Assessment of Density Functional Methods for the Calculation of Ionization Potentials of Unsaturated Molecules

S. Joantéguy,[†] G. Pfister-Guillouzo,[†] and H. Chermette*[,‡]

Laboratoire de Physico-Chimie Moléculaire, UMR-CNRS 5624, Avenue de l'Université, 64000 Pau, France, Laboratoire de Chimie Physique Théorique, Bat. 210, Université Claude Bernard Lyon-1, 43 blv. du 11 novembre 1918, F-69622 Villeurbanne Cedex, France, and Institut de Recherches sur la Catalyse, UPR CNRS 5401, 2 av. A. Einstein, F-69626 Villeurbanne Cedex, France

The suitability of density functional (DFT) methods for an accurate determination of ionization potentials is the object of a systematic analysis. The studied systems are unsaturated molecules containing 14 and 15 main group elements. The results, which have involved five different functionals, are compared to experimental results and to values estimated from calculations performed at the Møller−Plesset level up to second order.

I. Introduction

Ab initio quantum mechanical calculations are now widely used for investigating many experimental chemical problems. Photoelectron spectroscopy (UV radiation) is typically an experimental technique, which necessarily implies a theory/experiment comparison; indeed, good evaluation of ionization energies (IE) is essential for the interpretation of spectra and for reliable identification of molecules.

For rather small systems involving no transition metals, theoretical ionization energies have mostly been determined as the difference between the cation and the neutral molecule energies (IE = $E_{cation} - E_{neut.mol.}$) at MP2//HF level (MP2 energies calculated at self-consistent geometries calculated at the Hartree−Fock (HF) level). Nevertheless, this way of proceeding presents many disadvantages. (i) The important computation cost precludes the study of large systems (the CPU time dependence on the size N of the system is N^5). (ii) Post-Hartree−Fock methods, such as MP2, or even at a high-quality level, do not lead to satisfactory evaluations of ionization potentials of molecules containing third or fourth row atoms.

Considering these two drawbacks, the use of density functional theory (DFT) within its Kohn−Sham (KS) formulation is very appealing. First, because the cost of a KS-DFT calculation is at most of the same order of magnitude as a Hartree−Fock one, whereas most of the description of electron correlation is taken into account, it is substantially less expensive than traditional correlated techniques. Indeed, in a number of systematic validation studies,[1] DFT has been shown successfully to predict various molecular properties, often giving results of quality comparable to or better than second-order Moller−Plesset (MP2) perturbation theory. It appears logical to think that the use of DFT techniques could lead to a reliable theoretical evaluation of ionization potentials.

Nevertheless, despite these advantages, only few studies concern the performance of DF methods for the evaluations of ionization potentials (IP). Veszpremi et al.[2] have calculated the first ionization energy of small molecules such as H_2O, NH_3, SiH_3 and those of larger systems such as furane or thiophene,

using both DFT and unrestricted Hartree−Fock (UHF) methods. These authors obtained ionization potentials with reasonable accuracy, using the density functional method, whereas the UHF underestimates the IPs drastically. Fox and Kollman[3] have estimated the ionization potentials of several toluene derivatives with both MP2//HF and DFT methods (with SVWN, BLYP, B3LYP functionals). The local spin density approximation (LSDA) overestimates the IP systematically. Using functionals with gradient corrections (BLYP or B3LYP) leads to IPs that are underestimated, although the values obtained with the B3LYP functional are the closest to the experimental data and are comparable to the MP2 results. De Proft and Geerlings[4] have tested the performance of B3LYP and B3PW91 functionals in the calculation of ionization energies using a subset of molecules from the G2 thermochemical data set.[5] B3PW91 seems to perform considerably better for some molecules containing multiple bonds, such as CO, N_2, CS, or O_2, whereas B3LYP performs better for CH_4 and NH_3. The authors specify that no obvious reasons exist to explain this different behavior. On the other hand, this work shows that the largest mean deviation is obtained with the LDA method; it also appears that the P86 correlation functional performs somewhat better in the calculation of ionization energies than the LYP functional does.

The aim of the present work is to realize a systematic, although not exhaustive, comparison between theoretical IE obtained at different DF and MP2 levels of theory. This study is restricted to molecules containing 14 and 15 main group elements for which experimental spectra are well characterized.

Previous experimental work concerned the characterization by photoelectron spectroscopy in the gas phase of these highly reactive molecules containing low coordinated atoms of groups 14 and 15. These molecules RR′X = Y−R″ [where X is an element of group 14 (Si, Ge) and Y is an element of group 15 (N, P, As)] are generally characterized by two IPs corresponding to the ejection of an electron from the nonbonding orbital (n_Y) and the $\pi_{X=Y}$ orbital. The two corresponding IPs have the peculiarity of being generally close so that it is difficult to assign them unambiguously without theoretical help.

The rest of the paper is organized as follows. After some computational details given in section II, we will discuss the results in section III, which is split into two subsections devoted

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[†] Université de Pau.
[‡] Université Claude Bernard Lyon-1.

to molecules RR′X = X′−R″R‴ and RR′X = Y−R″, respectively. In section IV, we will enlarge the discussion on the accuracy of IPs to the dependence of molecule binding energies with the nature of the functionals.

