The Arsenic Fluorides AsF_n ($n = 1-6$) and Their Anions: Structures, Thermochemistry, and Electron Affinities

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The molecular structures, electron affinities, and dissociation energies of the AsF_n/AsF_n^- ($n = 1-6$) species have been examined using four hybrid and pure density functional theory (DFT) methods. The basis set used in this work is of double-ζ plus polarization quality with additional diffuse s- and p-type functions, denoted DZP++. The geometries are fully optimized with each DFT method independently. Three types of energy separations reported in this work are the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE). The first As−F dissociation energies $D_e(F_{n-1}As-F)$ for AsF_n, and both $D_e(F_{n-1}As^--F)$ and $D_e(F_{n-1}As-F^-)$ for AsF_n^- species have also been reported. The best method for predicting molecular structures was found to be BHLYP, while other methods generally overestimated bond lengths. For the closed-shell anions the As−F bond distances are ∼0.1 Å longer than those for the analogous neutrals. In contrast, when the neutral AsF_n is a closed shell, the anion As−F distances is ∼0.2 Å longer. The most reliable adiabatic electron affinities, obtained at the DZP++ BHLYP level of theory, are 0.74 eV (As), 0.94 eV (AsF), 1.17 eV(AsF_2), 0.80 eV (AsF_3), 4.42 eV (AsF_4), and 2.79 eV (AsF_5), respectively. Those for As and AsF_2 are in good agreement with experiment, but that for AsF is smaller than the available experimental value (1.3 ± 0.1 eV). The predicted vertical detachment energy for AsF_6^- is remarkable, as large as 10.54 eV (BHLYP), indicating AsF_6^- is stable. The general trend for predicting the first dissociation energies is BP86 $\sim$ BLYP $>$ B3LYP $\gg$ BHLYP. The first dissociation energies for the neutral arsenic fluorides predicted by the DFT methods except BHLYP are 4.22−4.50 eV (AsF), 4.45−4.74 eV (AsF_2), 4.76−5.03 eV (AsF_3), 1.46−1.84 eV (AsF_4), and 3.87−4.11 eV (AsF_5). Compared to the experimental dissociation energies, the theoretical predictions are very reasonable. The anion bond dissociation energies are largely unknown experimentally. The dissociation energy for $AsF^- \rightarrow As + F^-$ is predicted to be 1.73 eV (BHLYP), 1.82 eV (B3LYP), 1.93 eV (BP86), and 1.87 eV (BLYP), which values are in good agreement with experiment (1.9 ± 0.2 eV). The predicted bond dissociation energies for $D_e(F_3As-F^-)$ are in the range of 2.45−2.57 eV, which is close to the previous theoretical results using the HF and MP2/ECP methods. For the vibrational frequencies of the AsF_n series, the BHLYP method also produces good predictions with the average error only about 10 cm^{-1} from available experimental values. The other three methods underestimate the vibrational frequencies, with the worst predictions given by the BLYP method.

Introduction

The arsenic fluorides have received considerable attention because of their importance in the semiconductor industry: for example, AsF_3 and AsF_5 have been used as fluorinating reagents,[1] and AsF_3 also as a dopant.[2] Some other AsF_n species have also been observed. The excited photofragment AsF_2* is produced by the decomposition of AsF_3 under UV vacuum radiation.[3] AsF_6^- is a very stable ion, and the novel homoleptic polynitrogen N_5+ has been synthesized in the form of $N_5^+AsF_6^-$ salt.[4]

There have been some previous theoretical studies on AsF_n. Moc and Morokuma[5] have theoretically investigated the structure, stability, and electronic properties of the AsF_4^- anion using both effective core potentials (ECP) and all-electron (AE) ab initio methods, and found the C_{2v} structure to be the global minima. Latifzadeh and Balasubramanian[6] have studied the spectroscopic constants and potential energy curves of a number of electronic states of AsF/AsF^+ and AsF_2/AsF_2^+ using the complete active space self-consistent field (CASSCF) method followed by multireference singles and doubles configuration interaction (MRSDCI), and reported the bond dissociation energies of AsF and AsF_2. Other theoretical studies on AsF_3 and AsF_5 have been also published.[7−9] But little is known theoretically or experimentally about the electron affinities, a fundamental property of AsF_n molecules. Pabst, Bennett, Margrave, and Franklin[10,11] reported the experimental adiabatic electron affinity of AsF radical to be ≥1.3 eV and that of AsF_2 at 0.8 or 0.9 eV from their negative ion electron impact studies in 1970s. The only theoretical prediction of the AsF_n electron affinities is found in the 1973 study of O'Hare and Wahl,[12] who estimated an vertical electron affinity value (1.1 eV) for the AsF radical.

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Density functional theory (DFT)[13,14] has evolved into a widely applicable computational technique, while requiring less computational effort than convergent quantum mechanical methods such as coupled cluster theory. The application of gradient-corrected density functionals theory has been shown to be effective for many inorganic species such as the SiF_n/SiF_n^-, PF_n/PF_n^-, SF_n/SF_n^-, ClF_n/ClF_n^-, GeF_n/GeF_n^-, SeF_n/SeF_n^-, and BrF_n/BrF_n^- systems.[15−21] The theoretical prediction of electron affinities has historically been generally difficult due to the desired result being a small difference between two large energies; but recent work has shown that the DFT methods are dependable for EA predictions. For a general discussion of the reliability of DFT studies of anions, the reader is referred to the 2002 review of Rienstra-Kiracofe, Tschumper, Schaefer, Nandi, and Ellison.[22]

The objective of the present study is to systematically apply several contemporary forms of density functional theory[14] to the determination of the electron affinities and other properties of the AsF_n ($n = 1-6$) series. Of specific interest is (a) the comparison of the electron affinities with the limited available experimental results; (b) the relationship between the neutral AsF_n molecules and their anions as measured by the three types of energy separations, e.g., the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy of the anion (VDE); (c) the predictions of other properties including dissociation energies and vibrational frequencies; and (d) the comparison of the different DFT methods. We would like to establish reliable theoretical predictions for those arsenic fluorides in the absence of experimental results and in some cases to challenge existing experiments.

Theoretical Methods

The four different density functional or hybrid Hartree−Fock/density functional forms used here are as follow:

(a) Becke's 1988 exchange functional[23] with Lee, Yang and Parr's correlation functional[24] (BLYP);

(b) the half and half exchange functional[25] with the LYP correlation functional (BHLYP);

(c) Becke's three-parameter hybrid exchange functional[26] with the LYP correlation functional (B3LYP); and

(d) Becke's 1988 exchange functional with Perdew's correlation functional[27](BP86).

Restricted methods were used for all closed-shell systems, while unrestricted methods were employed for the open-shell species. All the electron affinities and molecular structures have been determined using the Gaussian 94[28] program suites. The default numerical integration grid (75,302) of Gaussian 94 was applied.

A standard double-ζ plus polarization (DZP) basis set for fluorine was constructed from the Huzinage−Dunning[29] contracted double-ζ Gaussian basis set by adding a set of five pure angular momentum d-like polarization functions on each atom. The contraction scheme for this fluorine basis is F(9s5p1d/4s2p1d). The DZP basis set for arsenic was constructed from the Schäfer-Horn-Ahlrichs[30] set of contracted Gaussian functions by adding a set of five pure d-type polarization functions on each atom. The contraction scheme for the arsenic basis is As(14s11p6d/8s6p3d).

