Benchmark of density functional theory methods on the prediction of bond energies and bond distances of noble-gas containing molecules

Tai-Yuan Lai, Chun-Yu Yang, Hsiao-Jing Lin, Chang-Yu Yang, and Wei-Ping Hu[a)]

Department of Chemistry and Biochemistry, National Chung Cheng University, Chia-Yi 621, Taiwan

We have tested three pure density functional theory (DFT) functionals, BLYP, MPWPW91, MPWB95, and ten hybrid DFT functionals, B3LYP, B3P86, B98, MPW1B95, MPW1PW91, BMK, M05-2X, M06-2X, B2GP-PLYP, and DSD-BLYP with a series of commonly used basis sets on the performance of predicting the bond energies and bond distances of 31 small neutral noble-gas containing molecules. The reference structures were obtained using the CCSD(T)/aug-cc-pVTZ theory and the reference energies were based on the calculation at the CCSD(T)/CBS level. While in general the hybrid functionals performed significantly better than the pure functionals, our tests showed a range of performance by these hybrid functionals. For the bond energies, the MPW1B95/6-311+G(2df,2pd), BMK/aug-cc-pVTZ, B2GP-PLYP/aug-cc-pVTZ, and DSD-BLYP/aug-cc-pVTZ methods stood out with mean unsigned errors of $2.0-2.3$ kcal/mol per molecule. For the bond distances, the MPW1B95/6-311+G(2df,2pd), MPW1PW91/6-311+G(2df,2pd), and B3P86/6-311+G(2df,2pd), DSD-BLYP/6-311+G(2df,2pd), and DSD-BLYP/aug-cc-pVTZ methods stood out with mean unsigned errors of $0.008-0.013$ Å per bond. The current study showed that a careful selection of DFT functionals is very important in the study of noble-gas chemistry, and the most recommended methods are MPW1B95/6-311+G(2df,2pd) and DSD-BLYP/aug-cc-pVTZ. © *2011 American Institute of Physics*. [doi:10.1063/1.3603455]

I. INTRODUCTION

The beginning of the noble-gas chemistry is usually dated to 1962 when Bartlett synthesized the first noble-gas compound $XePtF_6$.[1] The study of noble-gas chemistry has regained significant attention in recent years due to the successful detection of many neutral noble-gas hydride molecules using the matrix photolysis/isolation techniques, notably by Räsänen and co-workers.[2–11] In particular, the first Ar-containing molecules HArF was identified spectroscopically in 2000,[12,13] and it remains as the only observed Ar-containing molecules to this date. The noble gas is also known to form ligands to transition-metal ions[14,15] and to form actinide complexes with the uranium carbide-oxide (CUO) molecule.[16–18] In addition, the advent of computational chemistry has now made the accurate prediction of the structures and stability of small noble-gas molecule possible.[19] A few new types of noble-gas molecules or ions, such as FNgBO (Ng = Ar, Kr, Xe),[20] FNgCCH (Ng = Kr, Xe),[21,22] $F^-(NgO)_n$ (Ng = He, Ar, Kr, Xe),[23,24] $FNgBN^-$ (Ar, Kr, Xe),[25] M(NBeHe)$_n$,[26] Ng@cryptand (Ng = Ar, Kr),[27] NgMX (Ng = He, Ar, Kr, Xe; M = Cu, Ag, Au; X = F, Cl, Br),[28–33] He@Mo$_6$Cl$_8$F$_6$,[34] $NXeO_2^-$,[35] $NXeO_3^-$,[35] $HNgFNgH^+$ (Ng = Ar, Kr, Xe),[36] etc., have been predicted to be stable in the gas phase at least at low temperature. The FKrCCH (Ref. 37) and many of the NgMX (Refs. 38–48) molecules have been observed by experiments. While for small noble-gas molecules, the coupled-cluster method,[49–51] multi-reference CI,[52] and CASPT2 (Ref. 53) methods with a large basis set can possibly give reliable results on the bond energies (or

stability) and structures, these calculations usually become intractable with five or more heavy atoms. The frequently used MP2 theory[54] has been shown to be unreliable in predicting the stability for noble-gas hydrides.[22,55] As for the study of "normal" larger molecules, the various density functional theory (DFT) methods seem to be good alternatives. However, due to the very unusual types of bonding in the noble-gas containing molecules and the small bond energies (if any), the experience gained (or benchmark made) from the "normal molecules" on the accuracy of the DFT methods may not apply to the study of the noble-gas chemistry. Currently, the choices of the DFT methods in the theoretical study of noble-gas containing molecules have been more or less arbitrary, and thus the accuracy of the DFT results obtained without comparing to high-level electronic structure calculation was certainly questionable. Thus, it is desirable to perform a new benchmark study on the prediction of the structures and bond energies of the noble-gas containing molecules. In particular, the energy changes of the following reaction:

$$XNgY \rightarrow X + Ng + Y \qquad (R1)$$
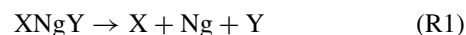
can be defined as the total noble-gas bond energy (TNGBE) of the molecule XNgY where X and Y are suitable functional groups or atoms. The bond distances between the noble gas and the closest atom in X or Y (Ng−X or Ng−Y) are defined as noble-gas bond distances (NGBD). For the molecules of the type NgMX, where MX can be, for example, BeO or AuF, the corresponding TNGBE can be defined as the energy change of the following reaction:

$$NgMX \rightarrow Ng + MX \qquad (R2)$$

a)Electronic mail: chewph@ccu.edu.tw.