II. Computational Details

All calculations were performed using the Gaussian 94 program.[6] The DF methods considered were the following.

(i) One method is the local density approximation (LDA), which uses Dirac−Slater expression for exchange (*S*)[7] and the Vosko, Wilk, and Nusair expression for the correlation energy of a uniform electron gas (VWN).[8]

(ii) Another method is the gradient-corrected BP86 functional consisting of Becke 88 gradient corrections[9] for exchange and Perdew 86 expression[10] for the correlation energy. This kind of functional, widely used, belongs to the so-called generalized gradient approximation (GGA) family.

(iii) A third method is the hybrid exchange functionals[11] B3LYP, B3P86, and B3PW91 as implemented in the Gaussian 94 program. In their formulation, these energy functionals include a linear combination of a small amount (20%) of exact exchange with the Becke 88 gradient-corrected exchange[9] and with the correlation energy functional (P86,[10] LYP,[12] PW91[13])

$$E_{xc} = aE_x^{HF} + bE_x^{LDA} + cE_x^{GGA} + dE_c^{LDA} + eE_c^{GGA}$$

Standard parametrization have been retained ($a = 0.20$, $b = 1 - a$, $c = 0.72$ for Becke's exchange, $e = 0.81$ for the gradient-corrected part of the correlation energy functional, and $d = 1 - e$).

Geometry optimizations were performed at both the HF level and DFT levels of theory and confirmed as true minima through vibrational analysis. Ionization energies were calculated with the ΔSCF method using energies of neutral and ionized molecules calculated at the MP2//HF and DFT levels of theory, at ground-state geometries in order to obtain vertical ionizations, in agreement with the time scale of the photoemission process.

The basis sets retained for all calculations were the 6-31G-(d,p) and 6-311G(d,p) sets, since the inclusion of polarization functions is necessary for the obtention of accurate energies. Indeed, as will be shown in the following, the 6-311G(d,p) may be still unsufficient for some MP2 calculations, whereas the 6-31G(d,p) will be found to be convenient for DFT calculations. The greater sensitivity of post-Hartree−Fock to the extent of the basis set is related to the necessity to describe properly virtual orbitals for the construction of excited states, whereas only occupied KS orbitals are necessary for DF methods, which need only a good description of the ground-state density. Because small energy differences are calculated, the addition of diffuse function has been checked on a subset of the molecules studied in this paper, with some functionals among those used in this work. It has been found that the ionization energies are modified by less than 0.03 eV for all the DFT calculations using the 6-311++G(d,p) (with respect to 6-311G-(d,p)). Much larger deviations (as far as 0.8 eV) are obtained with the 6-31++G(d,p) with respect to 6-31G(d,p) but only for hybrid functionals, i.e., those that include a pure exchange (HF-like) term. For pure GGAs, the deviation between the 6-31++G(d,p) with respect to 6-31G(d,p) remains smaller than 0.1 eV. This is in agreement with the following facts. (1) DFT methods do not require extensive basis sets, although hybrid functionals are more demanding than pure GGAs, as already known. (2) Whereas diffuse functions are essential for an accurate description of anions, cations, with a more contracted

TABLE 1: Bond Length and Ionization Energy of Ethylene

	6-31G(d,p)	6-311G(d,p)
(A) Experimental and Theoretical C=C Bond Length (Å)		
HF	1.335	1.337
SVWN	1.329	1.323
BP86	1.339	1.336
B3P86	1.328	1.325
B3LYP	1.330	1.326
B3PW91	1.329	1.326
exptl		1.339
(B) Experimental and Calculated Ionization Energy[a] (eV)		
MP2//HF	10.23 (−0.27)	10.45 (−0.05)
SVWN	11.28 (+0.78)	11.50 (+1.0)
BP86	10.51 (+0.01)	10.69 (−0.19)
B3P86	10.99 (+0.49)	11.14 (+0.64)
B3LYP	10.37 (+0.13)	10.56 (+0.06)
B3PW91	10.41 (+0.10)	10.56 (+0.06)
exptl		10.50

[a] Value in parentheses are deviations from experimental values.

density, do not require an addition of diffuse functions to a sufficiently flexible basis set.

Because of the large computing demand of computing resources of post-HF methods and because the aim of this work is to select a cheap, but sufficiently accurate, method for the determination of ionization energies of middle-size molecules, the addition of diffuse functions for MP2 calculations has not been checked.

III. Results and Discussion

III.A. Compounds Containing 14 Main Group Elements. *i. C=C. 1. Ethylene H₂C=CH₂. Geometrical Parameters.* We have reported in Table 1A the C=C bond length optimized with different DFs and HF formalism. The C=C lengths are calculated to be around 1.330 Å with the local functional SVWN and the hybrid functionals B3P86, B3LYP, B3PW91. On the other hand, the C=C length evaluated with the functional BP86 (6-31G(d,p) 1.339 Å; 6-311G(d,p) 1.336 Å) is slightly longer and closer to the one obtained with the MP2 method (6-31G-(d,p) 1.335 Å; 6-311G(d,p) 1.337 Å).