Since diffuse functions are important for the anions, the DZP basis was augmented with diffuse functions; each atom received one additional s-type and one additional set of p-type functions. The diffuse function orbital exponents were determined in an "even tempered sense" as a mathematical extension of the primitive set, according to the prescription of Lee and Schaefer.[31]

TABLE 1: Zero-point Vibrational Energies within the Harmonic Approximation for AsF_n/AsF_n^- ($n = 1-6$) in eV(kcal/mol in parentheses)[a]

compounds	BHLYP	B3LYP	BP86	BLYP
AsF	0.043(0.99)	0.041(0.94)	0.040(0.92)	0.039(0.90)
AsF^-	0.034(0.78)	0.032(0.74)	0.032(0.73)	0.030(0.70)
AsF_2	0.103(2.37)	0.098(2.25)	0.095(2.19)	0.092(2.13)
AsF_2^-	0.085(1.95)	0.076(1.76)	0.072(1.67)	0.069(1.60)
AsF_3	0.190(4.37)	0.176(4.07)	0.169(3.90)	0.165(3.80)
AsF_3^-	0.130(3.01)	0.121(2.79)	0.117(2.69)	0.112(2.58)
AsF_4	0.252(5.81)	0.228(5.25)	0.214(4.95)	0.206(4.75)
AsF_4^-	0.221(5.11)	0.203(4.69)	0.193(4.45)	0.186(4.29)
AsF_5	0.376(8.68)	0.350(8.05)	0.332(7.65)	0.324(7.47)
AsF_5^-	0.304(7.01)	0.273(6.30)	0.256(5.91)	0.245(5.64)
AsF_6^-	0.442(10.20)	0.409(9.44)	0.389(8.97)	0.371(8.74)

[a] All results obtained with the DZP++ basis set.

The diffuse function exponents were thus taken to be $\alpha_s(F) = 0.1049$, $\alpha_p(F) = 0.0826$ for fluorine, and $\alpha_s(As) = 0.031455$, $\alpha_p(As) = 0.031639$ for arsenic. The final basis was thus As(15s12p6d/9s7p3d), F(10s6p1d/5s3p1d). This extended basis will be denoted as "DZP++". The total number of DZP++ basis functions ranged from 64 for AsF/AsF^- to 159 for AsF_6/AsF_6^-.

All AsF_n($n = 1-6$) stationary point geometries were interrogated by the evaluation of their harmonic vibrational frequencies at the four different levels of theory. Zero-point vibrational energies (ZPVE) evaluated at the four levels are presented in Table 1. The ZPVE differences between AsF_n and AsF_n^- ($n = 1-5$) are quite small, in the range from 0.008 to 0.079 eV. These differences could be used as a correction to the adiabatic electron affinities.

The electron affinities are evaluated as the difference of total energies in the following manner: the adiabatic electron affinity is determined as

$$EA_{ad} = E(\text{optimized neutral}) - E(\text{optimized anion})$$

the vertical electron affinity by

$$EA_{vert} = E(\text{optimized neutral}) - E(\text{anion at optimized neutral geometry})$$

and the vertical detachment energy of the anion by

$$VDE = E(\text{neutral at optimized anion geometry}) - E(\text{optimized anion}).$$

The dissociation energies for AsF_n/AsF_n^- are determined from differences in total energies in the following manner: the first dissociation energies for the neutrals refer to the reaction

$$AsF_n \rightarrow AsF_{n-1} + F \quad (1)$$

while the first dissociation energies for the anions refer to the two different reactions

$$AsF_n^- \rightarrow AsF_{n-1}^- + F \quad (2)$$

$$AsF_n^- \rightarrow AsF_{n-1} + F^- \quad (3)$$

Results and Discussion

A. As and As^-. The electron affinity of the $^4S_{3/2}$ state of the As atom was estimated to be 0.6(5) eV with an empirical method by Ginsberg and Miller as early as 1958.[32] Later a value of 0.74 eV was estimated using a simple vertical analysis by

TABLE 2: Electron Affinities of As in eV (kcal/mol in parentheses)

method	EA
BHLYP	0.74(17.0)
B3LYP	0.96(22.2)
BP86	1.04(24.0)
BLYP	0.90(20.7)
experiment	0.81 ± 0.03[a], 0.814 ± 0.01[b]

[a] Ref 35c,d. [b] Ref 35e.

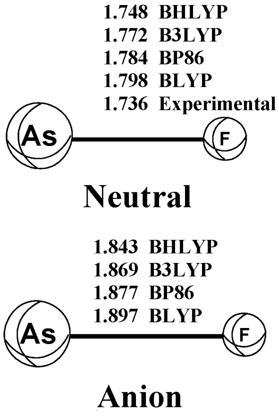

Figure 1. Molecular geometries of the X $^3\Sigma^-$ state of neutral AsF and the X $^2\Pi$ state of the AsF$^-$ anion. All bond lengths are in Å and all results were obtained with the DZP++ basis set.

Politzer[33] in 1968, and then 1.07 ± 0.1 eV using an analogous horizontal analysis by Zollweg[34] in 1969. These empirical EA values for the As atom were extrapolated from the known EAs of other elements in either the vertical group or in the same row of the periodic table. An experimental value of 0.80 ± 0.05 eV was given by Feldmann and co-workers in 1973 from their laser-photodetachment threshold spectroscopy study.[35a,b] A more precise value of 0.810 ± 0.03 eV was given by the same authors in 1977.[35c,d] In 1998, EA = 0.814 ± 0.008 eV was reported by Lippa et al. using negative-ion photoelectron spectroscopy.[35e] Our theoretical EA at various levels as well as the experimental electron affinity data are reported in Table 2. The EA values predicted by DZP++ BHLYP (0.74 eV) and DZP++ BLYP (0.90 eV) are closest to the most recent experimental result, 0.814 ± 0.008 eV. The BHLYP method predicts an EA only 0.07 eV lower than the experimental value. The fact that BHLYP gives the best predictions for electron affinities was also noted in earlier work on the second-row fluorides[15−18] and the third-row fluorides.[19−21] The predictions of the other two DFT methods are higher than the experimental value.

B. AsF and AsF$^-$. The geometries of the ground state of AsF and its anion are given in Figure 1. The AsF radical has a X $^3\Sigma^-$ ground state and an experimental bond length of 1.736 Å.[36] Latifzadeh and Balasubramanian[6] reported a theoretical bond length of 1.772 Å at the CASSCF/SOCI level of theory in conjunction with an ECP core and a 3s3p2d valence basis set. Theoretical bond lengths of 1.754 and 1.788 Å for AsF were also given by Schwerdtfeger et al.[7] with the HF and MP2 methods, using the 6-311+G* basis set for the F atom and a (6111111111s/6111111p/411d) basis set for As. The present DZP++ BHLYP bond length (1.748 Å) provides the most favorable comparison with experiment, while the other DFT methods predict longer bond lengths by up to 0.062 Å (BLYP). The general trend for bond lengths for the arsenic fluorides is BLYP > BP86 > B3LYP > BHLYP.

For the $^2\Pi$ ground state of the diatomic anion AsF$^-$, the predicted bond lengths agree with each other to 0.05 Å among the different DFT methods, with the r_e values being roughly 0.10 Å longer than those of the neutral species. The DZP++ BHLYP bond length, deemed to be the most reliable, is 1.843 Å.

