[100]$, $[010]$ and $[001]$ their length being included within the range 2.89Å – 3.18Å .

Evolution of the structure from AsF_3E from (a) DFT-ELF to; (b) 3 GPa application indicating the coherent large As–F interactions contraction; (c) an example at 20 GPa; (d) 70 GPa situation which indicate that the structure evolution as raised a state where a polymer circuit is traced along $[100]$ (as an example) marked by large blue sticks from ... F1b–Asb–F1a–Asa–F1b–Asb ... corresponding eventually to a potential phase $\{\text{As}_2\text{F}_6\text{E}_2\}_n$, therefore, also the beginning of phase $[\text{AsE}]\text{F}_3$ formation isostructural to orthorhombic β $[\text{Bi.E}]\text{F}_3$ phase with Bi–E = 0.28Å (SG $Pnam$, $a = 6.56$, $b = 4.84$, $c = 7.15\text{Å}$, $V = 222.9\text{Å}^3$ [5]) or a cubic one the synthetic γ $[\text{Bi.E}]\text{F}_3$ with Bi–E = 0.13Å (SG $P43m$, $a = 5.853\text{Å}$, $V = 200.5\text{Å}^3$) [21].

Then, the cell parameters evolution up to 100 GPa associated to the lengthening of primary As–F and As–E distances show that the last pressure was decisive to settle

a new phase $[\text{AsE}]\text{F}_3$ with a tri-dimensional network and a volume of 123.8\AA^3 (Table 1). A perspective view of the structure is given in Figure 6a. The detail of the crystal unit $[\text{AsE}]\text{F}_3$ in its CN = 9 number as a form of tri-capped triangular prism (TTP) is displayed in Figure 6b. Such virtual $[\text{AsE}]\text{F}_3$ phase under 100 GPa is directly comparable to β $[\text{BiE}]\text{F}_3$. Both formulae correspond astonishingly to an isostructural network. Following the As-E evolution (Figure 4d) and its formula of the curve; a value for its derivative is found at $P = 102$ GPa, and $d(\text{As-E}) = 0.467\text{\AA}$ is identified as very close to the data corresponding to $P = 100$ GPa.

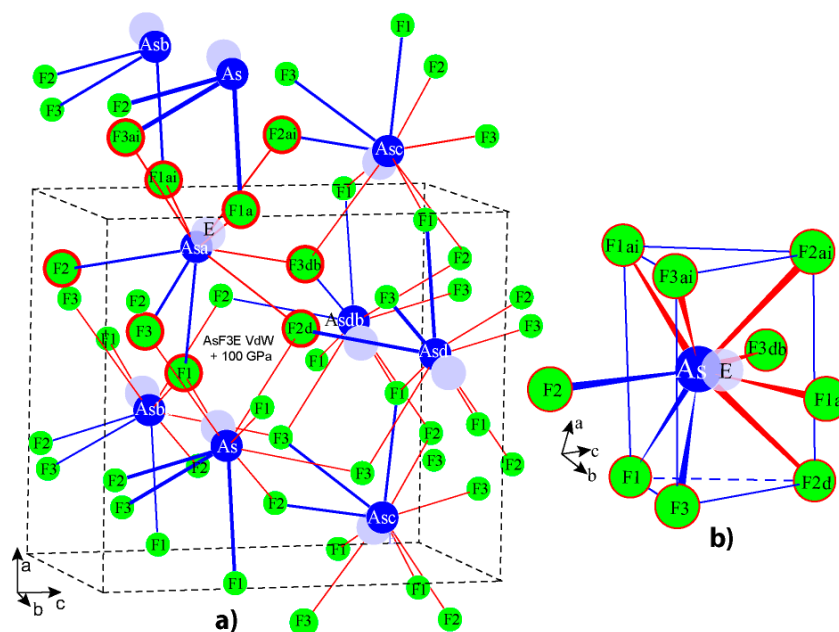


Figure 6. (a) Detail of the AsF_3E structure under 100 GPa pressure; all 9 fluorine atoms setting As and E are the green-red circles. (b) The formed fluorine tri-capped triangular prism (TTP) surrounding $[\text{AsE}]^{3+}$, which behaves like large K^+ , Ba^{2+} or more precisely like $[\text{BiE}]^{3+}$ cations in γ and α $[\text{BiE}]\text{F}_3$ forms.