TABLE I. The noble gas molecules used in the current benchmark study.

							HeBeO	HeAuF
HHeF							NeBeO	NeAuF
HArF		FArBO	FArCN	FArCH$_3$	FArBNH	FArCCH	ArBeO	ArAuF
HKrF	HKrCCH	FKrBO	FKrCN	FKrCH$_3$	FKrBNH	FKrCCH	KrBeO	KrAuF
HXeF	HXeCCH	FXeBO	FXeCN	FXeCH$_3$	FXeBNH	FXeCCH	XeBeO	XeAuF

and the NGBD is defined as the Ng−M bond distance. The study described in this article focused on the prediction accuracy on the TNGBE and NGBD for a database of 31 neutral noble-gas molecules using a few popular and newer DFT functionals with a series of commonly used basis sets. The results of the present study would be valuable to researchers in this field for choosing suitable theoretical tools for the study of larger noble-gas containing molecules. Also, the results would test the applicability and limitation of these DFT methods which might also be valuable for future development of new density functionals.

II. METHODS

A. Database of TNGBE and NGBD

We have chosen 31 small neutral noble gas molecules of the type XNgY and NgMX as our test set. These molecules, as listed in Table I, were chosen from literature or from our current research in this area. The structures of these molecules were optimized using the coupled-cluster theory CCSD(T) (Ref. 51) with the aug-cc-pVTZ basis set.[56–59] Using these structures, the TNGBE were also calculated using the CCSD(T) theory with the aug-cc-pVQZ basis set. The CCSD(T) energies were then extrapolated (using the aug-cc-pVTZ and aug-cc-pVQZ energies) to the complete basis set (CBS) limit using the inverse cubic formula by Halkier *et al.*[60] These data constituted the reference values for the current benchmark study. As a consequence of our choice of the theoretical method, an additional requirement for the test molecules was that they need to be an energy minimum at the CCSD(T)/aug-cc-pVTZ level.

B. Theoretical methods

We tested three pure density functionals: BLYP,[61, 62] MPWPW91,[63, 64] and MPWB95,[63–65] and ten hybrid density functionals: B3LYP,[61, 62, 66] MPW1B95,[63–65, 67] MPW1PW91,[63, 64] B98,[68] BMK,[69] B3P86,[66, 70] M05-2X,[71] M06-2X,[72] B2GP-PLYP,[73] and DSD-BLYP.[74] The traditional wavefunction-based MP2 method has also been tested for comparison.

C. Basis sets

A series of basis sets have been tested with the theories mentioned above. They include the Pople-type basis sets 6-31+G(d,p), 6-311+G(d,p), 6-311+G(2df,2dp),[75, 76] and the Dunning-type basis sets aug-cc-pVDZ, and aug-cc-pVTZ.[56–59] For Xe and Au atoms, basis sets with

pseudo-potentials (pp) for core electrons have been used.[77, 78] For example, the Stuttgart/Dresden (SDD) basis set[77] for Xe and Au was used with the 6-31+G(d,p) and 6-311+G(d,p) basis sets for H and other first-row elements, the aug-cc-pVDZ-pp basis set[78] was used with the aug-cc-pVDZ basis set, and the aug-cc-pVTZ-pp basis sets[78] were used with the 6-311+G(2df,2dp) and aug-cc-pVTZ basis sets.

III. RESULTS AND DISCUSSION

A. Reference data

Table II shows the reference TNGBE and Table III shows the reference NGBD calculated in the current study. In Table II, except for FArCH$_3$,[79] FArCN, and HHeF,[80, 81] all other molecules were found to have positive and sizable TNGBEs, which mean they are stable, to different extents, from the three-body dissociation channel of R1. The intrinsic stability[22] of noble-gas molecules sometimes also depends on the "bending" dissociation pathway:

$$\text{XNgY} \rightarrow \text{Ng} + \text{XY}. \qquad \text{(R3)}$$

However, the energy of the reaction and the barrier height of R2 depend also on the bonding strength of XY in addition to the noble-gas bond energy. The benchmark on R3 is also of great interest and will be investigated in a future study. We concentrated on the TNGBE obtained from R1 and R2 in the current study. We noted that due to the homolytic bond-breaking process, the reaction path of R1 is in principle a multi-configurational problem. However, since we are interested only in the energy of the reaction here, and the CCSD(T) method which is size-consistent should give accurate estimate of the TNGBE at the asymptotic limit and the NGBD at the energy minima. Some of the smallest molecules in the test set have been studied at higher theoretical levels.