TABLE 3: Adiabatic and Vertical Electron Affinities of the Neutral Arsenic Monofluoride (AsF), Arsenic Difluoride (AsF$_2$), Arsenic Trifluoride (AsF$_3$), Arsenic Tetrafluoride (AsF$_4$), Arsenic Pentafluoride (AsF$_5$), and Arsenic Hexafluoride (AsF$_6$), and Vertical Detachment Energies of Their Anions in eV (kcal/mol in parentheses)[a]

compound	method	EA$_{ad}$	EA$_{vert}$	VDE
AsF	BHLYP	0.94(21.8)	0.83(19.2)	1.08(24.8)
	B3LYP	1.14(26.1)	1.02(23.5)	1.27(29.2)
	BP86	1.18(27.1)	1.04(24.1)	1.29(29.9)
	BLYP	1.04(24.0)	0.91(20.9)	1.15(26.5)
	expt.	≥1.3[b]		
AsF$_2$	BHLYP	1.17(27.0)	0.99(22.9)	1.36(31.4)
	B3LYP	1.35(31.0)	1.19(27.4)	1.52(35.0)
	BP86	1.34(30.8)	1.19(27.5)	1.49(34.4)
	BLYP	1.22(28.2)	1.08(24.8)	1.39(32.0)
	expt.	0.8/0.9[b]		
AsF$_3$	BHLYP	0.80(18.5)	−0.54(−12.4)	3.31(76.3)
	B3LYP	1.06(24.3)	−0.26(−6.0)	3.22(74.2)
	BP86	1.09(25.1)	−0.16(−3.8)	3.00(69.2)
	BLYP	1.02(23.6)	−0.27(−6.3)	2.88(66.4)
AsF$_4$	BHLYP	4.42(102.0)	3.18(73.4)	5.38(124.0)
	B3LYP	4.58(105.7)	3.52(81.1)	5.39(124.2)
	BP86	4.45(102.6)	3.47(80.1)	5.17(119.2)
	BLYP	4.42(102.0)	4.42(102.0)	5.09(117.5)
AsF$_5$	BHLYP	2.79(64.3)	0.42(9.8)	4.80(110.6)
	B3LYP	3.14(72.4)	1.26(29.1)	4.87(112.3)
	BP86	3.17(73.2)	1.54(35.6)	4.69(108.2)
	BLYP	3.22(74.3)	1.08(24.9)	4.69(108.0)

[a] Values are not corrected for ZPVE and were obtained with the DZP++ basis set. [b] Ref 10.

Our theoretical neutral-anion energy separations for AsF, as well as experimental electron affinity data, are given in Table 3. The adiabatic electron affinity EA$_{ad}$ is predicted to be 0.94 eV (BHLYP), 1.14 eV (B3LYP), 1.18 eV (BP86), and 1.04 eV (BLYP). The zero-point vibrational energy correction is very small, around +0.01 eV (Table 1). The theoretical values are all lower than the experimental value (≥1.3 eV) reported by Pabst et al.[10] from their electron impact study in 1976. Relying upon BHLYP, we report 0.94 eV as the most reliable adiabatic electron affinity for AsF based on the previous studies of other main group fluorides.[15−22] The experimental value (≥1.3 eV[10]) for EA$_{ad}$ of AsF appears to us to be slightly too large. Higher level theoretical studies or new experiments would be most welcome for this species. The range for the theoretical vertical electron affinity EA$_{vert}$ is from 0.83 to 1.04 eV, among which the BHLYP method again predicts the smallest and most reliable value (0.83 eV). O'Hare and Wahl[12] estimated EA$_{vert}$ to be 1.1 eV in 1973, but they stated that the circuitous procedure used leads to some uncertainty. They also noted that the electron added to AsF to form AsF$^-$ goes into an essentially pure arsenic orbital, and thus EA$_{vert}$ for AsF should be similar to that for arsenic atom (0.81 ± 0.03 eV[35c,d] or 0.814 ± 0.008 eV,[35e] in Table 2). The range of VDE (AsF$^-$) is 1.08−1.29 eV, and thus the anion is quite stable with respect to electron detachment. The values of EA$_{ad}$, EA$_{vert}$, and VDE are close to each other due to the small difference in geometry between the neutral and its anion.

C. AsF$_2$ and AsF$_2^-$. The equilibrium geometries of the $^2B_1$ ground state of neutral AsF$_2$ and the $^1A_1$ ground state of AsF$_2^-$ are displayed in Figure 2. For the C_{2v} AsF$_2$ structure, the theoretical As−F bond lengths are in the range from 1.733 to 1.789 Å. As was case for AsF, the BHLYP method gives the

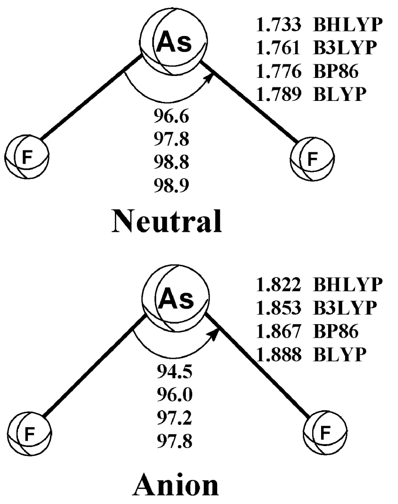

Figure 2. Molecular geometries in C_{2v}-symmetry of the X $^2B_1$ state of neutral AsF_2 and the C_{2v}-symmetry geometry of the $^1A_1$ state of the AsF_2^- anion. Bond lengths and bond angles are in Å and degrees, respectively. All results were obtained with the DZP++ basis set.

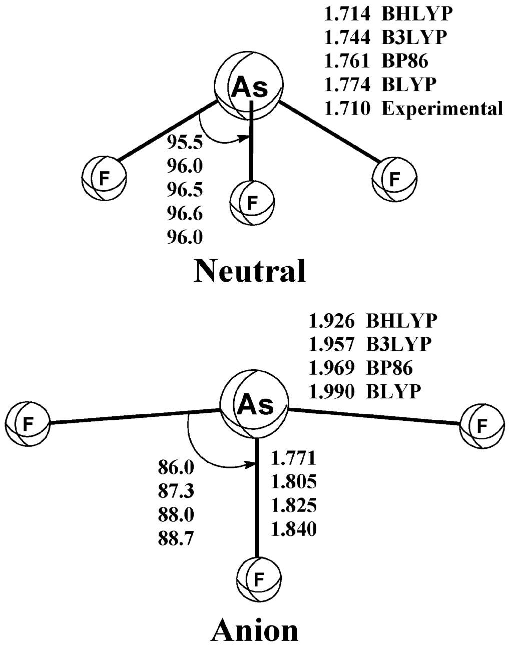

Figure 3. Molecular geometries in C_{3v}-symmetry of the X $^1A_1$ state of neutral AsF_3 and the C_{2v}-symmetry geometry of the X $^2B_1$ state of the AsF_3^- anion. Bond lengths and bond angles are in Å and degrees, respectively.

shortest and most reliable bond length. F−As−F bond angles of 96.6−98.9° are predicted by the four different functions. No experimental geometries are available for either AsF_2 or AsF_2^-. Latifzadeh and Balasubramanian[6] reported a theoretical bond length of 1.740 Å and a bond angle of 96.0° at the CASSCF/MRSDCI level of theory with the ECP+3s3p2d basis sets. Schwerdtfeger et al.[7] have optimized the geometry with $r = 1.732$ Å, $\theta = 95.5°$ at the HF level, and $r = 1.769$ Å, $\theta = 96.8°$ at the MP2 level with the same basis sets used for AsF. Their MP2 bond distance is longer than our BHLYP result, not surprising given the fact that MP2 theory sometimes yields long equilibrium bond distances even in the complete basis set limit.[37] Our BHLYP results are the closest to the earlier CASSCF and HF result. The other three DFT methods predict longer bond distances and larger bond angles.

The anion AsF_2^- also has C_{2v} symmetry, with the As−F bond distances predicted to be 1.822−1.888 Å. These distances are about 0.09 Å longer than their neutral counterparts, while the bond angles are about 2° smaller.

