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A new database and benchmark of the bond energies of noble-gas-containing molecules

Cheng-Cheng Tsai | **Zhi-Yao Tsai** | **Ming-Yu Tseng** | **Wei-Ping Hu** [ORCID]

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

Correspondence
Wei-Ping Hu, Department of Chemistry and Biochemistry, National Chung Cheng University, Chia-Yi, Taiwan, Republic of China.
Email: chewph@ccu.edu.tw

Abstract

We have developed a new database of structures and bond energies of 59 noble-gas-containing molecules. The structures were calculated by CCSD(T)/aug-cc-pVTZ methods and the bond energies were obtained using the CCSD(T)/complete basis set method. Many wavefunction-based and density functional theory methods have been benchmarked against the 59 accurate bond energies. Our results show that the MPW1B95, B2GP-PLYP, and DSD-BLYP functionals with the aug-cc-pVTZ basis set excel in predicting the bond energies of noble-gas molecules with mean unsigned errors (MUEs) of 2.0 to 2.1 kcal/mol. When combinations of Dunning's basis sets are used, the MPW1B95, B2GP-PLYP, DSD-BLYP, and BMK functionals give significantly lower MUEs of 1.6 to 1.9 kcal/mol. Doubly hybrid methods using B2GP-PLYP and DSD-BLYP functionals and MP2 calculation also provide satisfactory accuracy with MUEs of 1.4 to 1.5 kcal/mol. If the Ng bond energies and the total atomization energies of a group of 109 main-group molecules are considered at the same time, the MPW1B95/aug-cc-pVTZ single-level method (MUE = 2.7 kcal/mol) and the B2GP-PLYP and DSD-PLYP functionals with combinations of basis sets or using the doubly hybrid method (MUEs = 1.9-2.2 kcal/mol) give the overall best result.

KEYWORDS
doubly hybrid method, multi-coefficient density functional theory, noble gas chemistry, noble-gas molecule, noble gas bond energies

1 | INTRODUCTION

The noble gases have been thought to be inert in forming compounds or participating in chemical reactions since their surprising discovery in the 1890s.[1,2] The reactivity of Xe has been suggested in the 1930s[3] but the first noble-gas-containing molecule, $XePtF_6$, was not synthesized until 1962.[4] A few Xe- and Kr- containing molecules were synthesized soon after.[5] By using method of matrix isolation, many noble-gas molecules have been prepared and observed by infrared (IR) spectroscopy in the 1990s and 2000s.[6–13] In particular, the first Ar-containing molecule, HArF, was observed in 2000.[10]

With the advent of experimental and computational techniques, noble gas chemistry has been flourishing in recent years with many new observed and predicted noble-gas-containing molecules.[14–34] Computational study has played an integral role in noble gas chemistry. Predictions on the stability and spectral properties of noble-gas molecules have not only provided directions for their experimental synthesis but also helped in confirming the identities of new such molecules.[14,18,20,21,24,25,27,29,33,35–38]

However, it has been known that some commonly used theoretical methods do not give satisfactory accuracy on the bond energies, and hence the stability, of the noble-gas molecules, which may seriously hinder the progress of this field.[35,37,38] For example, the bond-energy prediction by the popular MP2 and some hybrid density functional methods would give average errors as large as 5 to 10 kcal/mol for several types of noble-gas molecules.[14,18,23,25,35,37,38] We have benchmarked many commonly used theoretical methods on the bond energies of noble-gas molecules based on a

database of 31 such molecules.[37] The values for the database were obtained by very high level electronic structure calculations, which gave standard bond energies for simple noble-gas-containing molecules observed in experiments or predicted by theoretical calculations.

The main goal of the current study is to find or develop methods that can give even more accurate prediction on the stability of noble-gas molecules and at the same time provide good bond energies for normal main-group molecules. In this study, we have increased the size of the database to 59 neutral noble-gas molecules and their anions with "saturated" electron configuration on all the atoms. Of course, many interesting noble-gas-containing cations have been observed or theoretically predicted, [34,39–46] which will be included in future studies. In addition, to test 16 frequently used wavefunction-based and density functional theories (DFTs) with different basis sets, we have also developed the new multi-coefficient density functional theory (MC-DFT, ie, DFT methods using more than one basis set)[47–49] and the doubly hybrid (DH; ie, DFT + MP2) methods[49,50] for predicting the bond energies of noble-gas-containing molecules and other main-group molecules. The new database and bench-mark results would benefit future theoretical prediction and experimental exploration in the field of noble gas chemistry.

