Atomization Energies, Formation Enthalpies, Bond Dissociation Energies, and Adiabatic Electron Affinities of the PF_n/PF_n^- Series, $n = 1-6$

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The Gaussian-2 theory (G2) and its modified versions (G2MP2, G2M(CC5), and G2M(CC6)) were applied to predict electron properties such as electron affinity and thermochemistry properties such as atomization energy, enthalpy of formation, and the bond dissociation energies of the PF_n/PF_n^- series. The atomization energies, enthalpies of formation, bond dissociation energies, and adiabatic electron affinities of the PF_n/PF_n^- series calculated according to the G2 theory and its modified versions are congruous with the available experimental data. Among the four tested G2 versions, the G2M(CC5) method is the most reliable for all of the calculated properties. It underestimates the $\Delta_f H°$ of PF_3 and PF_5 by about 4 kcal/mol and the EA of P and PF by 0.19 and 0.05 eV. G2M(CC5) has less error accumulation than the G2 theory. Moreover, fewer computational demands makes the G2M(CC5) theory more suitable for larger system than the G2 method. This study also reveals that all bond dissociation energies of $PF_{n-1}-F^-$ predicted by the BHLYP/DZP++ approach are quite close to those predicted by the G2 theory and its modifications with a difference of approximately 2 kcal/mol. However, the BHLYP/DZP++ method seriously underestimates the $PF_{n-1}-F$ and PF_{n-1}^--F bond dissociation energies (by 10−20 kcal/mol).

Introduction

Small molecules and molecular ions are prime targets for accurate quantum-mechanical predictions. The relatively small size of such species allows for the application of the most rigorous methods and comparison of their results to experimental data. Among the AB_n series of compounds, the PF_n species have attracted considerable attention from theoretical and experimental groups. The molecular structure, stability, electronic properties, and themochemistry of PF_n/PF_n^- ($n = 1-6$) have been studied theoretically by Gutsev[1] and by Tschumper et al.[2] Systematic investigations by Tschumper, Fermann, and Schaefer using the various DFT methods demonstrate that the DFT approach reproduces the molecular parameters of six experimentally known PF_n/PF_n^- species remarkably well.[2] It can be also expected that the PF_n/PF_n^- geometries not yet determined experimentally are accurately predicted by the DFT method. However, reliable experimental adiabatic values of electron affinity (EA) and bond dissociation energy of the PF_n/PF_n^- series are still scarce. A reliable experimental value of electron affinity for PF_5 is reported by Miller et al. utilizing charge-transfer reactions.[3] The well-established PF_5-F^- bond dissociation energy has been determined from fluorine anion affinity experiments by Larson et al.[4] Less reliable experimental estimations of the EA of PF and PF_2[5,7] have not been confirmed by high level theoretical studies.[2,8] However, the set of less reliable experimental bond dissociation energies of PF and PF_3[9] agree reasonably with the DFT result.[2]

Although a recent high level theoretical study of the EA of PF and PF_2 indicates that the BHLYP/DZP++ approach is quite reliable in predicting these two quantities, the well-established experimental study of the electron affinity of PF_5 suggests that the best DFT method used (BHLYP/DZP++) overestimates the adiabatic electron affinity of PF_5 by about 0.35 eV (∼40%).[2,3] Moreover, this DFT approach seriously underestimates the EA of fluorine.[2] Therefore, the theoretical estimations of the EA's of other species in the PF_n series as well as the predictions of thermochemical properties with the DFT methods are still inconclusive. To give credible and reliable theoretical estimations for those electron affinities and bond dissociation energies that have not been well determined, an accurate theoretical method is necessary. As a test of its reliability, such a method should be able to reproduce those well-established experimental and theoretical data.

The Gaussian-1 and -2 theory (G1 and G2) elaborated by Pople and co-workers has shown its excellency in reproducing the thermodynamics properties for most of the first and second row element compounds.[10−15] Recent study has demonstrated that the EA of PF and PF_2 revealed by the G2 method is consistent with those predicted by other reliable high levels of theory (CCSD(T)/aug-cc-pVQZ). Although the G2 theory slightly underestimates the EA of P by 0.09 eV, it gives a good prediction of the EA for F (3.48 eV in comparison to the experimental value of 3.40 eV).[8]

One of the flaws of the G2 theory is the use of the MP2 geometry, which is less reliable than the B3LYP/6-311G(d,p) approach.[16] The modifications of the G2 model (G2M) with the B3LYP/6-311G(d,p) geometry and zero-point energy and the couple cluster electron correlation suggested by Mebel and co-workers[16] are comparable to the G2 theory in accuracy. Moreover, the G2M approaches require less intensive computations than G2.