Such evolution lets us propose that a supplement of pressure could transform this $[\text{AsE}]\text{F}_3$ structure into isostructural cubic form of BiF_3 $P43m$ (215) [21] and perhaps α gananite form [22] that are related to typical YF_3 crystal structure as shown by Hyde and Andersson [23].

5. Electronic Band Structures, Density of States and Chemical Bonding

Further assessment of the van der Waals (vdW) effects, on one hand, and of the influence of pressure, on the other hand, regarding the electronic structure in AsF_3 were subsequently carried out using the full potential augmented spherical wave method (ASW) [17]. ASW method also implements the crystal orbital overlap population (COOP) criterion following Hoffmann [18] to address the chemical bonding as based on the overlap population. The calculations were done using the crystal parameters in Table 1.

Figures 7 and 8 present the results at Normal Pressure (N.P.) and $P = 3$ GPa, respectively, for the band structure calculated along the main lines of the simple orthorhombic Brillouin zone (BZ), followed by the site projected density of states (DOS) and the bonding rationalized through the integrated COOP (iCOOP). In all panels, the zero of energy is with respect to the top of the (filled) valence band VB, separated from the (empty) conduction band (CB) by an energy gap at different magnitudes (*vide infra*) indication insulating character of the trifluoride.

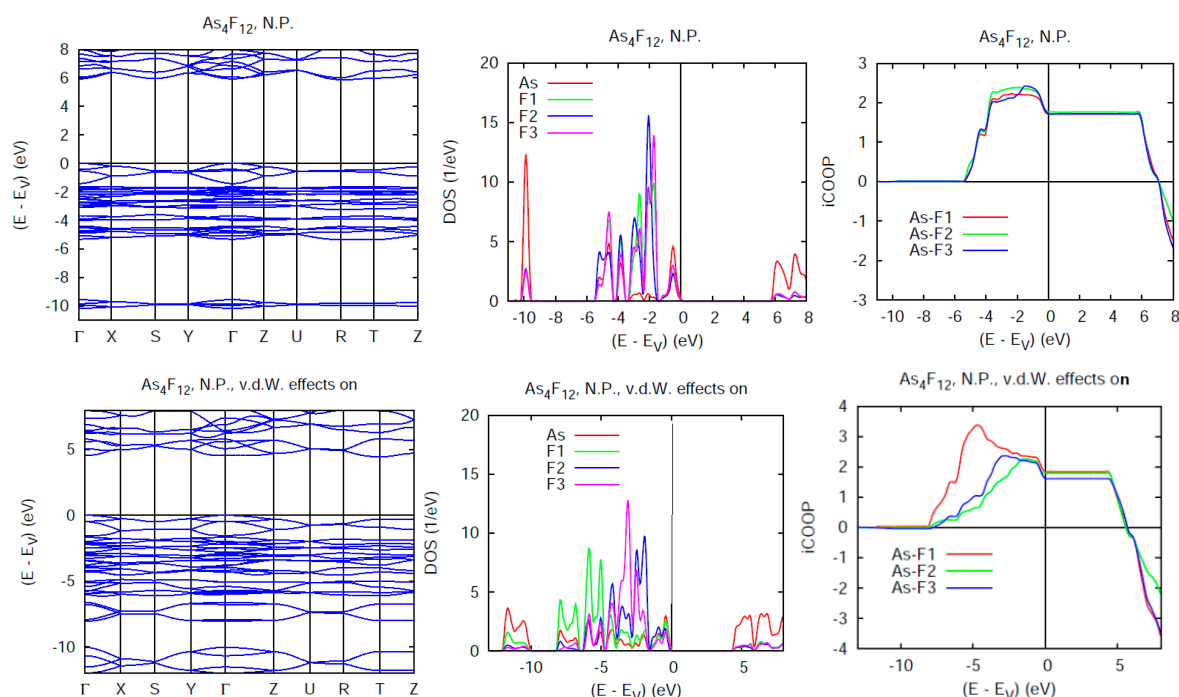


Figure 7. AsF₃ electronic structure at normal pressure: band dispersion (**left**), DOS (**middle**) and bonding (**right**), without (**top**) and with (**bottom**) van der Waals effects.