2 | METHODS

2.1 | Noble-gas molecules

In addition to the 31 molecules we previously studied,[37] we have added FNgNBH (Ng = Kr, Xe), HNgNBH (Ng = Kr, Xe), HXeH, HNgCl (Ng = Kr, Xe), HNgCN (Ng = Ar, Kr, Xe), HNgNC (Ng = Ar, Kr, Xe), FNgCC$^-$ (Ng = He, Ar, Kr, Xe),[23] FNgO$^-$ (Ng = He, Ar, Kr, Xe),[14] HBNNgO$^-$ (Ng = Kr, Xe), and FNgBN$^{-[16]}$ (Ng = He, Ne, Ar, Kr, Xe). The complete list of the 59 molecules studied in the current work is given in Table 1, and their schematic molecular structures are shown in Figure 1. Some of the new molecules contain Ng–N bonding, which was not included in previous studies. Four types of noble-gas-containing anions are included in the current study because it has been suggested that there could be rich anion chemistry in this field.[14,16,23]

2.2 | Basis sets

We used Dunning's correlation-consistent polarization basis sets, including cc-pVnZ and aug-cc-pVnZ (n = D, T, Q). [51,52] For Ar and Cl, the cc-pV(n+d)Z and aug-cc-pV(n+d)Z basis sets were used for better performance in basis set extrapolation.[53] For Au and Xe, the cc-pVnZ-pp and aug-cc-pVnZ-pp[54] basis sets, where the inner 28 electrons were represented by relativistic pseudo-potentials, were employed. For brevity, in the rest of this article all the valence double-zeta basis sets are abbreviated as pdz and apdz (pdz with diffuse functions), and the valence triple-zeta basis sets are abbreviated as ptz and aptz. The aug-cc-pVQZ basis set, which was used in the CCSD(T)[55] energy calculation, is abbreviated as apqz.

TABLE 1 List of the 59 noble-gas-containing molecules in the current study

HHeF		HArF	HKrF	HXeF
			HKrCCH	HXeCCH
		FArCCH	FKrCCH	FXeCCH
		FArBO	FKrBO	FXeBO
		FArCN	FKrCN	FXeCN
		FArCH$_3$	FKrCH$_3$	FXeCH$_3$
		FArBNH	FKrBNH	FXeBNH
			FKrNBH	FXeNBH
			HKrNBH	HXeNBH
				HXeH
			HKrCl	HXeCl
		HArCN	HKrCN	HXeCN
		HArNC	HKrNC	HXeNC
HeBeO	NeBeO	ArBeO	KrBeO	XeBeO
HeAuF	NeAuF	ArAuF	KrAuF	XeAuF
FHeCC$^-$		FArCC$^-$	FKrCC$^-$	FXeCC$^-$
FHeO$^-$		FArO$^-$	FKrO$^-$	FXeO$^-$
			HBNKrO$^-$	HBNXeO$^-$
FHeBN$^-$	FNeBN$^-$	FArBN$^-$	FKrBN$^-$	FXeBN$^-$

2.3 | Geometry optimization

The molecular geometries were fully optimized at the CCSD(T)/aug-cc-pVTZ level. Vibrational frequency calculations were performed at the same level of theory to ensure that the molecular structures obtained were true energy minima. All subsequent electronic structure calculations were based on the molecular structures obtained at this level. This restricted that the molecules studied must be true energy minima at the CCSD(T)/aug-cc-pVTZ level of theory.