TABLE II. Total noble-gas bond energies^a (TNGBEs) (in kcal/mol).

	He	Ne	Ar	Kr	Xe
HNgF	−15.0		9.5	28.5	54.6
HNgCCH				9.3	34.4
FNgBO			5.2	26.8	56.9
FNgCN			− 2.4	25.7	62.4
FNgCH$_3$			0.3	19.2	46.1
FNgBNH			12.6	32.5	61.3
FNgCCH			7.9	33.2	70.9
NgBeO	5.2	5.5	11.7	14.5	19.3
NgAuF	6.5	2.5	13.2	19.0	28.2

^{a}Calculated at CCSD(T)/CBS/CCSD(T)/aug-cc-pVTZ level.

TABLE III. Noble-gas bond distance (NGBD, in Å) calculated at CCSD(T)/aug-cc-pVTZ level.

	R_{X-Ng}	R_{Ng-Y}
	HNgF	
	H$-$Ng	Ng$-$F
He	0.811	1.415
Ar	1.329	1.979
Kr	1.477	2.042
Xe	1.663	2.116
	HNgCCH	
	H$-$Ng	Ng$-$C
Kr	1.614	2.271
Xe	1.754	2.354
	FNgBO	
	F$-$Ng	Ng$-$B
Ar	1.977	1.813
Kr	2.031	1.971
Xe	2.098	2.162
	FNgCN	
	F$-$Ng	Ng$-$C
Ar	1.889	1.908
Kr	1.940	1.975
Xe	2.031	2.123
	FNgCH$_3$	
	F$-$Ng	Ng$-$C
Ar	2.024	1.951
Kr	2.076	2.047
Xe	2.135	2.195
	FNgBNH	
	F$-$Ng	Ng$-$B
Ar	2.019	1.790
Kr	2.064	1.953
Xe	2.128	2.148
	FNgCCH	
	F$-$Ng	Ng$-$C
Ar	1.910	1.800
Kr	1.978	1.923
Xe	2.064	2.084
	NgBeO	
		Ng$-$Be
He		1.524
Ne		1.799
Ar		2.073
Kr		2.201
Xe		2.370
	NgAuF	
		Ng$-$Au
He		1.843
Ne		2.452
Ar		2.402
Kr		2.473
Xe		2.564

For example, the HArF has been calculated at CCSD(T) theory with basis sets up to aug-cc-pV5Z,[82] and the resulting CBS extrapolation predicted a TNGBE of 9.2 kcal/mol which is only 0.3 kcal/mol different from our current value in Table II. Thus, for the consistency of the reference data, we adopted our current CCSD(T)/CBS values throughout the database. We note that due to the lack of experimental data on the TNGBE, the uncertainties of the reference data could not be judged very objectively and are probably slightly higher than those in the benchmark studies on "normal" molecules. However, we believe that the reference data obtained here represent currently one of the best estimation that could be performed on a consistent basis. In addition to the stable noble-gas molecules that have been reported in literature, the FNgBNH (Ar, Kr, Xe) were also found to be stable with respect to the three-body dissociation with TNGBE of 13−61 kcal/mol. The noble-gas bonding in NgMX molecules is more electrostatic in nature, and the TNGBEs were found to be 5−19 kcal/mol for NgBeO and 3−28 kcal/mol for NgAuF. These values were slightly larger than those reported from previous study.[28–33,83–85] In Table III we noticed that for the more "ionic" F−Ng bonds, the bond distances were *not* very sensitive to the identity of the noble gas with increments <0.1 Å for Ng = Ar, Kr, and Xe, while for the more "covalent" H−Ng, Ng−B, and Ng−C bonds, the bond distances increased steadily from Ar to Xe with increments of 0.1−0.2 Å. The F−Ng and Ng−C bonds in FNgCN and FNgCCH were significantly shorter (0.1−0.2 Å) than in other molecules, perhaps due to the polarizing effects of the F atom and the multiple bonds on the carbon sides. For NgBeO, the Ng−Be distances were also sensitive to the identity of the noble gas with increments of 0.2−0.3 Å from He to Xe, while for the NgAuF, the Ng−Au distances were kept at 2.4−2.6 Å from Ne to Xe. We noted that the Ng−Au distances obtained in the current study were in good agreement (within 0.02 Å) with the experiments,[40,45,47] and were slightly different from the values obtained by similar methods in previous studies.[29–32]