The bond length optimized with SVWN, B3P86, B3LYP, and B3PW91 functionals is underestimated (around 0.01 Å) compared to the experimental results. On the other hand, the BP86 and HF results are in good agreement with the experimental bond length.[14]

Ionization Potentials. The first ionization potential of the ethylene corresponding to the ejection of an electron from the $\pi_{C=C}$ orbital is 10.50 eV.[15]

Table 1B lists the ionization energies calculated with the MP2, SVWN, BP86, B3P86, B3LYP, and B3PW91 and with the 6-31G(d,p) and 6-311G(d,p) basis sets. The deviation from experiment is also given for each combination of basis sets and methods. The B3LYP, B3PW91, and BP86 functionals show comparable performance in the calculation of the first ionization energy of ethylene. The theoretical results are in very good agreement with the experimental results, since the deviations from experiment are inferior to 0.1 eV.

The performance of the MP2//HF method becomes comparable to those of the B3LYP, B3PW91, or BP86 functionals only when the large basis set 6-311G(d,p) is used. This fact points out an interest in the DF calculation with respect to the MP2 approach.

On the other hand, the local functional SVWN and the hybrid functional B3P86 overestimate IEs by ca. 0.8 eV (6-31G(d,p)

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TABLE 2: Calculated Ionization Energy (eV) of Isobutene[a]

	6-31G(d,p)	6-311G(d,p)
MP2//HF	9.10 (−0.35)	9.29 (−0.16)
SVWN	9.57 (+0.12)	9.78 (+0.33)
BP86	8.98 (−0.47)	9.16 (−0.29)
B3P86	9.57 (+0.12)	9.71 (+0.26)
B3LYP	8.97 (−0.48)	9.16 (−0.29)
B3PW91	9.00 (−0.45)	9.14 (−0.31)
exptl		9.45

[a] Values in parentheses are deviations from experimental values.

TABLE 3: Bond Length and Ionization Energy of Silaethene

	6-31G(d,p)	6-311G(d,p)
(A) Theoretical Bond Length		
$d_{Si=C}$ (Å)		
HF	1.713	1.711
SVWN	1.704	1.702
BP86	1.702	1.718
B3P86	1.706	1.703
B3LYP	1.706	1.707
B3PW91	1.709	1.705
d_{Si-H} (Å)		
HF	1.467	1.468
SVWN	1.491	1.489
BP86	1.490	1.489
B3P86	1.478	1.477
B3LYP	1.477	1.476
B3PW91	1.481	1.480
(B) Calculated Ionization Energy[a] (eV)		
MP2//HF	8.42 (−0.53)	8.59 (−0.36)
SVWN	9.56 (+0.61)	9.69 (+0.74)
BP86	8.86 (−0.09)	8.97 (+0.04)
B3P86	9.29 (+0.34)	9.39 (+0.44)
B3LYP	8.80 (−0.15)	8.82 (−0.13)
B3PW91	8.74 (−0.21)	8.82 (−0.13)
exptl		8.95

[a] Values in parentheses are deviations from experimental values.

+0.78 eV; 6-311G(d,p) +1.0 eV) and ca. 0.5 eV (6-31G(d,p) +0.49 eV; 6-311G(d,p) +0.64 eV), respectively.

2. Isobutene $(CH_3)_2C=CH_2$. To observe the effect of the methylation, we have calculated the first ionization energy of the isobutene (Table 2). The deviation from experiment calculated with the BP86, B3LYP, B3PW91/6-31G(d,p) increases and becomes more important (around −0.5 eV) than those observed for the ethylene. However, the use of the 6-311G(d,p) basis sets allows us to reduce this gap (to around −0.3 eV). The results obtained with MP2 are comparable and even better than those found with the DF methods mentioned above. Thus, all these methods do not appear to be able to estimate accurately the first IP of the isobutene.

Finally and surprisingly, contrary to the ethylene results, the smallest deviation is found with the hybrid functional B3P86 and the local functional SVWN. Again, the use of the 6-311G-(d,p) basis sets with these two methods does not improve the results.

ii. Si = X. 1. Silaethene $H_2Si=CH_2$. Geometrical Parameters. Geometrical parameters optimized with 6-31G(d,p), 6-311G-(d,p) and MP2, SVWN, BP86, B3P86, B3LYP, B3PW91 methods are reported in Table 3A.

Few differences between the different methods are observed. Only the Si=C bond length as calculated with the MP2 method is longer, whereas the Si−H length is estimated to be shorter. The theoretical Si=C bond lengths are in good agreement with the X-ray diffraction bond length[16] (d = 1.702) of a substituted silaethene.

TABLE 4: Calculated Ionization Energy (eV) of Dimethylsilaethene[a]

	6-31G(d,p)	6-311G(d,p)
MP2//HF	7.54 (−0.76)	7.78 (−0.52)
SVWN	8.49 (+0.19)	9.01 (+0.71)
BP86	7.84 (−0.46)	8.01 (−0.29)
B3P86	8.31 (+0.01))	9.64 (1.34)
B3LYP	7.73 (−0.57)	7.90 (−0.40)
B3PW91	7.74 (−0.56)	7.89 (−0.41)
exptl		8.3

[a] Values in parentheses are deviations from experimental values (ref 18).