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In this study, the G2 theory and its modified versions (G2MP2, G2M(CC5), and G2M(CC6)) were applied to predict the electron properties of the PF_n/PF_n^- series in order to supply reliable data to test the performance of the G2 theory and its modified versions.

Methods of Calculation

Gaussian-2[12] and its modified versions G2MP2,[13] G2M(CC5), and G2M(CC6) (G2M(RCC5) and G2M(RCC6) for closed shell systems)[16] were used in this study to evaluate the energetic properties of the PF_n/PF_n^- series. In addition, the geometries of the smaller species ($n = 1-3$) were optimized at the CCSD(T)/6-311G(d,p) level. G2 and G2MP2 have been coded in the GAUSSIAN-94 program package. The G2M(CC5) and G2M(CC6) approaches were applied according to the models proposed by Mebel et al.[16]

In the G2M method the B3LYP/6-311G(d,p) level of theory was used for the geometric optimization and for the calculations of vibrational frequencies. The ZPE contributions evaluated at the B3LYP/6-311G(d,p) level were used without scaling. The energy is calculated for G2M(CC5) as

$$E = E[\mathrm{CCSD(T)/6\text{-}311G(d,p)}] + \Delta E(\mathrm{+3df\ 2p}) + \Delta E(\mathrm{HLC}) + \mathrm{ZPE} \quad (1)$$

and for G2M(CC6) as

$$E = E[\mathrm{PMP4/6\text{-}311G(d,p)}] + E[\mathrm{CCSD(T)/6\text{-}31G(d,p)}] - E[\mathrm{PMP4/6\text{-}31G(d,p)}] + \Delta E(\mathrm{+3df2p}) + \Delta E(\mathrm{HLC}) + \mathrm{ZPE} \quad (2)$$

where CCSD(T) is the unrestricted couple-cluster including calculations[17,18] for triple excitations for open shells and the restricted CCSD(T) (RCCSD(T)) calculation for closed shells; PMP4 stands for the spin-projected PMP4SDTQ energies for open shells and RMP4SDTQ energies for closed shell; ΔE(+3df2p) is the basis set correction:

$$\Delta E(\mathrm{+3df2p}) = E[\mathrm{MP2/6\text{-}311\text{+}G(3df,2p)}]\text{-}E[\mathrm{MP2/6\text{-}311G(d,p)}] \quad (3)$$

ΔE(HLC) is the "higher level correction" defined by the number of α and β valence electrons with $n_\alpha \geq n_\beta$ in mhartree:

$$\begin{aligned} \Delta E(\mathrm{HLC}) &= -5.25n_\beta - 0.19n_\alpha && \text{for} \quad \mathrm{G2M(RCC5)} \\ &= -5.30n_\beta - 0.19n_\alpha && \text{for} \quad \mathrm{G2M(CC5)} \\ &= -4.93n_\beta - 0.19n_\alpha && \text{for} \quad \mathrm{G2M(RCC6)} \\ &= -5.05n_\beta - 0.19n_\alpha && \text{for} \quad \mathrm{G2M(CC6)} \end{aligned}$$

Enthalpies of formation at 0 K ($\Delta_f H°(PF_n; 0\ K)$) are calculated according to

$$\Delta_f H°(\mathrm{PF}_n; 0\ \mathrm{K}) = \Delta_f H°(\mathrm{P}; 0\ \mathrm{K}) + n\Delta_f H°(\mathrm{F}; 0\ \mathrm{K}) - \Sigma D_o \quad (4)$$

where ΣD_o is the atomization energy. $\Delta_f H°$(P; 0 K) and $\Delta_f H°$(F; 0 K) were taken from the *JANAF* data.[9]