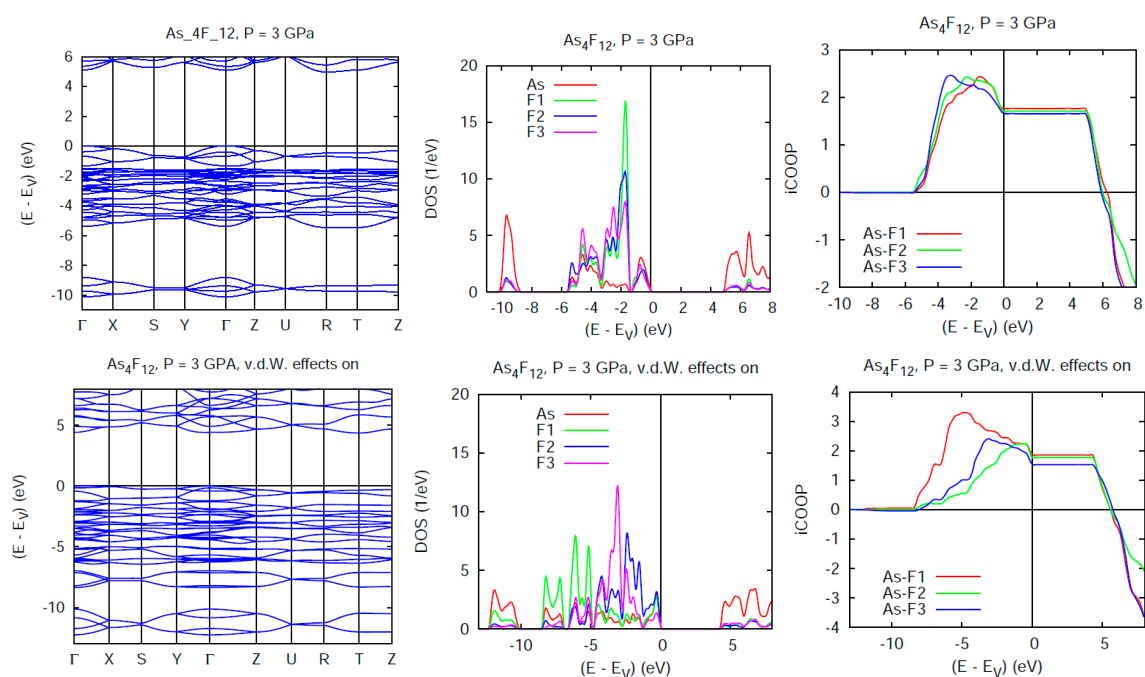


Figure 8. AsF₃ electronic structure at P = 3 GPa pressure: band dispersion (**left**), DOS (**middle**) and bonding (**right**), without (**top**) and with (**bottom**) van der Waals effects.

5.1. Normal Pressure Results

The energy band structures in Figure 7 exhibit differences between “off” and “on” vdW effects. Without vdW effects, the band gap E_{gap} is large, close to 6 eV. Upon including vdW effects, it decreases down to $E_{\text{gap}}(\text{vdW}) = 5$ eV. Additionally, the localized character of flat bands within both VB and CB is characteristic of a highly ionic chemical compound,

whereby there is a clear separation of s-like bands centered at -10 eV from p-like bands extending over 5 eV, up to E_V ; and finally a narrow CB of ~ 2 eV breadth is observed. Upon tuning on the vdW effects, drastic changes occur with a significant broadening of all of three band blocks, i.e., by 2 eV or s-like, 8 eV for p-like and 5 eV for the CB. The overall picture is that of a less-isolated chemical system with intermolecular electronic interactions.