Ionization Potentials. The silaethene has been synthesized by Maeïr[17] by thermolysis of a silabicyclo[2, 2, 2]octadiene and characterized by photoelectron spectroscopy. Its first ionization potential associated with the ejection of an electron from the $\pi_{Si=C}$ orbital is 8.95 eV.

The theoretical first ionization energy of the silaethene determined with the different methods is presented in Table 3B. The MP2 method significantly underestimates (around 0.5 eV) the IPs, showing the necessity of a greater treatment of correlation effects. As expected, the use of the 6-311G(d,p) basis set reduces the deviation from the experimental value from 0.53 to 0.36 eV.

On the other hand, consistent with most of the previous studies, the local functional SVWN overestimates the first IPs of the silaethene (6-31G(d,p) 0.61 eV; 6-311G(d,p) 0.74 eV) as a probable consequence of an overestimation of the binding energies. Likewise, the B3P86 hybrid functional shows a comparable performance, the deviation from the experience amounting to only 0.34 eV with 6-31G(d,p) and 0.44 eV with 6-311G(d,p). As usual for these methods, the use of larger basis does not lead to an improvement of the result. The B3LYP and B3PW91 functionals lead to small underestimations of −0.15, −0.21 eV with 6-31G(d,p) and 0.13, 0.13 eV with 6-311G-(d,p), respectively. These two methods allow a satisfactory agreement with the experimental results. Finally, the excellent performance of the pure gradient-corrected BP86 functional in the calculation of the first IP of silaethene may be emphasized.

2. Methylsilaethene $(CH_3)_2Si=CH_2$. The dimethylsilene was obtained by T. Koenig[18] by a retro-Diels reaction of 1,1-dimethylsilacyclobutane and characterized by photoelectron spectroscopy; its first IP associated with an electron ejection from the $\pi_{Si=C}$ orbital amounts to 8.3 eV.

Again, it was interesting to investigate the effects of the methylation on the quality of the theoretical IPs. The first IP of the dimethylsilene have been calculated within the MP2 and DFs methods with both the 6-31G(d,p) and the 6-311G(d,p) basis sets.

The results gathered in Table 4 show a clear deterioration of the performance of the MP2, BP86, B3LYP, and B3PW91 methods, the first IP of the dimethylsilene being overestimated by ca. 0.6 eV with 6-31G(d,p) and 0.5 eV with 6-311G(d,p). However, the DF methods still perform better than MP2.

Conclusion. The results obtained with the hybrid functionals are somewhat surprising. On one hand, the hybrid functional B3P86 clearly overestimates the IPs and delivers results comparable to those found with the nonlocal functional (SVWN). On the other hand, the B3LYP and B3PW91 give theoretical ionization energies close to the experimental values.

Nevertheless, a substitution effect as simple as a methylation is not well reproduced by these methods. In fact, their evaluation of the first IP of the isobutene or the dimethylsilaethene is disappointing. In this case, it appears that the hybrid functional

TABLE 5: Bond Length and Ionization Energy of Trimethylsilanimine

(A) Theoretical Bond Length

	6-31G(d,p)	6-311G(d,p)
	$d_{Si=N}$ (Å)	
HF	1.608	1.602
SVWN	1.596	1.592
BP86	1.615	1.612
B3P86	1.592	1.588
B3LYP	1.596	1.592
B3PW91	1.594	1.592
	d_{C-N} (Å)	
HF	1.442	1.440
SVWN	1.413	1.414
BP86	1.446	1.443
B3P86	1.430	1.426
B3LYP	1.437	1.434
B3PW91	1.428	1.428

(B) Calculated Ionization Energy[a] (eV)

	$^2A'$	$^2A''$
	6-311G(d,p)	
MP2//HF	7.99 (+0.08)	8.40 (+0.10)
SVWN	8.44 (+0.54)	8.95 (+0.65)
BP86	7.99 (+0.09)	8.37 (+0.07)
B3P86	8.49 (+0.59)	8.91 (+0.61)
B3LYP	7.89 (−0.01)	8.32 (+0.02)
B3PW91	7.87 (−0.03)	8.29 (+0.01)
	6-311G(d,p)	
SVWN	8.61 (+0.71)	9.11 (+0.81)
BP86	8.13 (+0.23)	8.52 (+0.22)
B3P86	8.59 (+0.69)	9.10 (+0.8)
B3LYP	8.03 (+0.13)	8.46 (+0.16)
B3PW91	8.02 (+0.12)	8.46 (+0.16)
exptl	7.9	8.3

[a] Values in parentheses are deviations from experimental values (ref 21).

B3P86 and the local functional SVWN associated with the 6-31G(d,p) basis sets apparently perform better and seem more attractive for estimating the IPs of molecules with methyl groups. We will come back to this point in Concluding Remarks.