The adiabatic electron affinities are calculated according to the ZPE-corrected energies of the neutral molecule and its anion:

$$\mathrm{EA} = E_{\mathrm{neutral}} - E_{\mathrm{anion}}$$

Bond dissociation energies were determined by the differences in total energies of the products and reactants for the following pathway

$$\mathrm{PF}_n \rightarrow \mathrm{PF}_{n-1} + \mathrm{F}$$

$$\mathrm{PF}_n^- \rightarrow \mathrm{PF}_{n-1} + \mathrm{F}^-$$

$$\mathrm{PF}_n^- \rightarrow \mathrm{PF}_{n-1}^- + \mathrm{F}$$

TABLE 1: Atomization Energies (ΣD_o) and Enthalpies of Formation at 0 K ($\Delta_f H°(PF_n; 0\ K)$) in kcal/mol Calculated According to Eq 4[a]

	G2M(CC5)	G2M(CC6)	G2	G2MP2	expt
			ΣD_o		
PF	105.24	104.97	105.17	105.26	106.08 ± 4.6[b]
PF_2	223.24	223.01	222.51	223.23	
PF_3	354.62	353.90	353.29	354.92	
PF_4	408.76	408.74	407.25	409.24	
PF_5	541.75	540.79	539.72	542.24	545.5[c]
			$\Delta_f H°(PF_n; 0\ K)$		
PF	−11.35	−11.08	−11.28	−11.37	−12.27 ± 5.0[b]
PF_2	−110.88	−110.65	−110.15	−110.87	−115.99 ± 5.0[b]
PF_3	−223.79	−223.07	−222.46	−224.09	−227.72 ± 0.9[b]
PF_4	−259.46	−259.44	−257.95	−259.94	
PF_5	−373.98	−373.02	−371.95	−374.47	−378.47 ± 0.7[b]

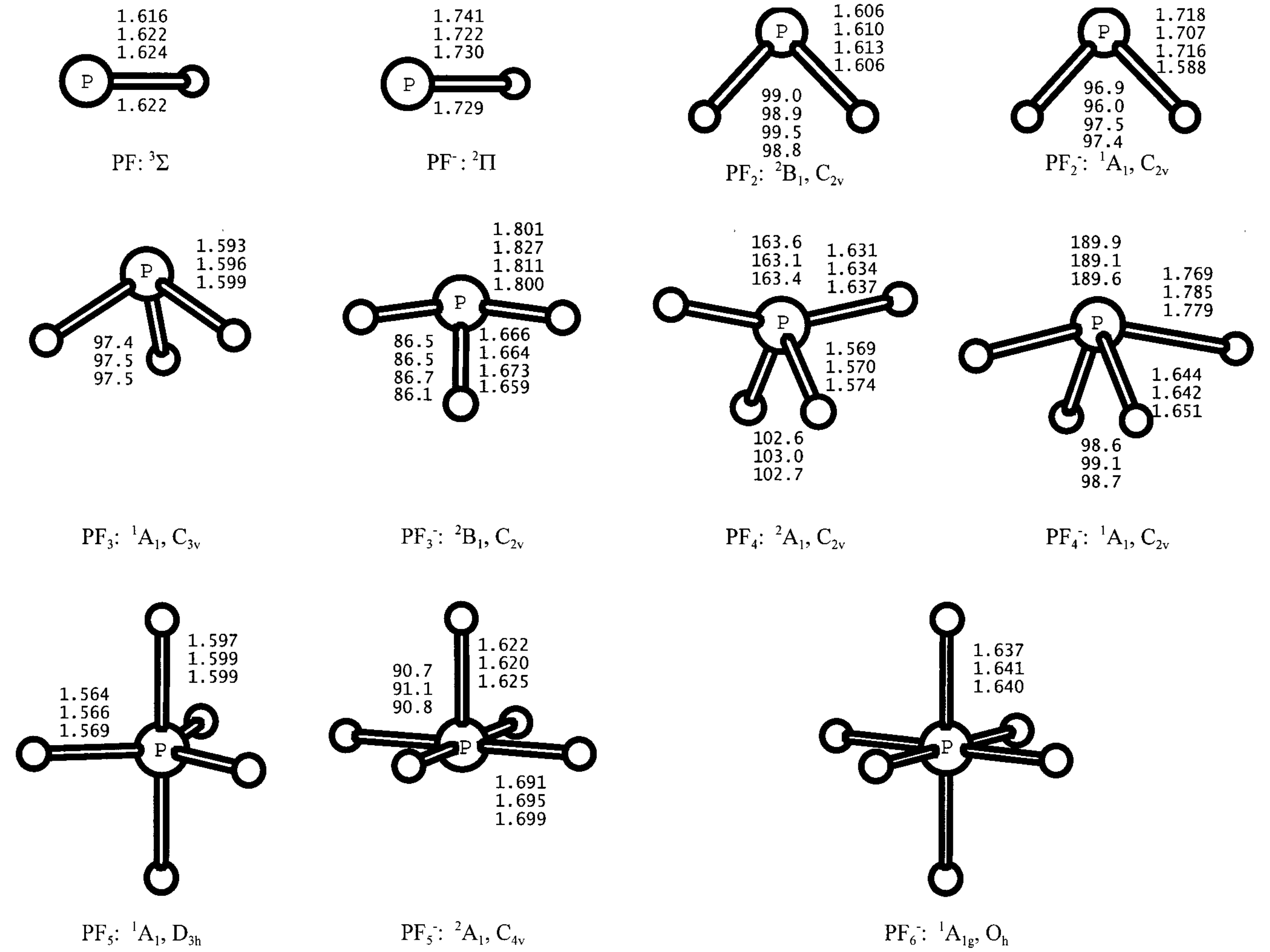
[a] *JANAF* data[9] of $\Delta_f H°$(P; 0 K) and $\Delta_f H°$(F; 0 K) were used in the calculation. [b] *JANAF* dat.[9] [c] Estimated in this work according to the averaged bond energy in PF_5 of 109.1 kcal/mol.