The observations are mirrored by the electronic density of states where the low energy lying DOS correspond to a broadening of the sharp As s-like states mixing specifically with F1 within a broad ~ 2 eV band. The p-block is broadened with a differentiation between the F states, especially F1, and the CB is mainly composed of As empty states.

In so far that the bonding is ensured by the directional p-states, the iCOOP top panel shows significant intensity essentially within the p-block energy range. The As-F bonds are almost identical for the three kinds of As-F_i ($i = 1,2,3$) interactions, but large changes occur in the lower panel upon accounting for vdW effects where As-F1 iCOOP intensity prevails versus As-F2 and As-F3 within the broader p-like VB, in perfect agreement with Figure 5b) showing infinite chains: ... F1-As-F1 ...

5.2. Pressure Effects

The major effects discussed above are reproduced in Figure 8, illustrating the consequence of exerting pressure. Expectedly, increasing pressure reduces the interatomic distances with the consequence of a larger overlap between the valence states, i.e., with broader bands. This is actually observed in the band structure panels exhibiting smaller band gaps.

The DOS panels show the same trends as in Figure 7 regarding the relative energy extension magnitudes of the s- and p-blocks, as well as the gap magnitudes.

Lastly, the iCOOP shows the remarkable As-F1 differentiated larger magnitude characterizing As-F1 bonding.

6. Conclusions

In this work a thorough analysis highlighting the major changes brought into the molecular structure of arsenic trifluoride AsF₃E submitted via DFT-ELF to van der Waals corrections and high pressure treatments was performed.

The first point concerns the valence ns^2 E lone pair of As, i.e., $4s^2$, which assumes with the three F atoms and its centroid Ec and electronic cloud E, the basal plane and the apex of the AsF₃E triangular pyramidal molecule. Around [AsE] we have noted the presence of six fluorine atoms which form, with the three fluorine atoms involved with the As-F bonds, a closed tricapped triangular prism [AsE]F₉ polyhedron.

The lone pair triplets of each fluorine atoms linked to As form a torus crowning each of them, and it is believed that such a dynamic of fluorine atoms of pending bonds must have a major impact in their high reactivity.

Coming to Van der Waals contraction of the cell, large length As-F interactions are all clearly reduced; this phenomenon being enhanced with the pressure increase.

However, a most astonishing fact is the increasing lengths of the three bonds As-F_{1,2,3}, which amounts to $\sim 117\%$ between room and 100 GPa pressures. Such a phenomenon is well-balanced by the contraction of As-Ec, which enclose them, after continuous bond diminution from 0.96\AA to 0.46\AA , into a tricapped triangular prism, noted [AsE]F₉. Accordingly, the volume [AsE]F₉³⁺ can be seen as a large cation like K⁺, Ba²⁺ or more precisely to [BiE]³⁺ in the series of α , β , and γ [BiE]F₃ fluorides. However, here we learn that with pressure increase, the distance As-E diminishes but [AsE] size increases, its combination being illustrated in another occurrence with bismuth, namely in orthorhombic γ [BiE]F₃ with Bi-E = 0.28\AA , γ [BiE]F₃ with Bi-E = 0.13\AA and β [BiE]F₃ with Bi-E = 0 the *Gananite* mineral with {[BiE]F₈ cube surrounded by six {F}F₈ cubes.

This stereochemical study indicates that it is possible with programmed high pressure to master the lone pair and to press it to merge into the cation, here As^{III}, thus inducing it to behave, structurally, like a heavy atom as Bismuth.

Author Contributions: Both authors J.G. and S.F.M. have contributed equally to the conceptualization, methodology, formal analysis and writing—original draft preparation. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data supporting reported results including CIF files can be made available on demand.

Acknowledgments: One of us (J.G.) thanks Gérard Vignoles, LCTS-CNRS, for providing facilities and enriching discussions. Computational facilities from the University of Bordeaux and from the Lebanese German University are gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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