III.B. Compounds Containing a 15 Main Group Element. *i. N═C. Trimethylsilanimine (CH₃)₂Si═N─(CH₃). Geometrical Parameters.* Geometrical parameters optimized with the 6-31G-(d,p) basis set are reported in Table 5A. The hybrid functionals (B3LYP, B3P86, and B3PW91) perform equivalently for the optimization of the geometry of the trimethylsilanimine. The Si═N and C─N bond lengths are slightly shorter (by ca. 0.01−0.02 Å) than those obtained with the BP86 method. In agreement with the studies of Andzelm[19] and St Amant,[20] the SVWN functional underestimates the C─N lengths (around 0.03 Å compared to the lengths obtained with BP86 and 0.01 Å compared to the optimization performed with the hybrid functionals). The geometrical parameters calculated with BP86 are close to those obtained with the MP2 approach.

Ionization Potentials. The trimethylsilanimine was synthesized and characterized by photoelectron spectroscopy by V. Metail;[21] its first ionization potential corresponding to an ejection of an electron from the nitrogen atom lone pair amounts to 7.9 eV, and the second ionization potential associated with the ionization of $\pi_{Si=N}$ is 8.3 eV.

The two theoretical first ionization potentials are reported in Table 5B. The SVWN functional overestimates the IPs of the trimethylsilanimine by ca. 0.5 eV. A similar deviation from the experimental value is obtained with the B3P86 functional. Like for the calculation of the first IP of the silaethene or the ethene, these two functionals are unsuitable for the evaluation of the

TABLE 6: Bond Length and Ionization Energy of Phosphaethene

(A) Theoretical Bond Length

	6-31G(d,p)	6-311G(d,p)
	$d_{C=P}$ (Å)	
MP2//HF	1.676	1.674
SVWN	1.669	1.664
BP86	1.686	1.683
B3LYP	1.675	1.671
B3P86	1.669	1.665
B3PW91	1.671	1.667
exptl	1.673, 1.671	
	d_{P-H} (Å)	
MP2//HF	1.413	1.415
SVWN	1.444	1.442
BP86	1.446	1.443
B3LYP	1.432	1.431
B3P86	1.430	1.429
B3PW91	1.431	1.431
exptl[a]	1.420, 1.425	

(B) Calculated Ionization Energy[b] (eV)

	$^2A''$	$^2A'$
	6-31G(d,p)	
MP2//HF	9.94 (−0.36)	10.15 (−0.55)
SVWN	11.02 (+0.72)	10.91 (+0.21)
BP86	10.26 (−0.04)	10.43 (−0.27)
B3P86	10.74 (+0.44)	10.99 (+0.29)
B3LYP	10.11 (−0.19)	10.43 (−0.27)
B3PW91	10.17 (−0.13)	10.40 (−0.30)
	6-311G(d,p)	
MP2//HF	10.11 (−0.19)	10.26 (−0.44)
SVWN	11.13 (+0.83)	10.97 (+0.27)
BP86	10.37 (−0.07)	10.49 (−0.21)
B3P86	10.83 (+0.53)	11.05 (−0.35)
B3LYP	10.24 (−0.06)	10.51 (−0.19)
B3PW91	10.27 (−0.03)	10.48 (−0.22)
exptl[a]	10.3	10.7

[a] From refs 22 and 23. [b] Values in parentheses are deviations from experimental values (ref 21).

first two IPs of the trimethylsilanimine. On the other hand, the IPs calculated with the BP86, B3LYP, B3PW91, and MP2 approaches are in good agreement with the experimental values, the deviations from the experiment being almost equivalent for the four methods (around −0.1 to +0.2 eV) and for the two bases.

ii. P═C. 1. Phosphaethene HP═CH₂. Geometrical Parameters. Phosphaethene has been synthesized by Hopkinson et al.[22] by pyrolysis of the dimethylphosphine and characterized by microwave spectroscopy. Then Kroto[23] and Brown[24] completed this work. These two studies allowed the characterization of the geometrical parameters of the phosphaethene (error inferior to 2%). Table 6A lists the C═P and P─H bond lengths optimized with the DF methods and MP2 for both of the 6-31G-(d,p) and 6-311G(d,p) basis sets, as well as the experimental values.

Concerning the C═P bond length, there are rather small differences among the B3P86, B3PW91, B3LYP, and MP2 results and the reported distances C═P are all in good agreement with the experimental values. In contrast, the BP86 value is too long (around 0.01 Å) compared to the experimental value. For the P─H bond length, a larger difference between the MP2 and DFT values is observed. In fact, the MP2 underestimates greatly the P─H distances (around 0.06 Å) whereas the DF methods underestimate the P─H bond length too, but to a smaller extent (around 0.02 Å). On the other hand, a slight and rather insignificant shortening of the bond lengths is obtained when the 6-311G(d,p) basis set is used.

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Ionization Potentials. The phosphaethene has been synthesized in the gas phase by vacuum dehydrochlorination of chloromethylphosphine and characterized by UV photoelectron spectroscopy.[25] The first two bands measured at 10.3 and 10.7 eV are assigned to the ionization of the $\pi_{C=P}$ orbital and the nonbonding orbital n_P, respectively.

A few theoretical studies in which the two first ionization potentials were calculated can be found in the literature. Bruna et al.[26] employed a large-scale multireference single- and double-excitation configuration interaction (MRD-CI) calculations for the study of the isovalent compounds ($H_2C=N-H$; $H_2C=P-H$). In particular, the first two ionization potentials of $H_2C=P-H$ are estimated at 10.09 eV (ionization of $\pi_{C=P}$ orbital) and 10.30 eV (ionization of n_P orbital). More recently, the ionization potentials of $\pi_{C=P}$ and n_P orbitals have been calculated by David et al.[27] at 9.94 and 10.19 eV, respectively.