The Gaussian 94 program package[19] was used in the calculations.

Results and Discussion

The geometric parameters optimized at the B3LYP/6-311G(d,p) level are displayed in Figure 1 along with those obtained with different basis sets. All structures are consistent with those predicted by Tschumper, Fermann, and Schaefer in the previous study.[2] No significant changes were observed for the parameters at the B3LYP/6-311G(d,p) level in comparison with the B3LYP/DZP and B3LYP/DZP++ approximations. This confirms that the geometry of the PF_n/PF_n^- series is well-converged for the B3LYP approach with respect to the present basis set used.

Atomization energies of the neutral PF_n series calculated as the energy differences between the molecule and the atoms are listed in Table 1. Also the enthalpies of formation at 0 K (eq 4) are listed in Table 1. The enthalpies of the P and F atoms at 0 K (75.42 and 18.47 kcal/mol, respectively) taken from the *JANAF* data[9] were used in calculating the enthalpies of formation. The obtained data can be compared with the only experimental estimations for the atomization energies. The ΣD_o value calculated according to the G2 theory and its modified versions agree well with the only available experimental estimations for PF and PF_5. Four different G2 versions reveal consistent predictions for the atomization energies of PF_n. However, the G2 theory gives the lowest estimations among the methods used (except for PF for which the G2M(CC6) method results in the lowest value of the atomization energy). This trend is also revealed in the calculated values of the heat of formation for PF_n. The theoretical enthalpies of formation in Table 1 show good agreement between the theories and experiments. The available reliable experimental values for the $\Delta_f H°$ of the members of the PF_n series are $\Delta_f H°(PF_3; 0\ K)$ and $\Delta_f H°(PF_5; 0\ K)$.[9] The G2M(CC5) method underestimates the $\Delta_f H°$ of PF_3 and PF_5 by approximately 4 kcal/mol. The G2MP2 results are very close to those of G2M(CC5). The heat of formation predicted by the G2 theory for PF_3 and PF_5 is ~5−6 kcal/mol lower than the experimental value. The difference



PF: $^3\Sigma$ PF$^-$: $^2\Pi$ PF$_2$: $^2B_1$, C_{2v} PF$_2^-$: $^1A_1$, C_{2v}

PF$_3$: $^1A_1$, C_{3v} PF$_3^-$: $^2B_1$, C_{2v} PF$_4$: $^2A_1$, C_{2v} PF$_4^-$: $^1A_1$, C_{2v}

PF$_5$: $^1A_1$, D_{3h} PF$_5^-$: $^2A_1$, C_{4v} PF$_6^-$: $^1A_{1g}$, O_h

Figure 1. Geometric parameters of the PF_n/PF_n^- series obtained by the B3LYP method. Bond lengths are in Å, and bond angle, in degrees. From top to bottom, the basis set used are DZP,[2] DZP++,[2] and 6-311G(d,p). The last set of numbers for the $n = 1,2,3$ species of the series relates to the structures optimized at the CCSD(T)/6-311G(d,p) level.