The theoretical EA_{ad}, EA_{vert}, and VDE, as well as the experimental electron affinity data, are listed in Table 3. The range of EA_{ad} is from 1.17 to 1.35 eV from the four different functionals, and these values are all larger than the experimental values (0.8 or 0.9 eV with two different experimental methods) given by Pabst, Bennett, Margrave, and Franklin[10,11] in the 1970s from their electron impact study. The BHLYP method predicts the smallest EA_{ad} for AsF_2 (1.17 eV), and it should be recognized as the most reliable value based on the previous studies.[15−22] The BHLYP result is also the closest to the experiment (0.8 or 0.9 eV). The experimental value for the electron affinity of AsF_2 may be slightly too small. The range of EA_{vert} is from 0.99 to 1.19 eV and the range of VDE is from 1.36 to 1.52 eV. The values for EA_{ad}, EA_{vert}, and VDE are fairly similar due to the small differences in geometry between neutral and anion, unlike those for SeF_2,[20] which show significant differences for the bond lengths and bond angles between the neutral and the anion.

D. AsF_3 and AsF_3^-. The geometries of the ground state of AsF_3 and its anion are displayed in Figure 3. The neutral AsF_3 molecule, like the valence isoelectronic PF_3, has C_{3v}-symmetry for the $^1A_1$ ground state. AsF_3 is a stable species, and many experimental and theoretical studies have been reported. As early as the 1930s, Yost and Sherborne[38] estimated that the F−As−F angle was about 97° on the basis of their Raman investigation. Howard and Wilson[39] estimated the As−F bond length of 1.80 Å, based on the bond angle of Yost and Sheborne. Pauling and Brockway[40] reported an As−F bond distance of 1.70 Å from electron diffraction, and they gave the final value (weighted average) to be 1.72 ± 0.02 Å. Later, in the 1940s, Dailey and Townes[41] reported the microwave As−F distance as 1.712 ± 0.006 Å. Subsequently, Kisliuk and Geschwind[42] estimated an ∠FAsF of 102 ± 2° from quadrupole interactions. In the 1970s, Clippard and Bartell[43] reported an experimental $r_g = 1.706 \pm 0.002$ Å and ∠FAsF = 96.2° ± 2° from electron diffraction (ED). Also in 1970 Konaka et al.[44] reported 1.7089 ± 0.0016 Å and 95°53′ ± 22′ (ED). In 1978 Smith[45] reported an experimental value $r_e = 1.704 \pm 0.010$ Å and ∠FAsF = 95°46′ ± 7′ from the rotational spectra. The currently accepted experimental results appear to be 1.710 Å and 95.9°.[46]

The previous theoretical studies of the AsF_3 geometry include the 1990 work by Schneider, Thiel, and Komornicki,[47] and the 1992 work by Breidung and Thiel[9a] with the effective core potentials(ECP) method; they reported the As−F distance and the F−As−F angle to be 1.683 Å and 95.7°, respectively. Later, Schwerdtfeger et al.[7] reported the As−F distance and the F−As−F angle to be 1.709 Å, 95.3°; 1.748 Å, 96.0°; and 1.706 Å, 96.0°, at the HF, MP2, and PM3 levels of theory, respectively. They also adopted the DFT methods (with the VWN functional) along with a number of different basis sets, and reported As−F distances in the range 1.702−1.764 Å, and the F−As−F angles as 96.0°−97.7°. Moc and Morokuma[5] predicted the neutral AsF_3 geometry as 1.693 Å, 95.4°; 1.683 Å, 95.5°; and 1.699 Å, 95.5°, with all-electron (AE), effective core potentials (ECP), and model potential methods, respectively. Kraatz, Jacobsen, Ziegler, and Boorman[8] using density functional theory within the local density approximation (LDA), reported 1.756 Å, 95.4°. Most of the previous theoretical As−F bonds are longer than the experiment. Usually the Becke gradient-corrected exchange functional increases the bond distance. The Perdew gradient-corrected correlation functional slightly offsets this error. From the present study, the trend of the bond distances is BLYP > BP86 > B3LYP > BHLYP. Our BHLYP bond distance 1.714 Å and bond angle 95.5° are closest to the experiment data, and the agreement is somewhat better than the previous theoretical results, while our other three DFT functionals predict longer As−F bonds with the longest being the value 1.774 Å given by BLYP. The bond angles from the different theoretical methods change only slightly.

For the $^2B_1$ ground state of the AsF_3^- anion, which is predicted to have a T-shaped structure with C_{2v}-symmetry (Figure 3), there are no experimental data available. Our theoretical predictions show that the As−F bonds have been elongated from the neutral structure by ~0.06 Å (axial) or ~0.21 Å (equatorial). The trend for the theoretical bond lengths with the different theoretical methods is similar to that for the neutral radical, i.e., BLYP > BP86 > B3LYP > BHLYP. The DFT $F_{ax}-As-F_{eq}$ bond angles range from 86.0 to 88.7°. The BHLYP method, the most reliable, predicts the geometrical parameters to be $r(As-F_{eq}) = 1.926$ Å, $r(As-F_{ax}) = 1.771$ Å, and $\angle FAsF = 86.0°$. We also tried to optimized structures for the C_{2v}, C_{3v}, and D_{3h} symmetries reported by Gutsev for PF_3^-,[48,49] but these stationary points all have multiple imaginary vibrational frequencies and higher energies.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 3. Unlike PF_3, which has a negative EA_{ad} (−0.32 eV),[16] the predicted EA_{ad} for AsF_3 ranges from 0.8 to 1.09 eV, among which the BHLYP method predicts the smallest value (0.80 eV). Thus we predict a major difference between the EAs of PF_3 and AsF_3. The EA_{vert} values are negative, ranging from −0.16 to −0.54 eV, while the VDE values are large and vary from 2.88 to 3.31 eV. One readily sees that the values for EA_{ad}, EA_{vert}, and VDE are significantly different due to the large difference in geometries between the neutral AsF_3 (pyramidal) and the anion AsF_3^- (T-shaped). There are no experimental results for comparison.

E. AsF_4 and AsF_4^-. The pseudo-trigonal-bipyramidal structure of C_{2v}-symmetry for the $^2A_1$ ground state for AsF_4 and the C_{2v}-symmetry geometry of the $^1A_1$ ground state for AsF_4^- are given in Figure 4. There are no experimental data. For the neutral AsF_4, the axial bond lengths given by the four DFT methods are longer than those for the equatorial bonds, by ~0.08 Å. The BHLYP method gives the shortest bond lengths 1.757 Å (for $As-F_{ax}$) and 1.686 Å (for $As-F_{eq}$). The other methods predict bond distances longer by up to 0.076 Å. The BHLYP bond distances are considered to be the most reliable results based on previous experience.[15−22]

With attachment of an extra electron to the neutral AsF_4 to form the AsF_4^- anion, the symmetry does not change, but the $F_{ax}-As-F_{ax}$ bond angle changes by 27−28°, and the $F_{eq}-As-F_{eq}$ bond angles decrease by about 3°. The bond lengths are longer than those of the neutral species by ~0.12 Å for $As-F_{ax}$ bonds, and by ~0.07 Å for $As-F_{eq}$ bonds. Moc and Morokuma[5] optimized the AsF_4^- structure, predicting the bond distances to be 1.716 Å ($As-F_{eq}$) and 1.850 Å ($As-F_{ax}$) at the HF/ECP level, and 1.725 Å ($As-F_{eq}$) and 1.855 Å ($As-F_{ax}$) at the HF/AE level. Their bond distances are shorter than our BHLYP results (1.752 and 1.881 Å), perhaps because the HF method usually underestimates bond lengths due to neglect of electron correlation. Moc and Morokuma's bond angles (191.1° at HF/ECP and 194.5° at HF/AE) are in good agreement with our BHLYP bond angle (191.6°).