B. Test results on TNGBE

Table IV shows the mean unsigned errors (MUEs) on the TNGBE by various theoretical methods for all 31 molecules. The results by the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ methods were on average 1.8 and 0.8 kcal/mol from the reference values. Thus, it seemed that the reference TNGBE were well converged with respect to the size of the basis set. For the MP2 method, the average errors were 4–8 kcal/mol which were significant considering that the TNGBE of many stable Ar-containing molecules were predicted to be only around 10 kcal/mol. The best choice of basis set was aug-cc-pVDZ with an MUE of 4.5 kcal/mol. The MUEs using the 6-31+G(d,p), 6-311+G(d,p), and aug-cc-pVTZ basis sets were as high as 8 kcal/mol and are thus not recommended basis sets for the MP2 theory. For the DFT method, the three pure functionals did not give good prediction on the TNGBE with MUEs on the order of 10 kcal/mol. Among these methods, the BLYP/6-311+G(d,p) gave the best results of 6.3 kcal/mol in MUE which was not satisfactory. Overall speaking, the hybrid functionals performed much better than the pure functional, as shown in Table IV, with the smallest MUEs around 2 kcal/mol. For all the hybrid functionals tested, we could find at least a basis set with MUEs ∼3 kcal/mol or smaller except for the M05-2X and

TABLE IV. Mean unsigned errors (MUEs) on the TNGBE (in kcal/mol) by various theoretical methods.[a]

Theory/basis set	6-31+G(d,p)	6-311+G(d,p)	6-311+G(2df,2pd)	aug-cc-pVDZ	aug-cc-pVTZ
MP2	7.1	8.1	5.0	4.5	7.4
B3LYP	4.9	5.2	3.1	3.8	3.6
MPW1B95	4.3	5.0	2.1	2.8	2.5
MPW1PW91	5.6	6.7	2.9	3.7	2.9
B98	4.2	4.0	2.9	3.4	3.4
BMK	4.5	5.3	3.2	4.6	2.3
B3P86	3.9	3.1	3.8	3.9	4.4
M05-2X	6.9	7.8	5.4	6.7	4.3
M06-2X	8.8	10.1	7.4	8.2	5.6
B2GP-PLYP	7.9	9.6	3.3	4.9	2.2
DSD-BLYP	7.1	8.9	2.5	3.8	2.0
BLYP	7.8	6.3	8.0	8.0	8.9
MPWB95	12.3	11.0	13.7	13.1	14.0
MPWPW91	8.4	7.1	9.7	9.4	10.3

[a]MUEs for the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ methods are 1.8 and 0.8 kcal/mol, respectively.

M06-2X functionals which, on the other hand, performed extremely well on many other types of main-group chemical bonding.[72,86–91] For the B3LYP, MPW1B95, MPW1PW91, and B98 functionals, the best choice of basis set was 6-311+G(2df,2pd) with MUEs of 3.1, 2.1, 2.9, and 2.9 kcal/mol, respectively. The B3P86/6-311+G(d,p) method also performed well with an MUE of 3.1 kcal/mol. The best basis set for the BMK, B2GP-PLYP, and DSD-BLYP functionals was aug-cc-pVTZ with MUEs of 2.0−2.3 kcal/mol. The four methods that stood out in the test on TNGBE were MPW1B95/6-311+G(2df,2dp), BMK/aug-cc-pVTZ, B2GP-PLYP/aug-cc-pVTZ, and DSD-BLYP/aug-cc-pVTZ. Their MUEs on TNGBEs, ∼2 kcal/mol, were only half of the best MP2 method. We also note that the dispersion terms in the DSD-BLYP functional were almost negligible in the current study. Excluding the dispersion terms in most cases would only make differences less than 0.1 kcal/mol on the MUEs for TNGBE.

We could also categorize the test molecules into seven groups (HNgF, HNgCCH, FNgBO/FNgBNH, FNgCCH/FNgCN, FNgCH$_3$, NgBeO, and NgAuF) and study the performance of the various theoretical methods on different groups. The detailed data on MUEs by all the tested methods on these groups are included in the supplementary material.[92] For the HNgF (Ng = He, Ar, Kr, Xe) group, the MP2/aug-cc-pVTZ method performed very well with MUE of 1.8 kcal/mol, and are among the best methods with MPW1B95/6-311+G(2df,2pd), B98/6-311+G(2df,2pd), B2GP-PLYP/aug-cc-pVTZ, and DSD-BLYP/aug-cc-pVTZ with MUEs of 1.9−2.5 kcal/mol. The performance of the DFT methods on this group basically followed the trends of the overall performance described earlier. In comparison, the CCSD(T) theory with aug-cc-pVTZ and aug-cc-pVQZ basis sets gave MUE of 2.4 and 1.0 kcal/mol, respectively, on this group.

For the HNgCCH group (Ng = Kr, Xe), the only acceptable MP2 method was with the aug-cc-pVDZ basis set. (The HArCCH is not a minimum at the CCSD(T)/aug-cc-pVTZ level, and is thus not included in the test molecules.) The MP2/aug-cc-pVTZ method significantly overestimated the TNGBE of this type of molecule as discussed in

earlier studies.[22,55] The DSD-BLYP functional gave the smallest MUE of 1.5 kcal/mol using the basis aug-cc-pVTZ set. The B3LYP functional performed well on this group, with the best MUE of 2.2 kcal/mol using the 6-311+G(2df,2pd) basis set. The B98 functional performed very well on HNgCCH, with MUEs of 1.9 and 2.0 kcal/mol using 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets, respectively. The MPW1B95/6-311+G(2df,2pd) and B2GP-PLYP/aug-cc-pVTZ methods also performed satisfactorily. In comparison, the CCSD(T) theory with aug-cc-pVTZ and aug-cc-pVQZ basis sets gave MUE of 1.0 and 0.4 kcal/mol, respectively, on this group.