2.4 | Noble-gas bond energies

The noble-gas bond energy (NGBE) has been defined as in the previous study.[37] If the molecules are of the type XNgY, where X and Y are atoms or chemical groups, NGBEs are the energy changes of XNgY → X + Ng + Y. If the molecules are of the type NgZ, where Z is BeO or AuF, NGBEs are defined as the energy changes of NgZ → Ng + Z. For anions of the type XNgY⁻, where X = F, HBN and Y = O, CC, BN, NGBEs are defined as the energy changes of XNgY⁻ → X + Ng + Y⁻ for consistency. All energies in the current study are Born-Oppenheimer energies.
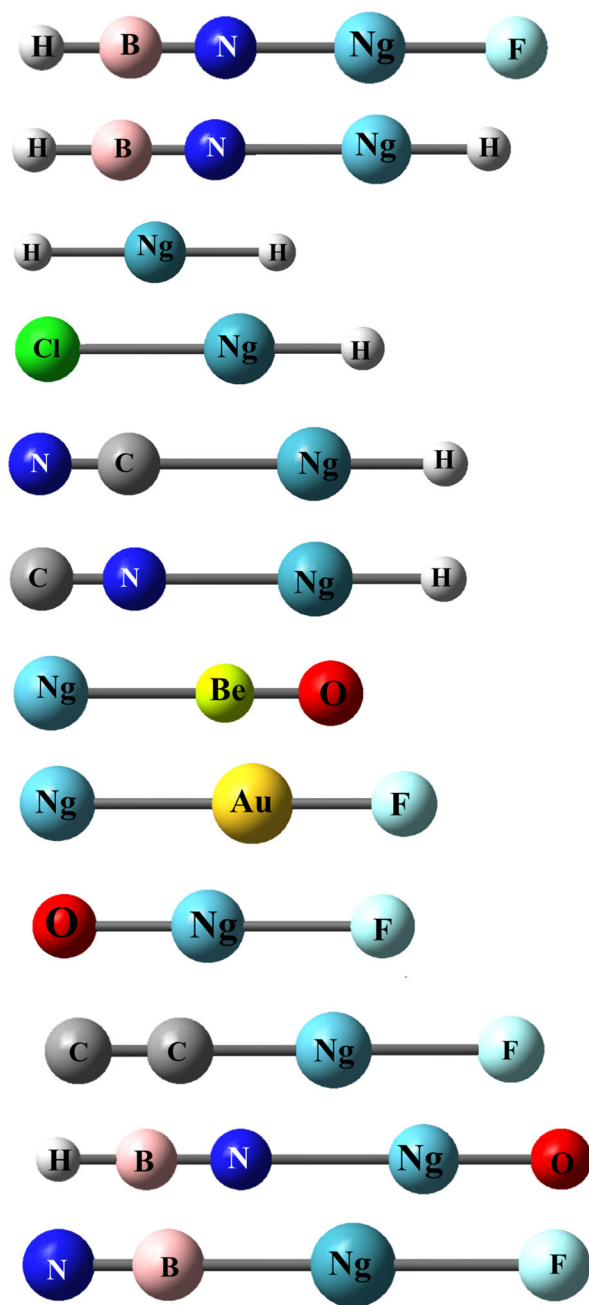
2.5 | Complete basis set energies

The CCSD(T)/complete basis set (CBS) energies for all species were obtained using the following formula[56]:

$$E_n = E_{CBS} + Cn^{-3} \qquad (n = 3 \text{ or } 4) \tag{1}$$

$$E_{CBS} = E_4 - \left(\frac{E_3 - E_4}{3^{-3} - 4^{-3}} \right) 4^{-3} \tag{2}$$
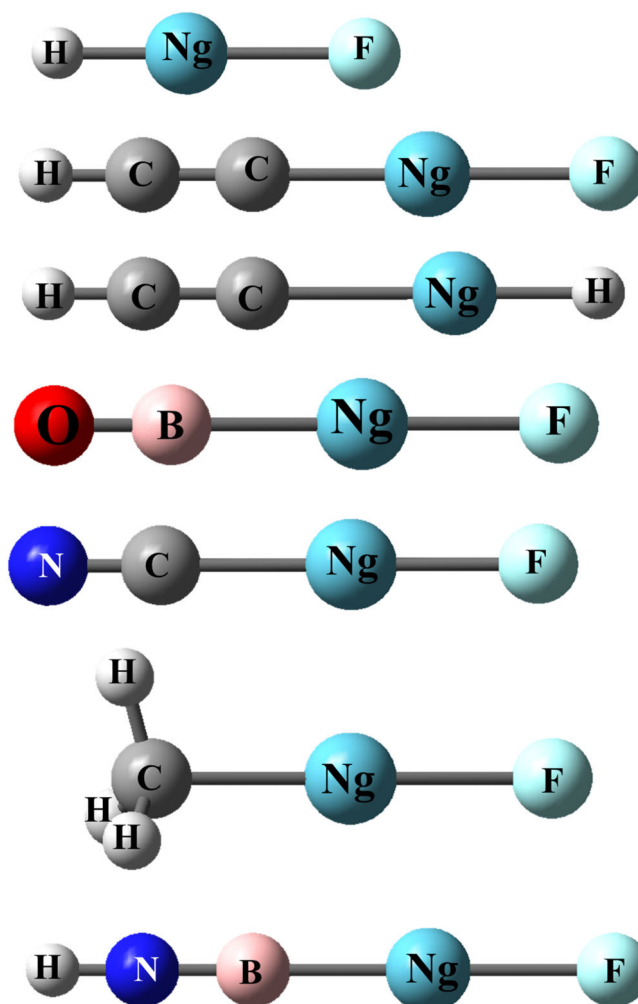
FIGURE 1 Schematic plot of the molecular structures of the noble-gas-containing molecules in the current study