The electron affinities of AsF_4 are given in Table 3. There are no experimental or other theoretical data available. The BHLYP method gives the lowest EA_{ad} (4.42 eV) and EA_{vert} (3.18 eV). The EA_{vert} ranges from 3.18 to 4.42 eV. The VDE ranges from 5.09 to 5.39 eV, indicating that the anion is quite stable with respect to electron detachment. Again, the differences between EA_{ad}, EA_{vert}, and VDE are due to the changes in geometry between AsF_4 and AsF_4^-.

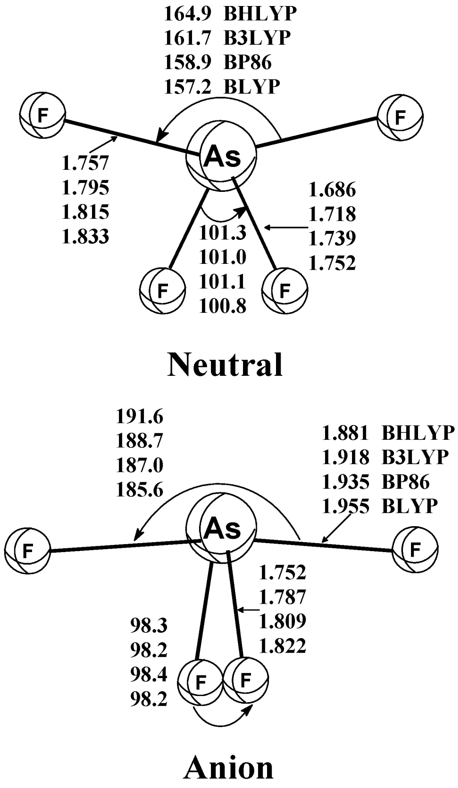

Figure 4. Molecular geometries in C_{2v}-symmetry of the X $^2A_1$ state of neutral AsF_4 and the C_{2v}-symmetry geometry of the X $^1A_1$ state of the AsF_4^- anion. Bond lengths and bond angles are in Å and degrees, respectively.

F. AsF_5 and AsF_5^-. The D_{3h} symmetry structure of the $^1A_1$ ground state for the neutral AsF_5 and the C_{4v}-symmetry structure of the $^2A_1$ ground state for the anionic AsF_5^- are shown in Figure 5. The experimental bond distances of Clippard and Bartell for neutral AsF_5 are 1.711 ± 0.005 Å ($As-F_{ax}$) and 1.656 ± 0.004 Å ($As-F_{eq}$).[43] The BHLYP method predicts 1.698 Å for the $As-F_{ax}$ bond and 1.674 Å for the $As-F_{eq}$ bond, giving the shortest and most reliable bond lengths for comparison with the experiment. The other methods predict longer bond distances by as much as 0.044 Å for $As-F_{ax}$ and 0.079 Å for $As-F_{eq}$, showing the same trend discussed above. For comparison with other theoretical work on AsF_5, the $As-F_{ax}$ and $As-F_{eq}$ bond distances obtained by Breidung and Thiel[9a] at the SCF/ECP level were reported as 1.672 and 1.644 Å, respectively. Moc and Morokuma[9b] reported the $As-F_{ax}$ and $As-F_{eq}$ bond distances as 1.671 and 1.641 Å at the RHF/ECP level, 1.680 and 1.654 Å at the RHF/AE level, and 1.715 and 1.692 Å at the MP2/AE level, respectively. Their work seems to underestimate both the $As-F_{ax}$ and $As-F_{eq}$ distances, as is normal for the HF method when the low-lying unoccupied MOs are nonbonding or antibonding. The AsF_5^- ion displays C_{4v} symmetry, and it has longer As−F bond distances than the neutral. The qualitative structural differences show that bonding in the AsF_5^- anion is quite distinct from that for the neutral species.

The EA_{ad}, EA_{vert}, and VDE values are reported in Table 3. No previous estimates or experimental values were found. Our predicted EA_{ad} is in the range from 2.79 to 3.22 eV, among which the BHLYP method predicts the smallest value, $EA_{ad} = 2.79$ eV. In the work on the valence-isoelectronic phosphorus

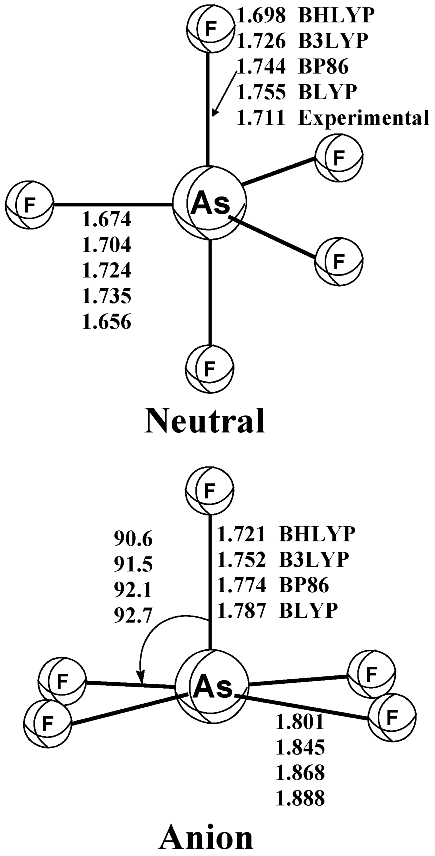

Figure 5. Molecular geometries in D_{3h}-symmetry of the X $^1A_1$ state of neutral AsF$_5$ and the C_{4v}-symmetry geometry of the X $^2A_1$ state of the AsF$_5^-$ anion. Bond lengths and bond angles are in Å and degrees, respectively.

analogues,[16] it was found that the DFT methods provided reasonable agreement with the experiment. Thus the EA$_{ad}$ value for AsF$_5$ from the BHLYP method should be regarded as dependable. The range of EA$_{vert}$ is predicted from 0.42 to 1.54 eV, and we note the BHLYP result (0.42 eV) is surprisingly much lower than others (1.08−1.54 eV). The range of VDE is from 4.69 to 4.80 eV. The BLYP method yields the highest EA$_{ad}$, but this is not the case for EA$_{vert}$ and VDE. Again, the significant divergence among EA$_{ad}$, EA$_{vert}$, and VDE for AsF$_5$/AsF$_5^-$ are due to the large difference in geometries between AsF$_5$ and AsF$_5^-$.

G. AsF$_6$ and AsF$_6^-$. No minimum was found on the potential energy surface for the neutral AsF$_6$ species. For the O_h structure, since the degenerate HOMO is not fully occupied, it will distort to a structure with lower symmetry. The optimization of the C_{2v} structure with two equatorial atoms below the plane leads to the rupture of one of the As−F bonds. Further optimizations carried out in C_s symmetry also lead to the dissociation of a fluorine atom, leaving the trigonal bipyramidal AsF$_5$ structure discussed in the previous section.