For the FNgBO/FNgBNH group (Ng = Ar, Kr, Xe), the MP2/6-311+G(2df,2pd) and MP2/aug-cc-pVDZ method gave good MUEs of 2.1 and 1.7 kcal/mol, respectively, while other MP2 methods were not satisfactory. Most of the hybrid functionals with larger basis sets gave MUEs of 2−5 kcal/mol, and the best methods were MPW1B95/6-311+G(2df,2pd) and DSD-BLYP/aug-cc-pVTZ with MUEs of 2.0 and 2.2 kcal/mol, respectively. In comparison, the CCSD(T) theory with aug-cc-pVTZ and aug-cc-pVQZ basis sets gave MUE of 2.5 and 1.2 kcal/mol, respectively on this group.

For the FNgCCH/FNgCN group (Ng = Ar, Kr, Xe), the MP2 results were very unsatisfactory with MUEs of 4−22 kcal/mol. A few of the hybrid functionals performed rather well on this group. In particular, the MPW1B95, BMK, and DSD-BLYP functionals with 6-311+G(2df,2pd) basis set and the BMK functional with aug-cc-pVTZ basis set gave MUEs of 2.3, 2.1, 2.3, and 1.2 kcal/mol, respectively. In comparison, the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ methods gave MUEs of 2.6 and 1.1 kcal/mol, respectively.

For the FNgCH$_3$ group (Ng = Ar, Kr, Xe), the MP2/6-311+G(2df,2pd) method performed very well with an MUE of only 1.2 kcal/mol. Most of the hybrid functionals performed reasonably well (MUEs 2−6 kcal/mol) except for M05-2X and M06-2X. The best results were obtained from the MPW1B95/6-311+G(2df,2pd), B3P86/6-311+G(d,p), and DSD-BLYP/aug-cc-pVTZ methods with MUEs of 2.2, 2.2, and 2.1 kcal/mol, respectively. In comparison,

the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ methods gave MUEs of 2.5 and 1.0 kcal/mol, respectively.

For the NgBeO group (Ng = He, Ne, Ar, Kr, Xe), all the MP2 methods performed rather well. It is not surprising since the interactions between Ng and BeO are mostly electrostatic. The most accurate results were obtained using the 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets with MUEs of 0.6 and 0.4 kcal/mol, respectively. Almost all the DFT methods, including the pure functionals, gave good results. Most of the functionals tested could reach MUEs below 1 kcal/mol with suitable basis sets and it is difficult to tell which ones were best. The averaged differences between the reference values and the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ methods were 0.4 and 0.2 kcal/mol, respectively.

For the NgAuF group (Ng = He, Ne, Ar, Kr, Xe), the prediction seemed to be more difficult than the NgBeO group. In the MP2 methods, only the aug-cc-pVDZ basis set gave good result with MUE of 0.8 kcal/mol. The MUEs by all the DFT methods were significantly larger than on the NgBeO group. The best result was obtained from the DSD-BLYP functional with 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets with MUEs of 1.5 and 1.4 kcal/mol, respectively. The MPW1B95, BMK, B3P86, M05-2X, and B2GP-PLYP functionals with 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets also gave reasonable MUEs of 2−3 kcal/mol. In comparison, the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ methods gave MUEs of 1.0 and 0.4 kcal/mol, respectively. On both NgBeO and NgAuF groups, the performance of pure and hybrid functionals was similar.

We also compiled the benchmark results on TNGBE by the identity of the noble gas atom. The detailed MUE data are listed in the supplementary material.[92] Of course, very few molecules in the database contain He or Ne and thus the average errors are less statistically meaningful for these two noble gases. There are three helium-containing molecules in our current database, HHeF, HeBeO, and HeAuF of which the reference TNGBE values are −15.0, 5.2, and 6.5 kcal/mol, respectively. The best MP2 results were from 6-311+G(2df,2pd) basis sets with MUE of 1.0 kcal/mol, respectively. The most accurate DFT results came from the DSD-BLYP/6-311+G(2df,2dp) method with an MUE of 0.4 kcal/mol. The B2GP-PLYP functional with larger basis sets also gave very satisfactory MUEs of ∼0.7 kcal/mol. There are only two neon-containing molecules in our current database, NeBeO and NeAuF. Since the TNGBEs are mostly electrostatic in nature, most of the methods performed well and gave MUEs below 1 kcal/mol while absolute values of the TNGBEs are 5.5 and 2.5 kcal/mol, respectively. For the two data, the best agreement came from MPW1B95/6-311+G(2df,2pd), MPWB95/6-311+G(2df,2pd), M05-2X/6-311+G(d,p), B2GP-PLYP/aug-cc-pVTZ, and DSD-BLYP with aug-cc-pVDZ and aug-cc-pVTZ basis sets with MUEs of ∼0.1 kcal/mol. For the Ar-containing molecules, none of the MP2 methods gave MUEs below 5 kcal/mol. The smallest MUEs (<2.0 kcal/mol) were obtained from MPW1B95/6-311+G(2df,2pd), MPW1PW91 with 6-311+G(2df,2pd) and aug-cc-pVDZ basis sets, BMK/aug-cc-pVTZ, B2GP-PLYP/aug-cc-pVTZ, and DSD-BLYP/6-311+G(2df,2pd).