TABLE 2: Bond Dissociation Energies of $PF_{n-1}-F$ in kcal/mol

	G2M(CC5)	G2M(CC6)	G2	G2MP2	BHLYP/DZP++[a]	expt
$PF \rightarrow P + F$	105.24	104.97	105.17	105.26	95.8	106 ± 5[b]
$PF_2 \rightarrow PF + F$	118.00	118.03	117.34	117.97	104.0	122 ± 10[b]
$PF_3 \rightarrow PF_2 + F$	131.38	130.89	130.78	131.69	114.6	124 ± 2[c]
$PF_4 \rightarrow PF_3 + F$	54.14	54.84	53.96	54.32	42.8	
$PF_5 \rightarrow PF_4 + F$	132.99	132.05	132.47	133.00	115.3	

[a] Reference 2. [b] Reference 9. [c] References 1 and 2.

between the G2 theory and its modifications increases proportionately to an increase in the size of the calculated species. The underestimation of the heat of formation for PF_3 and PF_5 can be explained as the result of an accumulation of errors that arises in the application of the G2 theory.[15] The relatively lower estimations of $\Delta_f H°$ for PF_3 and PF_5 compared to the other methods used in this study and to the experiments suggest that this error accumulation is more severe for the G2 theory than for the G2MP2, G2M(CC5), and G2M(CC6) modifications.

Bond dissociation energies of the neutral and anionic forms of the PF_n series are listed in Tables 2 and 3, respectively. In their systematic study of PF_n with various DFT approaches, Tschumper, Fermann, and Schaefer suggest that among all DFT versions used, the BHLYP/DZP++ level is best for predicting the electronic properties and thermochemistries of the PF_n series.[2] The BHLYP/DZP++ predictions[2] are also listed in the tables for comparison. As can be seen from the data collected in Tables 2 and 3, all theoretical estimations are in excellent agreement with the available experimental data. The theoretical PF_2-F bond dissociation energy value of 131 kcal/mol is a little higher than the experimental estimation of 124 kcal/mol. However, the experimental value is estimated from the averaged bond dissociation energy of PF_3 by multiplying by a factor of 1.1, as described in refs 9 and 20, and we expect this estimation to be lower than the real value. It is interesting to notice that all bond dissociation energies of $PF_{n-1}-F^-$ predicted by the BHLYP/DZP++ approach are quite close to those predicted by the G2 theory and its modifications with differences of approximately 2 kcal/mol. However, the BHLYP/DZP++ method seriously underestimates the $PF_{n-1}-F$ and $PF_{n-1}^{-}-F$ bond dissociation energy by 10−20 kcal/mol compared to the G2 theories and to the experimental data. In this case the BHLYP/DZP++ theory is not appropriate for a bond dissociation energy study of the PF_n series.

Adiabatic electron affinities of P, F, and PF_n are given in Table 4 along with other theoretical predictions and the available

TABLE 3: Bond Dissociation Energies of PF_n^- in kcal/mol

	G2M(CC5)	G2M(CC6)	G2	G2MP2	BHLYP/DZP++[a]	expt
$PF^- \rightarrow P + F^-$	41.33	41.02	42.23	41.11	44.3	53.10 ± 17[b]
$PF^- \rightarrow P^- + F$	108.00	107.96	107.71	107.93	96.4	
$PF_2^- \rightarrow PF + F^-$	55.62	55.23	56.26	55.66	53.5	
$PF_2^- \rightarrow PF^- + F$	119.54	119.19	119.19	119.81	105.0	
$PF_3^- \rightarrow PF_2 + F^-$	42.95	43.03	43.08	42.81	39.3	
$PF_3^- \rightarrow PF_2^- + F$	105.33	105.83	104.16	105.13	89.8	
$PF_4^- \rightarrow PF_3 + F^-$	46.93	46.85	47.16	47.10	48.1	
$PF_4^- \rightarrow PF_3^- + F$	135.36	134.71	134.86	135.97	123.4	
$PF_5^- \rightarrow PF_4 + F^-$	73.94	74.04	74.25	74.28	76.3	
$PF_5^- \rightarrow PF_4^- + F$	81.15	82.03	81.05	81.50	71.0	
$PF_6^- \rightarrow PF_5 + F^-$	92.06	91.90			94.9	84.9 ± 9.9[c]
$PF_6^- \rightarrow PF_5^- + F$	151.11	149.91			133.9	

[a] Reference 2. [b] Reference 9. [c] Reference 4.