The octahedral geometry of the closed-shell $^1A_{1g}$ ground state of AsF$_6^-$ is given in Figure 6. The BHLYP As−F distance (1.734 Å) and the B3LYP result (1.764 Å) are in good agreement with the experimental values for various known AsF$_6^-$ crystalline salts, e.g., 1.719 + 0.003 Å (KAsF$_6$),[50] 1.695−1.734 Å [HON(CH$_2$)CF$_3^+$AsF$_6^-$],[51] and 1.701−1.742 Å (H$_3$OAsF$_6$).[52]

The vertical detachment of energy VDE for AsF$_6^-$ is predicted as 10.54 eV (BHLYP), 8.43 eV (B3LYP), 8.07 eV (BP86), and 7.95 eV (BLYP). Thus, the anion is remarkably stable with respect to electron detachment.

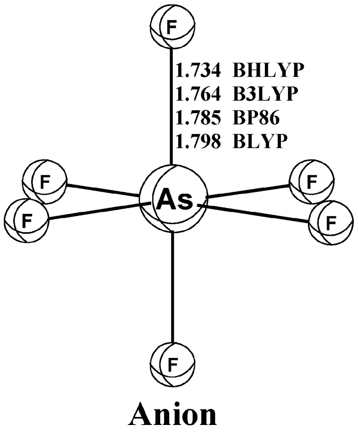

Figure 6. Molecular geometries of the O_h-symmetry structure of the X $^1A_{1g}$ state of the AsF$_6^-$ anion. Bond lengths and bond angles are in Å and degrees, respectively.

H. Dissociation Energies and Vibrational Frequencies. The first bond dissociation energies for AsF$_n$/AsF$_n^-$(n = 1−6) are given in Tables 4 and 5. The BHLYP dissociation energies are much lower than those from the other three methods. It was found in the previous studies[15−22] that the BHLYP predictions for dissociation energies were the least reliable of the four functionals employed. This emphasizes the necessity of being very selective in choosing DFT results for the theoretical predictions. While the BHLYP method is excellent for the structures and electron affinities of these main group fluorides, the thermochemistry predicted by this method is generally unreliable. As the DFT/HF hybrid BHLYP functional incorporates the standard Hartree−Fock theory to the greatest degree of all the functionals used in this study, this finding is not surprising. It is well-known that the Hartree−Fock method performs poorly for bond-breaking processes.[53]

Table 4 shows the dissociation energies (for the process AsF$_n$ → AsF$_{n-1}$ + F) of the neutral molecules. Except for BHLYP, the theoretical results for the diatomic AsF dissociation energy predicted by other three DFT functionals are in good agreement with each other. D_e(As−F) ranges from 4.22 to 4.52 eV, and the B3LYP result (4.22 eV) is the closest to the most probable experimental value 4.2 ± 0.2 eV estimated by O'Hare et al.[12] Latifzadeh and Balasubramanian[6] predicted the theoretical dissociation enegy of AsF to be 3.81 and 3.92 eV using the ECP+3s3p2d basis sets with the CASSCF/SOCI and CASSCF/SOCI+Q methods, respectively. Their theoretical results appear slightly low. Our theoretical As−F dissociation energies for AsF$_2$ range from 4.45 to 4.74 eV (excluding BHLYP). No experimental results are available, but there are some previous theoretical dissociation energies. Schwerdtfeger et al.[7] reported theoretical values of 2.89 eV (HF) and 4.75 eV (MP2) for the decomposition process AsF$_2$ → AsF + F. Obviously, the HF result is too low and unreliable. Latifzadeh and Balasubramanian[6] predicted the value of D(FAs−F) to be 4.20 eV at the CASSCF/MRSDCI level, and they stated that their result should be treated as a lower bound. Our DFT results are reasonably higher than this lower bound, and the B3LYP result 4.45 eV may be more reliable.

The predicted dissociation energies for AsF$_3$ range from 4.76 to 5.03 eV (BHLYP excluded). Sanderson[55] estimated the As−F D_0 bond energy in the AsF$_3$ molecule to be 5.03 eV. Our B3LYP bond dissociation energy (4.76 eV) is in reasonable agreement with Sanderson's estimate. For AsF$_4$, the experimental first dissociation energy is D_0 = 125 kJ/mol (i.e., 29.9 kcal/mol, or 1.30 eV), which indicates the expected weak As−F bond.[54]

TABLE 4: Dissociation Energies (D_e) for the Neutral AsF_n Species ($n = 1-5$) in eV (and kcal/mol in parentheses)[a]

dissociation	BHLYP	B3LYP	BP86	BLYP	expt.
$AsF \rightarrow As + F$	3.72(85.8)	4.22(97.2)	4.52(104.2)	4.50(103.8)	4.2 ± 0.2[b]
$AsF_2 \rightarrow AsF + F$	4.01(92.5)	4.45(102.6)	4.74(109.4)	4.67(107.7)	
$AsF_3 \rightarrow AsF_2 + F$	4.40(101.6)	4.76(109.8)	5.03(116.1)	4.92(113.2)	5.03[c]
$AsF_4 \rightarrow AsF_3 + F$	1.09(25.2)	1.46(33.7)	1.84(42.5)	1.70(39.2)	1.30[d]
$AsF_5 \rightarrow AsF_4 + F$	3.88(89.5)	3.96(91.4)	4.11(94.8)	3.87(89.3)	4.7 ± 0.2[d]

[a] Values are not corrected with ZPVE. [b] Ref 12. [c] Ref 55. [d] Ref 54.

TABLE 5: Dissociation Energies (D_e) for the Anionic AsF_n^- Species ($n = 1-6$) in eV (and kcal/mol, in parentheses)[a]

dissociation	BHLYP	B3LYP	BP86	BLYP	expt.
$AsF^- \rightarrow As + F^-$	1.73(39.8)	1.82(85.6)	1.93(44.5)	1.87(43.0)	1.9 ± 0.2[b]
$AsF_2^- \rightarrow AsF + F^-$	2.24(51.6)	2.25(51.9)	2.31(53.3)	2.22(51.1)	
$AsF_3^- \rightarrow AsF_2 + F^-$	2.27(52.3)	2.27(52.4)	2.36(54.3)	2.27(52.3)	
$AsF_4^- \rightarrow AsF_3 + F^-$	2.57(59.3)	2.50(57.8)	2.53(58.3)	2.45(56.4)	(48.2)[c]
$AsF_5^- \rightarrow AsF_4 + F^-$	3.73(86.0)	3.56(82.1)	3.52(81.2)	3.42(78.8)	
$AsF_6^- \rightarrow AsF_5 + F^-$	4.69(108.1)	4.38(100.9)	4.23(97.6)	4.11(94.8)	(>71)[d]
$AsF^- \rightarrow As^- + F$	3.93(90.7)	4.39(101.3)	4.65(107.3)	4.64(107.1)	4.7 ± 0.2[e]
$AsF_2^- \rightarrow AsF^- + F$	4.24(97.7)	4.65(107.2)	4.90(113.0)	4.85(111.9)	
$AsF_3^- \rightarrow AsF_2^- + F$	4.04(93.1)	4.99(115.1)	4.78(110.3)	4.72(108.9)	
$AsF_4^- \rightarrow AsF_3^- + F$	4.71(108.6)	4.99(115.1)	5.21(120.1)	5.10(117.6)	
$AsF_5^- \rightarrow AsF_4^- + F$	2.25(51.9)	2.52(58.1)	2.83(65.3)	2.67(61.6)	
$AsF_6^- \rightarrow AsF_5^- + F$	4.84(111.7)	4.78(110.2)	4.83(111.3)	4.56(105.3)	

[a] Values are not corrected for ZPVE. [b] Ref 12. [c] Ref 56. [d] Ref 59. [e] Estimated value from D_0(As−F) by Pabst et al.[10] combined with the experimental EA(AsF) and EA(As) values.[32]

[Note that the value of 1.30 eV in reference[54] may be dubious, because it comes from the average dissociation energy (288 kJ/mol), and the latter does not satisfy eq 8 therein.] Our DFT predictions excluding BHLYP fall in a range from 1.46 to 1.84 eV. Our B3LYP result (1.46 eV) is close to the experimental value of 1.30 eV. For AsF_5, our predicted first bond dissociation energies $D_e(F_4As-F)$ are 3.88 eV (BHLYP), 3.96 eV (B3LYP), 4.11 eV (BP86), and 3.87 eV (BLYP). O'Hare[54] reported the experimental value of the first bond-dissociation energy $D(AsF_4-F)_{axial} = 451 \pm 19$ kJ/mol (i.e., 108 ± 5 kcal/mol, or 4.7 ± 0.2 eV). O'Hare considered this value to be an upper-bound value, and a correction (as much as 20 kcal/mol is appropriate for some processes) would lower the $D(AsF_4-F)$ value.