For the Kr-containing molecules, the MP2 methods were also unsatisfactory. The smallest MUEs (<1.5 kcal/mol) were obtained from B3LYP/6-311+G(2df,2pd), B3LYP/aug-cc-pVDZ, MPW1B95 with 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets, and B2GP-PLYP/aug-cc-pVTZ. For most DFT methods, the MUEs for Kr-containing molecules were smaller than those for Ar-containing molecules. The prediction of the TNGBEs of the Xe-containing molecules seemed to be the most difficult. All the MP2 methods gave MUEs larger than 5 kcal/mol, and most of the DFT methods gave MUEs larger than 4 kcal/mol. The better results came from MPW1B95 and B98 with 6-311+G(2df,2dp) and aug-cc-pVTZ basis sets, BMK/6-311+G(d,p), B3P86 with 6-311+G(2df,2dp), aug-cc-pVDZ, and aug-cc-pVTZ basis sets, and DSD-BLYP/aug-cc-pVTZ. From the above discussion and the data in the supplementary material the MPW1B95/6-311+G(2df,2pd) method and the BMK, B2GP-PLYP, and DSD-BLYP functionals with the aug-cc-pVTZ basis set showed the most consistent performance on the TNGBEs regarding to the identity of the noble gas. This conclusion also parallels the results seen in Table IV.

C. Test results on NGBD

Table V shows the MUEs on the NGBD by various theoretical methods for all 31 molecules with 52 bond distances. For the MP2 theory, the 6-31+G(d,p) and 6-311+G(d,p) basis set gave rather large errors of ∼0.04 Å, and the other three basis sets gave errors of ∼0.02 Å. This is approximately twice the average errors for MP2 bond distance prediction on molecules containing first- and second-row elements.[93] The pure density functionals gave rather large errors on NGBD with MUEs of 0.03−0.10 Å. Thus the pure functionals are not recommended for the structure prediction of the noble-gas molecules. The prediction by the hybrid DFT was significantly better but was still very basis-set dependent, as shown in Table V. Generally speaking, the larger basis sets gave more reliable results, especially, the 6-311+G(2df,2pd) basis set gave significantly better results than the 6-31+G(d,p) and 6-311+G(d,p) basis sets. The aug-cc-pVTZ basis set also gave slightly better results than the aug-cc-pVDZ basis set. The most accurate prediction came from the MPW1B95, MPW1PW91, B3P86, B2GP-PLYP, and DSD-BLYP functionals using the 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets with MUEs of ∼0.01 Å. The DSD-BLYP/6-311+G(2df,2pd) method gave the smallest MUE of 0.008 Å.

The test results on NGBD by all the tested methods can also be categorized into six types (H−Ng, B−Ng, C−Ng, F−Ng, Be−Ng, and Au−Ng) of noble-gas bond distances. The detailed MUE data on these bond distances are listed in the supplementary material.[92] For the H−Ng group, the MP2 theory with the 6-311+G(d,p) and aug-cc-pVDZ performed very well with MUEs less than 0.01 Å. Other MP2 methods also performed reasonably well with MUEs less than 0.02 Å. The MPW1B95, MPW1PW91, M05-2X, M06-2X, B2GP-PLYP, and DSD-BLYP functionals all performed very

TABLE V. Mean unsigned errors (MUEs) on the noble-gas bond distances (NGBD, in Å) by various theoretical methods.

	6-31+G(d,p)	6-311+G(d,p)	6-311+G(2df,2pd)	aug-cc-pVDZ	aug-cc-pVTZ
MP2	0.036	0.040	0.019	0.018	0.022
B3LYP	0.050	0.056	0.027	0.034	0.024
MPW1B95	0.024	0.033	0.013	0.015	0.017
MPW1PW91	0.028	0.033	0.013	0.018	0.015
B98	0.045	0.050	0.019	0.028	0.017
BMK	0.031	0.037	0.020	0.019	0.019
B3P86	0.029	0.033	0.011	0.018	0.014
M05-2X	0.024	0.028	0.018	0.021	0.021
M06-2X	0.028	0.032	0.024	0.025	0.028
B2GP-PLYP	0.037	0.044	0.009	0.019	0.009
DSD-BLYP	0.039	0.045	0.008	0.019	0.009
BLYP	0.094	0.101	0.067	0.074	0.059
MPWB95	0.070	0.076	0.042	0.049	0.035
MPWPW91	0.066	0.071	0.037	0.044	0.031

well on the H−Ng bond distance with MUEs less than 0.02 Å in most cases.