On the other hand, Nguyen et al.[28] determined the first two ionization energies of phosphaethene, using both DF and HF methods. This work shows that the B3LYP method (6-31G-(d,p) $\pi_{P=C}$ 10.11 eV, n_P 10.43 eV; 6-311++G(3df,3pd) $\pi_{P=C}$, 10.19 eV, n_P 10.51 eV) yields improved values compared to the CCSD(T) results (6-31G(d,p) $\pi_{P=C}$ 9.92 eV, n_P 10.20 eV; 6-311++G(3df,3pd) $\pi_{P=C}$ 10.24 eV, n_P 10. 59 eV). The authors specify that the basis set dependence is found to be less severe for the DFT methods than for the post-HF methods (see comment vide supra for ethylene).

Our theoretical results of the first two ionization potentials of the phosphaethene are shown in Table 6B. The 6-31G(d,p)/MP2 results are particularly unsatisfactory; differences of -0.36 eV ($\pi_{P=C}$) to -0.56 eV (n_P) from experimental values are obtained. However, the values obtained with the 6-311G(d,p) are definitely better, the deviations from experiment becoming only -0.19 eV ($\pi_{P=C}$) and -0.44 eV (n_P). Concerning the DF methods, the SVWN functional not only overestimates the two IPs and in particular the first ionization potentials (deviation from experiment around of 0.7 eV) but also reverses the sequence of the ionizations. Although it reestablishes the good sequence, the B3P86 functional overestimates severely the first IP, too. Finally, the results obtained using the gradient-corrected functional BP86 and the hybrid functionals B3LYP and B3P86 represent a serious improvement with respect to the MP2 values. As expected and already mentioned, the use of the larger basis sets for these methods is not needed, contrary to the MP2 method.

2. 1-Phosphapropene HP=CH—CH$_3$. To investigate the capability of DF methods to estimate the effect of the methylation on the ionization potentials of the C=P skeleton, we have calculated the first two ionization potentials of HP=C(CH$_3$)H. The experimental vertical ionization energies of $\pi_{P=C}$ and n_P orbitals are observed at 9.75 and 10.35 eV, respectively. The theoretical values of the two first ionization potentials are reported in Table 7.

As in the case of the parent compound, we note the weakness of the MP2 method with the 6-31G(d,p) basis set; the deviation from experiment amounts to 0.5 eV. Concerning the DF methods, the B3P86 and SVWN methods produce results closest to the experimental values. The differences from experimental results for the BP86, B3LYP, and B3PW91 calculations are ca. 0.3 eV. Here again, the substitution by a methyl group leads to results less satisfactory than those reported for the phosphaethene. Thus, like for the silaethene, the BP86, B3LYP, and B3PW91 functionals overestimate the polarization effect during the methylation. However, the values determined with those methods are still better than the MP2/6-31G(d,p) ones.

TABLE 7: Calculated Ionization Energies (eV) of 1-Phosphapropene[a]

	$^2A''$	$^2A'$
	6-31G(d,p)	
MP2//HF	9.28 (-0.47)	9.80 (-0.55)
SVWN	10.05 ($+0.30$)	10.49 ($+0.14$)
BP86	9.45 (-0.30)	10.01 (-0.34)
B3P86	10.00 ($+0.25$)	10.62 ($+0.27$)
B3LYP	9.38 (-0.37)	10.05 (-0.30)
B3PW91		
	6-311G(d,p)	
MP2//HF	9.40 (-0.35)	10.09 (-0.26)
SVWN	10.18 ($+0.43$)	10.53 ($+0.18$)
BP86	9.55 (-0.20)	10.10 (-0.25)
B3P86	10.08 ($+0.33$)	10.70 ($+0.35$)
B3LYP	9.49 (-0.26)	10.12 (-0.23)
B3PW91	9.52 (-0.23)	10.21 (-0.14)
exptl	9.75	10.35

[a] Values in parentheses are deviations from experimental values (exptl from ref 25).

TABLE 8: Bond Length and Ionization Energy of Phosphaethyne

(A) Theoretical Bond Length

	6-31G(d,p)	6-311G(d,p)
	$d_{C\equiv P}$ (Å)	
MP2//HF	1.562	1.558
SVWN	1.546	1.541
BP86	1.557	1.553
B3LYP	1.543	1.539
B3P86	1.539	1.536
B3PW91	1.541	1.538
exptl[a]		1.540, 1.542

(B) Calculated Ionization Energy[b] (eV)