TABLE 4: Adiabatic Electron Affinities of PF_n (in eV)

	G2M(CC5)	G2M(CC6)	G2	G2MP2	theory	expt
P	0.56	0.55	0.64	0.55		0.75[d]
F	3.46	3.45	3.48	3.45		3.40[d]
PF	0.68	0.68	0.74[a]	0.67	0.73[b]	<3.4[e]
					0.71[c]	
PF_2	0.75	0.73	0.75[a]	0.75	0.74[b]	≈1.4[f]
					0.75[c]	≥1.6 ± 0.5[g]
PF_3	−0.38	−0.36	−0.33	−0.41	−0.32[c]	
PF_4	3.14	3.11	3.18	3.14	3.17[c]	
PF_5	0.90	0.94	0.95	0.90	1.25[c]	0.75 ± 0.15[h]

[a] Reference 8. [b] CCSD(T)/aug-cc-pVQZ.[8] [c] BHLYP/DZP++.[2] [d] References 9 and 12. [e] Reference 7. [f] Reference 6. [g] Reference 5. [h] Reference 3.

TABLE 5: Contributions of the Different Corrections to CCSD(T) in the G2(CC5) Approach in the Predicted Atomization Enegies (ΣD_o) and Adiabatic Electron Affinites (EA) of PF_n

	CCSD(T)	ZPE	Δ(+3df2p)	Δ(HLP)	G2(CC5)
			ΣD_o (kcal/mol)		
PF	86.44	1.16	16.75	3.21	105.24
PF_2	187.74	2.81	31.90	6.41	223.24
PF_3	304.73	5.18	45.85	9.21	354.62
PF_4	345.74	7.04	60.44	9.62	408.76
PF_5	464.40	10.24	75.38	12.20	541.75
			EA (eV)		
P	−0.054	0.0000	0.473	0.144	0.56
F	1.387	0.0000	1.930	0.139	3.46
PF	0.019	0.0116	0.510	0.144	0.68
PF_2	0.107	0.0255	0.488	0.131	0.75
PF_3	−1.015	0.0762	0.537	0.023	−0.38
PF_4	2.608	0.0461	0.368	0.121	3.14
PF_5	0.591	0.0875	0.184	0.032	0.90

experimental results. The three modified versions of the G2 theory underestimate the EA of P and PF. The EA of atom P predicted by G2M(CC5), G2M(CC6), and G2MP2 are 0.56, 0.55, and 0.55 eV; they are 0.19, 0.20, and 0.20 eV lower than the experimental value of 0.75 eV. Previous studies suggest that the accepting ability of the low coordinated phosphorus fluorides is determined mainly by the phosphorus atom.[1,8] Following this argument, it is not surprising that G2M(CC5), G2M(CC6), and G2MP2 underestimate the adiabatic electron affinity of PF by 0.05 eV compared to the highest theoretical level calculations (0.73 eV at the CCSD(T)/aug-cc-pVQZ level).[8] The EA values of PF_2 evaluated at the modified G2 levels are in excellent accord with the CCSD(T)/aug-cc-pVQZ prediction, as can be seen from Table 4. It is evident that the G2 and G2M(CC6) methods slightly (by 0.05 eV) overestimate the EA value of PF_5. However, the theoretical prediction of the EA of PF_5 of 0.90 eV by G2M(CC5) and G2MP2 lies within the well-established experimental measurement range (0.75 ± 0.15 eV). The overestimation of the EA of PF_5 by G2 suggests that the accumulation of errors in application of the G2 theory also appears in the adiabatic electron affinity calculations for which one expects that this accumulation of error should be small due to the error cancelation. This accumulation of errors implies that the G2 theory is not equally accurate for neutral molecules and anions of the PF_n series. Although the BHLYP/DZP++ method seriously overestimates the EA of PF_5, it gives very good estimations for other PF_n species, as can be seen from Table 4. There are no experimental data for the EA of PF_3 and PF_4; however, high consistency among the estimations by different highly theoretical levels ensures the reliability of the theoretical predictions. Considering that the G2 theory slightly overestimates the EA of PF_5, we believe that the EA of 3.14 eV for PF_4 and −0.38 eV for PF_3 are more reasonable.