For the Be−Ng group, the MP2 methods with largest basis sets gave excellent results. The MUEs obtained using the 6-311+G(2df,2pd) and aug-cc-pVTZ are 0.004 and 0.002 Å, respectively. It is noted that this is one of the rare cases that MP2/aug-cc-pVDZ method gave quite unsatisfactory results in bond lengths. Most of the hybrid functionals performed rather well and gave MUEs around 0.02 Å or smaller. The most accurate results were obtained using the MPW1B95/6-311+G(2df,2pd) method with an MUE of 0.004 Å. The prediction by MPW1PW91 and B3P86 functionals with several different basis sets was also excellent.

For the B−Ng group, all the MP2 methods made good prediction with MUEs ∼0.01 Å. The best method was MP2/aug-cc-pVDZ with MUE of only 0.004 Å. The MPW1B95, MPW1PW91, M05-2X, M06-2X, B2GP-PLYP, and DSD-BLYP functionals all performed very well on the B−Ng bond distance with MUEs less than 0.02 Å in most cases. The MPW1B95 functional with 6-311+G(2df,2pd) and aug-cc-pVDZ basis set both gave very small MUEs of 0.004 Å, and the B2GP-PLYP and DSD-BLYP functionals with 6-311+G(2df,2pd) basis set gave MUEs of only 0.003 Å.

For the C−Ng group, MP2 methods with larger basis sets made larger errors due to the over-predicted bond energies. The MP2/aug-cc-pVDZ method gave the best results of 0.018 Å in MUE. In comparison, the MP2/aug-cc-pVTZ method gave almost 80% higher MUE. The MPW1B95 functional with 6-31+G(d,p) and 6-311+G(d,p) basis sets and the B2GP-PLYP and DSD-BLYP functionals with 6-311+G(2df,2pd) basis set gave very small MUEs of ∼0.01 Å. Most of the other hybrid functional gave good prediction with MUEs of 0.01–0.03 Å, and in many cases better results were obtained using smaller basis sets.

For the F−Ng group, MP2 methods with larger basis sets made smaller errors, in contrast to the case in C−Ng group. The MUEs obtained using 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets were 0.011 Å. Thus if molecules contain both C−Ng and F−Ng bonds, the best compromise for the

MP2 theory seems to be using the aug-cc-pVDZ basis set. Using larger basis sets, most of the hybrid functionals gave good results with MUEs of 0.01−0.02 Å. The most accurate results came from the MPW1B95, MPW1PW91, and B3P86 functionals using the 6-311+G(2df,2pd) basis set and from the B2GP-PLYP and DSD-BLYP functionals using the aug-cc-pVTZ basis set with MUEs of ∼0.005 Å. The B3LYP functional performed less satisfactorily except when using the aug-cc-pVTZ basis set.

For the Au−Ng group, accurate prediction of the bond distances proved to be the most difficult. In most cases, the predicted Ng−Au distances were too long. Interestingly, the MP2/aug-cc-pVDZ method gave good result with MUE of 0.018 Å while other MP2 methods gave large MUEs of 0.06−0.16 Å. Very large MUEs (0.1−0.2 Å) were also obtained from almost all the hybrid and pure density functionals with smaller basis sets. The DFT methods that stood out were MPW1B95, MPW1PW91, B3P86, B2GP-PLYP, and DSD-BLYP with the 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets with MUEs less than 0.03 Å. The best result came from the DSD-BLYP/6-311+G(2df,2pd) method with an MUE of only 0.003 Å.

The benchmark results on the NGBD can also be compiled by the identity of the noble gas atom. The detailed MUE data are included in the supplementary material.[92] As mentioned earlier, the statistics was less meaningful for He and Ne because only a few molecules were available in the database. As a general trend, larger basis sets gave better results than smaller basis sets. For He-containing molecules, the MP2/6-311+G(2df,2pd) and MP2/aug-cc-pVTZ methods gave reasonable MUEs of ∼0.02 Å. The best predictions came from MPW1B95, MPW1PW91, B3P86, B2GP-PLYP, and DSD-BLYP functionals using the 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets with MUEs of ∼0.01 Å. For Ne-containing molecules, BMK/6-311+G(d,p), and B3P86 functionals with 6-311+G(2df,2pd) and aug-cc-pVDZ basis sets, B2GP-PLYP and DSD-BLYP functional with 6-311+G(2df,2pd) and aug-cc-p-VTZ basis sets performed best with MUEs of ∼0.01 Å. However, statistics with only two data cannot be taken too seriously. For Ar-containing