For the anions, AsF_n^-, there are two distinct types of dissociation: that is, dissociation to neutral AsF_{n-1} plus an ionic F^-, and the dissociation to ionic AsF_{n-1}^- plus a neutral F atom. The AsF_n^- anions are isoelectronic with the neutral SeF_n species, and valence-isoelectronic with the PF_n^- anionic species. Like the neutral SeF_n[20] and anionic PF_n^-,[16] Table 5 shows that the dissociation energies for $AsF_n^- \rightarrow AsF_{n-1}^- + F$ are larger when n is even, and are smaller when n is an odd number. This zigzag phenomenon may be readily explained. With even n, AsF_n^- has a closed-shell electronic structure, and so is more stable. In contrast the products AsF_{n-1}^- and F are both open-shell systems, so the analogous dissociation energies would be larger. With odd n, the situation is the opposite, and the dissociation energies are smaller. However, the zigzag feature is not noticeable for the dissociation $AsF_n^- \rightarrow AsF_{n-1} + F^-$, because in this process both AsF_n^- and AsF_{n-1} are either closed-shell or open-shell. The general trend for these F^- dissociation energies is upward with n. This explains the prediction that when the size of the molecule increases, dissociation to a AsF_{n-1}^- plus neutral F atom becomes less preferable. Compared with the value 1.9 ± 0.2 eV estimated by O'Hare, Batana, and Wahl[12] for $AsF^-(g) \rightarrow As(g) + F^-(g)$, all four functionals predict dissociation energies (BHLYP, 1.73 eV, B3LYP, 1.82 eV; BP86, 1.93 eV; BLYP, 1.87 eV) in good agreement. From the simple relationship $D_0(As^--F) = D_0(As-F) - EA(As) + EA(AsF)$, we may estimate $D_0(As^--F) = 4.7 \pm 0.2$ eV, based on the experimental data $D_0(As-F) = 4.2 \pm 0.2$ eV, EA(As) = 0.81 ± 0.03 eV,[32] and EA(AsF) = 1.3 eV.[10] Excluding the BHLYP method, the other functionals predict dissociation energies (B3LYP, 4.39 eV; BP86, 4.65 eV; BLYP, 4.64 eV) that are in good agreement with the above experimental estimate. The experimental bond dissociation energies D_0 for $AsF_4^- \rightarrow AsF_3 + F^-$ has been reported by Larson and McMahon as 48.2 kcal/mol (i.e., 2.09 eV).[56] Our predicted values $D_e(F_3As-F^-)$ = (BHLYP, 2.57 eV; B3LYP, 2.50 eV; BP86, 2.53 eV; BLYP, 2.45 eV) are slightly too large, albeit close to the previous theoretical results 2.51 eV (MP2/ECP) and 2.41 eV (RHF/ECP) of Moc and Morokuma.[5] An estimated experimental D_0 for $AsF_6^- \rightarrow AsF_5 + F^-$ is >71 kcal/mol.[57] Moc and Morokuma[9b] reported the theoretical results 107.3 kcal/mol (RHF/ECP) and 104.1 kcal/mol (MP2/ECP). Our results (95−108 kcal/mol) are in satisfactory agreement with this lower bound.

Harmonic vibrational frequencies have been predicted for each neutral molecule with each functional, and these are reported in Table 6. Available experimental fundamentals[58−63] are included for comparison. The BHLYP method gives the best predictions for the harmonic vibrational frequencies of the AsF_n series, compared to the limited experimental values in Table 6. For the AsF_n molecules, the average error for the BHLYP method is only about 10 cm^{-1}. The other three methods all underestimate the harmonic vibrational frequencies in the AsF_n series, with the worst predictions given by the BLYP method. The fact that the HF/DFT hybrid functionals produce higher vibrational frequencies than the pure DFT exchange functionals was also observed in previous studies.[64−66] The harmonic vibrational frequencies for the anionic AsF_n^- systems are listed in Table 7. The IR and Raman spectra for different kind of AsF_6^- salts were reported by Minkwitz et al.[51] Our BHLYP vibrational frequencies for AsF_6^- are in good agreement with experiment.

Conclusions

Carefully selected DFT methods applied with the DZP++ basis set are capable of reliably predicting the limited available experimental structures, EAs, and other properties for the arsenic fluorides. The BHLYP method is the most reliable method for

TABLE 6: Harmonic Vibrational Frequencies (cm^{-1}) for AsF$_n$ (n = 1−5)

	sym.	BHLYP	B3LYP	BP86	BLYP	expt.	
AsF	σ	693	660	646	628	685.8[a]	
AsF$_2$	a_1	712	677	661	645	705 ± 10[b]	
	a_1	261	239	225	219	285 ± 10[b]	
	b_2	684	657	645	626		
AsF$_3$	a_1	752	703	676	659	740.4 s[c]	738.5[d]
	a_1	349	321	303	295	336.5 m[c]	336.8[d]
	e	714	666	643	625	702.2 s[c]	698.8[d]
	e	265	244	231	226	262.3 m[c]	262.0[d]
AsF$_4$	a_1	182	157	138	131		
	b_2	189	169	156	148		
	a_2	283	251	231	220		
	a_1	321	285	262	252		
	b_2	333	294	269	256		
	a_1	589	541	519	498		
	b_1	623	562	543	511		
	a_1	770	705	669	651		
	b_2	775	711	678	658		
AsF$_5$	a_1'	753	688	650	631		734[f]
	a_1'	664	620	593	578		644[f]
	a_2''	808	748	713	692	787.4 vs[e]	
	a_2''	407	385	369	363	400.4 s[e]	
	e'	832	767	728	709	811.4 vs[e]	813[f]
	e'	372	348	332	326	372 s[e]	
	e'	126	114	105	104	123 w[e]	130[f]
	e''	389	365	349	343		386[f]

[a] Ref 58. [b] Ref 59 (REMPI spectra). [c] Ref 60 (Infrared). [d] Ref 61 (Raman). [e] Ref 62 (Infrared). [f] Ref 63 (Raman).