	Π	Σ^+
	6-31G(d,p)	
MP2//HF	10.73 (-0.07)	12.61 (-0.69)
SVWN	11.45 ($+0.65$)	12.94 ($+0.04$)
BP86	10.75 (-0.05)	12.75 (-0.15)
B3P86	11.22 ($+0.42$)	13.38 ($+0.48$)
B3LYP	10.63 (-0.17)	12.82 (-0.08)
B3PW91		
	6-311G(d,p)	
MP2//HF	10.81 ($+0.01$)	13.04 (-0.14)
SVWN	11.28 ($+0.48$)	13.42 ($+0.52$)
BP86	10.87 ($+0.07$)	12.87 (-0.18)
B3P86	11.30 ($+0.5$)	13.40 ($+0.90$)
B3LYP	10.76 (-0.04)	12.96 ($+0.06$)
B3PW91	10.80 (0.00)	12.93 ($+0.03$)
exptl[c]	10.8	12.9

[a] From refs 30 and 31. [b] Values in parentheses are deviations from experimental values. [c] From ref 32.

iii. P≡C. Phosphaethyne P≡CH and P≡C—CH$_3$. *Geometrical Parameters.* The experimental parameters of phosphaethyne synthesized in 1961 by Gier[29] have been determined by microwave spectroscopy.[30,31] Table 8A shows both the experimental and theoretical CP bond length.

The MP2 and BP86 methods overestimate the P≡C bond length by ca. 0.03 and 0.02 Å, respectively. The B3LYP, B3PW91, and SVWN results are, in contrast, in good agreement with the experimental value. Frost et al.[32] have determined the photoelectron spectrum of the phosphaethene. The first band at 10.8 eV is associated with the ejection of an electron from the π_{P+C} orbitals. The second band at 12.9 eV corresponds to the ionization of the lone pair on the phosphorus atom. The theoretical values listed in Table 8B show an overestimation of the ionization potentials by the SVWN and B3P86 functionals. The results obtained with the functionals BP86, B3LYP,

TABLE 9: Calculated Ionization Energies (eV) of Phosphapropyne[a]

	$^2A''$	$^2A'$
	6-31G(d,p)	
MP2//HF	9.85 (−0.05)	b
BP86	9.76 (−0.14)	11.98 (−0.12)
B3LYP	9.72 (−0.18)	12.11 (−0.01)
B3PW91	9.81 (−0.09)	12.13 (+0.03)
exptl	9.9	12.1

[a] Values in parentheses are deviations from experimental values (exptl from ref 33). [b] $\langle S^2 \rangle = 1.6$, superior to 0.75 (±10%) where $\langle S^2 \rangle$ is eigenvalue of the S^2 operator.

B3PW91, and MP2 are in satisfactory agreement with the experimental results. However, as usual, the MP2 method requires the use of the 6-311G(d,p) basis set to reach the DF method accuracy.

On the other hand, we have calculated the first two ionization potentials of 1-phosphapropyne to estimate the effect of the methylation. The experimental ionization potentials are 9.9 and 12.1 eV.[33] This example emphasizes another advantage of DF methods: the spin contamination is quite small, contrary to UHF calculations (Table 9). Moreover, despite the methylation of the molecule, good agreement of the BP86, B3PW91, and B3LYP values with the experimental values is observed (Table 9).

Conclusion. When the system, like silanimine, is strongly polarized (compared to the compounds containing only group 14 elements), the electronic relaxation of the ion occurring for both the ionization of the π system and the lone pair is more important than the correlation effects. In this case, the MP2//HF method leads to satisfactory results. On the other hand, the local functional that underestimates the polarization effects is not appropriate. Finally, the BP86 functional allows a good representation of both effects of correlation and polarization and leads to satisfactory values.

When the system is less polar, as are ethene or silaethene, correlation effects occurring during the ionization of the π system are important. In this case, the gradient-corrected functional BP86 and the hybrid functionals B3LYP and B3PW91 perform better than MP2//HF. For the phosphaalcenes, the conclusions are similar to the comments given for the silaethene class of compounds, namely, the following.

(1) The SVWN and B3P86 functionals systematically underestimate the IPs.

(2) Compared to the MP2 method, the use of the BP86, B3LYP, or B3PW91 functionals improves significantly the results. Moreover, in the case of the DFs methods, the use of a large basis set does not alter significantly the results and is not necessary, whereas in the case of the MP2 method, the need for a large basis set is essential.

(3) The methylation induces deterioration in the performance of all the functionals that gave the most accurate IPs, namely, BP86, B3LYP, and B3PW91.

For the phosphaalcynes, the results obtained with the BP86, B3LYP, and B3PW91 are in good agreement with experimental results. In addition, these methods do not suffer from the severe spin contamination present in UHF calculations.

IV. Concluding Remarks

For the evaluations of IPs, these selected examples exhibit the indefinable interest of the DF methods (BP86, B3LYP, B3PW91) over the MP2 method: improvement of the results, smaller basis sets dependence, reduced spin contamination.

One could assume that the performance of the BP86, B3LYP, and B3PW91 functionals may be credited to some error cancellation due to, on one hand, the original parametrization of Becke's Be88 exchange functional[9] and, on the other hand, the correlation functional, namely, Perdew's P86,[10] or some admixture of pure exchange in hybrid B3xxx functionals[11] with xxx = LYP[12] or PW91.[13] In the case of the B3P86, one can therefore suspect some overcompensation of errors. Finally, some attempts with other functionals, not reported here, lead to a somewhat erratic accuracy. This compensation of errors appears to be restricted to small molecules, since the methylation of the molecules studied here shuffles the previous conclusions. Indeed, this could be traced back to the parametrization of Be88 exchange GGA (one parameter, β, fitted) and Becke's hybrid functionals (three parameters in the standard form used here with Gaussian implementation).[11,6] Because the parametrization was obtained through fits bearing on a set of small molecules, namely, the G2 set,[5b] one can expect a better "universality" of the functional for small molecules than for bigger ones.