molecules, the MP2/6-311+G(2df,2pd) and MP2/aug-cc-pVDZ methods gave reasonable MUEs of ∼0.02 Å. Most of the hybrid functionals using large basis sets gave reasonable MUEs of 0.02−0.03 Å. The best predictions came from DSD-BLYP/6-311+G(2df,2pd) method with an MUE of 0.007 Å. The MPW1B95, MPW1PW91, B98, B3P86, and B2GP-PLYP functionals using the 6-311+G(2df,2pd) basis sets and B3LYP, B2GP-PLYP, and DSD-BLYP functionals with aug-cc-pVTZ basis sets also performed very well with MUEs less than 0.02 Å. For Kr-containing molecules, the MP2/aug-cc-pVDZ method was significantly better than other MP2 methods with small MUEs of 0.014 Å. Most of the hybrid functionals using large basis sets gave good predictions with MUEs less than 0.02 Å except for M06-2X. The best predictions came from B2GP-PLYP and DSD-BLYP functionals using the aug-cc-pVTZ basis sets with MUEs of 0.007 Å. The MPW1B95/aug-cc-pVDZ method, MPW1PW91, B3P86, B2GP-PLYP, and DSD-BLYP functionals using the 6-311+G(2df,2pd) basis sets also performed impressively well with MUEs ∼0.010 Å. For Xe-containing molecules, the MP2 theory with the aug-cc-pVDZ and aug-cc-pVTZ basis sets gave small MUEs of ∼0.015 Å. Most of the hybrid functionals performed rather well with MUEs of 0.01−0.02 Å using medium to large basis sets while the B3LYP functional performed unsatisfactorily with MUEs of 0.03−0.05 Å. The best predictions came from B2GP-PLYP and DSD-BLYP functionals using the aug-cc-pVTZ basis set with MUEs of 0.006 and 0.005 Å, respectively. The MPW1B95, MPW1PW91 functionals using the 6-311+G(2df,2pd) basis sets also performed very well with MUEs of 0.007 Å.

IV. SUMMARY

We have made benchmark study on the noble-gas bond energies and bond distances of a set of 31 neutral noble-gas molecules using the MP2 theory and various density functionals with a series of commonly used basis sets. Our results indicated that some of the hybrid density functionals with appropriate basis sets outperformed the best MP2 method by a wide margin. In particular, the MPW1B95/6-311+G(2df,2pd), BMK/aug-cc-pVTZ, DSD-BLYP/aug-cc-pVTZ, and B2GP-PLYP/aug-cc-pVTZ gave the best accuracy in bond energies with MUEs ∼2.0 kcal/mol while the most accurate MP2 method, MP2/aug-cc-pVDZ, gave an MUE of 4.5 kcal/mol. Interestingly, the M05-2X and M06-2X functionals which have been very successful on many types chemical bonding and on kinetics did not perform well on the noble-gas bond energies. The popular B3LYP functional did not perform particularly well, either. The pure density functionals performed relatively poor on bond energies, and gave significantly higher MUEs. For bond distances, the B2GP-PLYP and DSD-BLYP functionals with 6-311+G(2df,2pd) and aug-cc-pVTZ basis sets gave excellent results with MUEs ∼0.009 Å. The MPW1B95, MPW1PW91, and B3P86 functionals with the 6-311+G(2df,2pd) also gave accurate prediction with MUEs of 0.011−0.013 Å. Most of the other hybrid DFT methods with larger basis sets performed reasonably well on bond distances

with MUEs around 0.02 Å. The popular B3LYP functional with 6-31+G(d,p) and 6-311+G(d,p) basis sets gave very large MUEs of ∼0.05 Å. The pure density functionals gave significantly larger errors on bond lengths. The MP2 theory with 6-311+G(2df,2pd) and aug-cc-pVDZ basis sets gave reasonably accurate results with MUEs less than 0.02 Å. Overall speaking, the new DSD-BLYP functional with the aug-cc-pVTZ basis set and the MPW1B95 functional with 6-311+G(2df,2pd) basis set stood out as the best methods. As shown in Secs. III B–III C, they were among the best methods for almost all the individual test categories. These two functionals have also been shown to perform very well in general application in main-group thermochemistry.[66,74,94,95] We thus highly recommend MPW1B95/6-311+G(2df,2pd) and DSD-BLYP/aug-cc-pVTZ as the methods of choice for the computational study of noble gas chemistry. The DSD-BLYP/6-311+G(2df,2pd) method is also worth mentioning with the best result on NGBD and is only slightly less accurate on TNGBE. In addition, the BMK and B2GP-PLYP functionals, which have also been shown to perform very well on thermochemical kinetics,[68,73,94,96] gave good and balanced performance with the aug-cc-pVTZ basis sets, and are thus also good choices. For larger systems, however, the functionals that require second-order perturbation energy corrections (B2GP-PLYP and DSD-BLYP) would be significantly more demanding on the computational resources.

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