TABLE 7: Harmonic Vibrational Frequencies (cm^{-1}) for Anionic AsF$_n^-$ (n = 1−5)

	sym.	BHLYP	B3LYP	BP86	BLYP	expt.
AsF$^-$	σ	546	516	509	486	
AsF$_2^-$	a_1	225	197	183	180	
	b_2	554	499	475	453	
	a_1	587	535	508	484	
AsF$_3^-$	b_1	103	95	88	89	
	a_1	208	181	166	160	
	b_2	314	282	265	250	
	b_2	408	396	399	381	
	a_1	431	409	399	385	
	a_1	638	592	566	548	
AsF$_4^-$	a_1	158	145	135	131	
	b_2	208	180	164	154	
	a_2	310	276	258	247	
	a_1	328	292	270	258	
	b_1	348	311	290	278	
	a_1	454	425	412	398	
	b_1	457	433	429	410	
	b_2	640	594	564	543	
	a_1	672	625	596	578	
AsF$_5^-$	b_2	165	140	125	115	
	e	232	212	201	194	
	b_1	309	282	266	258	
	a_1	334	280	248	229	
	e	354	314	290	275	
	b_2	512	465	441	422	
	a_1	547	500	477	459	
	e	577	516	490	463	
	a_1	711	653	618	599	
AsF$_6^-$	t_{2u}	241	225	214	210	
	t_{2g}	371	346	328	322	373, 379, 374[a]
	t_{1u}	414	387	369	362	369, 392[b]
	e_g	590	547	522	507	581, 574, 573[a]
	a_{1g}	695	632	594	575	688, 684, 685[a]
	t_{1u}	728	669	634	614	692, 691[b]

[a] Raman spectra for three kind of AsF$_6^-$ salts.[51] [b] Infrared spectra for two kind of AsF$_6^-$ salts.[51]

predicting the geometries and electron affinities of these molecular systems. The adiabatic EAs are predicted to be 0.74 eV (As), 0.94 eV (AsF), 1.17 eV (AsF$_2$), 0.80 eV (AsF$_3$), 4.42 eV (AsF$_4$), and 2.79 eV (AsF$_5$). Although neutral AsF$_6$ has at best a fleeting existence, the anion AsF$_6^-$ is very stable, with a huge vertical detachment energy. Like other fluorides (e.g., SeF$_n$[20]), the EA$_{ad}$ values for AsF$_n$ increase in a zigzag pattern when n increases from 1 to 5. The larger EAs are related to the close-shell anionic systems (AsF$_2^-$, AsF$_4^-$, AsF$_6^-$), which are clearly more stable. Most of our theoretical EA values are in good agreement with the limited experimental results, but the experimental EA for AsF appears somewhat too large.

Compared with available experimental geometrical parameters (AsF, AsF$_3$, AsF$_5$, and AsF$_6^-$), the BHLYP method predicts the most reliable As−F bond distances. The mean errors for the As−F bond distances using the four density functionals are 0.013 Å (BHLYP), 0.029 Å (B3LYP), 0.047 Å (BP86), and 0.059 Å (BLYP). For the bond angles, the four DFT methods do not reveal significant differences. The As−F bond distances predicted by BHLYP for the neutral species are 1.748 Å (AsF), 1.733 Å (AsF$_2$), 1.714 Å (AsF$_3$), 1.686 and 1.757 Å (AsF$_4$), 1.674 and 1.698 Å (AsF$_5$), respectively. The As−F bond distances for the negative ions are all longer, namely 1.843 Å (AsF$^-$), 1.822 Å (AsF$_2^-$), 1.772 and 1.926 Å (AsF$_3^-$), 1.752 and 1.881 Å (AsF$_4^-$), 1.721 and 1.881 Å (AsF$_5^-$), 1.734 Å (AsF$_6^-$), respectively. For the closed-shell anionic systems (AsF$_2^-$, AsF$_4^-$), the As−F bond distances enlongate by ∼0.1 Å relative to the neutrals, but for the open-shell anionic systems (AsF$^-$, AsF$_3^-$, AsF$_5^-$) the As−F bond distances are lengthened by ∼0.2 Å. Badger's Rule suggests that unusually long bond distances might be associated with low electron affinities. Such an argument may indeed be applied to the AsF$_n$ systems, for which the closed-shell AsF, AsF$_3$, AsF$_5$ species have smaller EAs and longer anion bond distances.

Unlike its performance for the geometries and EAs of these molecules, the BHLYP method is found to yield the least reliable dissociation energies, as seen earlier for some related molecules.[15−22] This is surely due to the fact that the BHLYP method incorporates the largest fraction of exact (Hartree−Fock) exchange. The first dissociation energies for the neutral members of the arsenic fluoride series, excluding BHLYP values, are 4.22−4.52 eV (AsF), 4.45−4.74 eV (AsF$_2$), 4.76−5.03 eV (AsF$_3$), 1.46−1.84 eV (AsF$_4$), 3.87−4.11 eV (AsF$_5$). The general trend for dissociation energy values is BP86 ∼ BLYP > B3LYP ≫ BHLYP. Compared to the experimental dissociation energies for AsF$_n$ (Table 3), these predictions are reasonable. The smaller dissociation energy for AsF$_4$ indicates a weak As−F bond. This is consistent with the fact that AsF$_4$ has apparently not been observed via rotational, vibrational, or electronic spectroscopy. In comparison with the theoretical predictions of earlier authors, our results are in best agreement with those of CASSCF/SOCI, CASSCF/SOCI+Q, and MP2.

The dissociation energies for the anionic AsF$_n^-$ systems to lose an F atom are 4.39−4.65 eV (AsF$^-$), 4.65−4.90 eV (AsF$_2^-$), 4.72−4.99 eV (AsF$_3^-$), 4.99−5.21 eV (AsF$_4^-$), 2.52−2.83 eV (AsF$_5^-$), and 4.56−4.83 eV (AsF$_6^-$). The general trend for these dissociation energy values is BP86 > BLYP > B3LYP ≫ BHLYP. The dissociation energies for loss of an F$^-$ anion are 1.82−1.93 eV (AsF$^-$), 2.22−2.31 eV (AsF$_2^-$), 2.27−2.36 eV (AsF$_3^-$), 2.45−2.53 eV (AsF$_4^-$), 3.42−3.56 eV (AsF$_5^-$), and 4.11−4.38 eV (AsF$_6^-$). The general trend is BP86 ∼ BLYP ∼ B3LYP ∼ BHLYP. All four functionals predict dissociation energies (BHLYP, 1.73 eV; B3LYP, 1.82 eV; BP86, 1.93 eV; BLYP, 1.87 eV) for AsF$^-$ that are in agreement with the rough experimental value (1.9 ± 0.2 eV). Our predicted bond dissociation energies $D_e(F_3As{-}F^-)$ = (BHLYP, 2.57 eV; B3LYP, 2.50 eV; BP86, 2.53 eV; BLYP, 2.45 eV) are close to the theoretical value of 2.51 eV estimated by Moc and Morokuma[6] using MP2/ECP method, and larger than their RHF/ECP result (2.41 eV). Thus, except for AsF_5^-, the anionic dissociation to the F^- anion is preferable.

The BHLYP method also gave good predictions for the vibrational frequencies of the neutral AsF_n series, as shown by comparison to the experimental values in Table 6. For the neutral AsF_n molecules, the average error for the BHLYP method is about only 10 cm^{-1}. The other three methods all underestimate the vibrational frequencies, with the worst predictions given by BLYP method.

Including the present paper, we have systematically studied a series of fluorides for the second- and third-row elements,[15−21] including Si, P, S, Cl, Ge, As, Se, and Br. With the same quality basis sets (DZP++) for the different fluorides, the various DFT functionals perform in the same behavior for predicting the molecular properties. The BHLYP method is the most reliable method for predicting molecular geometries and electron affinities, but the BHLYP method predicts the worst dissociation energies. The BLYP method generally yields the longest bond distances and the worst vibrational frequencies, but it may predict reasonable electron affinities. The B3LYP method also gives good vibrational frequencies, while the B3P86 and BP86 methods predict the worst (too large) electron affinities. Thus far, there are no perfect density functionals available, and we have to employ several carefully selected functionals to allow reliable predictions.

We hope that our theoretical predictions will provide strong motivation for further experimental studies of these important arsenic fluorides and their anions.

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