It is possible that more recent functionals such as the new Becke's hybrid functional (10 parameters)[34] for which the molecular data set was enlarged, or Barone and Adamo's functional,[35] could lead to improved IPs, and work in this direction is in progress.

However, if one sticks to the three-parameter hybrid functional, one can legitimately suspect that the standard parametrization is less universal than it should be and that the amount of pure exchange should be modulated according to the class of molecule. In our case, one could classify our molecules into two groups. The first one consists of molecules containing two atoms belonging to the p block, linked by a π bond. The second group concerns the methylated species, which involve the same amount of π electrons, but with a larger molecular volume. This pragmatic point of view could be corroborated to Perdew and co-workers' recent attempt to rationalize the mixing of the exact exchange within the density functional approximation.[36] They concluded that an ideal hybrid functional would be sophisticated to optimize this coefficient for each system and property, but they suggested that for most standard molecules of the G1 data set,[5a] the best choice was an amount of exchange equal to 0.25, a value that compares to 0.20 in standard B3xxx and to 0.28 in Becke's one independent parameter Be1 functional,[37] 0.55 for the B3(H) functional especially designed for hydrogenic systems[38] but 0.00 for systems such as ozone (O_3),[39] which is typically a system with a high number of π electrons and lone pairs over the molecular volume ratio.

One could be tempted to conclude that with the functionals presently used, we have obtained the limit corresponding to the state of the art in the determination of ionization energies. Indeed, the accuracy of the ionization energies is strongly related to those of the geometrical structure. At first glance of the data gathered in Tables 1−8, one can extract a general trend that is a statistical negative correlation between bond lengths and IPs. To quantify more precisely this trend, we have performed a constrained geometry optimization of the ethene C_2H_4 molecule with the B3LYP functional, fixing the ethylenic C=C bond length to a value varying from 130 to 136 pm. A linear relation can be extracted, giving a decrease of 0.253 eV with 5 pm of bond length increase. Therefore, an accuracy of 0.1 eV in IPs is equivalent, at least, to an accuracy of 2 pm in the bond lengths.

Finally, one could also rationalize the preceding conclusions noting that systems for which no single determinant dominates its wave function are precisely those exhibiting two or more orbitals with closely spaced eigenvalues, i.e., those exhibiting two or more low-lying excited states close to its ground state. These systems have been qualified as "abnormal" by Grev and

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Schaefer[40] or Ernzerhof, Perdew and Burke.[41] The systems studied in the present work, and especially their corresponding cation involving a π orbital energetically close to lone pairs orbitals, are not far from belonging to such a class.

If one considers that hybrid functionals are a definite improvement over pure GGA belonging to the third generation of DF according to Ziegler's classification,[1b] the question of the universality of a hybrid functional remains open.

One of the main drawbacks of hybrids functionals is that they are parametrized from the G2 data set, which is dominated by the smallest molecules for which reliable experimental data are available. Indeed, the choice of small molecules is dictated by the computational effort for parametrization, but one must suspect this database to contain an exaggerated proportion of small molecules. Indeed, Pople extended recently this data set from 55 to 148 molecules.[5c]

Binding energies have been the key factor driving the elaboration of hybrid functionals. However, most of the improvement brought by GGAs in the calculation of binding energies comes from the energy of atoms because they are the systems where the relative contribution of large reduced density gradients $\nabla\rho/\rho^{4/3}$ is maximum.

This domain of large reduced density gradients comprises mostly the "molecular surface", and its relative importance decreases as long as the system grows. Indeed, it becomes relatively small for periodic systems where large values of reduced density gradients come only from the domains of large $\nabla\rho$, whereas for atoms large reduced density gradients come from parts where the density tends to zero.

Then one should not be surprised that the best functionals for molecules such as ethene or silathene lead to worse IPs or bond lengths when these molecules are methylated (isobutene, dimethylsilaethene, ...). More generally, the correlation IP−bond energy just mentioned emphasizes the fact that GGAs are less accurate for saturated systems than for systems involving lone pairs and multiple bonds. However, the results presented in this work show that this conclusion is less straightforward for phosphaethenes.

From a pragmatic point of view, it seems that the necessary amount of pure exchange in hybrid functionals has to be smaller for molecules involving π systems than for systems involving only σ bonds. This is exactly the conclusion drawn by Burke, Ernzerhof, and Perdew[42] in their study bearing on atomization energies. Therefore, if a functional is accurate for π molecules as small as C_2H_4, any substitution by σ groups should deteriorate the performance; in other words, the amount of pure exchange in a B3xxx functional should be modified (increased).

Nevertheless, if IPs with an accuracy better than 0.1 eV cannot yet be reached with functionals used in this work, the hybrid functionals are already a promising computational strategy for the study of ionizations potentials of large heteroatomic systems.

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