The coupled-cluster energy was introduced in the G2M theory to replace the QCISD(T) energy to correct the deficiencies of the Møller−Plesset theory truncated at the fourth order.[14−16] However, in the G2M(CC5) approach, the original method of calculation of the energy[16]

$$E = E_{\mathrm{bas}} + \Delta E(\mathrm{RCC}) + \Delta E(+3\mathrm{df2p}) + \Delta E(\mathrm{HLC}) + \mathrm{ZPE}$$

changes to

$$E = E[\mathrm{CCSD(T)/6\text{-}311G(d,p)}] + \Delta E(+3\mathrm{df2p}) + \Delta E(\mathrm{HLC}) + \mathrm{ZPE}$$

According to this energy expression, G2M(CC5) can be viewed as a correction of the contributions from the basis set, the zero point, and the HLC component to the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) approach. Although a previous study has demonstrated that the CCSD(T) theory excellently predicts the electron affinity of the PF_n species with very large basis sets, it is interesting to examine the performance of the CCSD(T) theory using relatively smaller basis sets. The geometries of the PF, PF^-, PF_2, PF_2^-, PF_3, and PF_3^- were reoptimized at the CCSD(T)/6-311G(d,p) level. No substantial difference was found in the comparison of the geometic parameters to those obtained at the B3LYP/6-311G(d,p) level (see Figure 1). The energy differences between the CCSD(T)/6-311G(d,p) and the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) levels were found to be less than 0.17 kcal/mol. To analyze the contribution of the different corrections, the atomization energies of the PF_n species were calculated on the basis of the CCSD(T) energy, the ZPE correction, the basis set correction, and the high-level correction, separately. The results are given in Table 5. One can see from Table 5 that the CCSD(T) energy covers about 80% of the atomization energy. Basis set corrections are very important in the calculation of atomization energy;

Δ(+3df2p) contributes around 15% to the energy values. The ZPE corrections are less important than the high-level correction and contribute less than 2% to ΣD_o. However, the CCSD(T)/6-311G(d,p) method fails in predicting the correct adiabatic electron affinities of PF_n, as can be seen from Table 5. The basis set corrections dominate the calculation of the EA. For P, F, PF, and PF_2, more than 50% of EA is covered by the Δ(+3df2p) contribution. The CCSD(T)/6-311G(d,p) value even gives the wrong sign for the EA of P.

Conclusions

All the molecular parameters predicted at the B3LYP/6-311G-(d,p) level are consistent with those calculated at the B3LYP/DZP and DZP++ levels. This confirms that the geometry of the PF_n/PF_n^- series is well converged for the applied B3LYP approach with respect to the present basis set used.

The ΣD_o calculated according to the G2 theory and its modified versions agree well with the experimental estimations. The theoretical enthalpies of formation show good agreement between the theoretical and reliable experimental values of $\Delta_f H°$. All theoretical estimations for the bond dissociation energies are in excellent agreement with the available experimental data. G2 and its modified versions reproduce the reliable experimental values and other high-level theoretical adiabatic electron affinity values. It can be expected that the PF_n/PF_n^- properties, such as atomization energy, enthalpy of formation, and bond dissociation energy, which are not yet well-characterized experimentally, are reliably predicted by the G2, G2M(CC5), G2M(CC6), and G2MP2 theories.

Among the four G2 versions tested, the G2M(CC5) method is the most reliable for all the properties calculated. The analysis of the contribution of the different corrections applied in the G2M(CC5) approach enables us to conclude that reliable atomization energies and adiabatic electron affinities obtained at the CCSD(T) level can only be reached by applying very large basis set.

This study also reveals that all bond dissociation energies for $PF_{n-1}-F^-$ predicted by the BHLYP/DZP++ approach are quite close to those predicted by the G2 theory and its modifications; the differences are around 2 kcal/mol. However, the BHLYP/DZP++ method seriously underestimates the $PF_{n-1}-F$ and $PF_{n-1}^- - F$ bond dissociation energies by 10−20 kcal/mol compared to the G2 theories and to the experimental data. In this case the BHLYP/DZP++ method is not very suitable for the bond dissociation energy study of the PF_n series.

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