FIGURE 1 (Continued)

where E_3 and E_4 were obtained from CCSD(T)/aptz and CCSD(T)/apqz calculation, respectively. The CBS energies thus obtained were used to evaluate the standard noble-gas bond energies in the NGBE database.

2.6 | Theoretical methods tested

The wavefunction-based theories MP2[57] and CCSD(T) and the density functional-based theories MPW1B95,[58] MPW1PW9,[59,60] B98,[61] B3LYP,[62] BMK,[63] B3P86,[64,65] M05-2X,[66] M06-2X,[67] BLYP,[65,68] MPWB95,[59,69] MPWPW91,[59,60] B2GP-PLYP,[70] DSD-BLYP,[71] and DSD-PBEP86[72] were benchmarked for the prediction of NGBEs against the CCSD(T)/CBS values described above.

2.7 | Main-group total atomization energies

Some of the methods in the current study were also benchmarked against the standard main-group total atomization energy database MGAE109[73] to check if they gave balanced performance in predicting both the bond energies of "non-noble" main-group molecules and noble-gas-containing molecules.

2.8 | Multi-coefficient DFT

The MC-DFT method[47–49] uses more than one basis set (B1, B2, B3, etc.) to extrapolate the Born-Oppenheimer energies according to the following formulas:

$$E_{2B}(B1/B2) = E(DFT/B1) + c_1 [E(DFT/B2) - E(DFT/B1)] \tag{3}$$

$$E_{3B}(B1/B2/B3) = E(DFT/B1) + c_1 [E(DFT/B2) - E(DFT/B1)] + c_2 [E(DFT/B3) - E(DFT/B2)] \tag{4}$$

where c_1 and c_2 are empirical coefficients to be determined by minimizing the mean unsigned errors (MUEs) against the standard NGBE or MGAE109 database.

2.9 | DH methods

The DH method[41,42] combines the Hartree-Fock (HF), MP2, and DFT energies according to the formula

$$E_{DH}(DFT/B1 + MP2/B2) = c_1 E(DFT/B1) + (1 - c_1) E(HF/B2) + c_2 (E2/B2) \tag{5}$$

where E2 is the second-order correction energy of MP2 theory, and c_1 and c_2 are empirical coefficients to be determined by minimizing the MUE against the standard NGBE or MGAE109 databases.

All the electronic structure calculations were performed using the Gaussian 16 program, revision A03.[74]

3 | RESULTS AND DISCUSSION

3.1 | Molecular structures

The calculated geometry parameters of the 59 noble-gas-containing molecules at the CCSD(T)/aptz level are listed in Table 2, and their Cartesian coordinates are included in Table S5. Except for FNgCH$_3$, which belongs to the point group C_{3v}, all other structures are linear with $C_{\infty v}$ symmetry. Thirty-one of the structures were included in our previous study,[37] but they are also re-calculated in the current study using Gaussian 16. Some of the molecule types do not include the lighter noble gases because they were found not to meet the energy minimum criterion at the CCSD(T)/aptz level. To our knowledge, FNgNBH, HNgNBH, and HBNNgO$^-$ have not been studied previously. The Ng–N bond lengths in FKrNBH and FXeNBH are 1.898 and 2.035 Å, respectively. They are similar to the F–Ng bond lengths in the same molecules. However, the Ng–N bonds in HNgNBH are 0.2 to 0.3 Å longer, which reflects the significantly larger NGBE of FNgNBH (see Table 3). The HBNNgO$^-$ molecules can also be viewed as ion-induced dipole complexes HBN$^-$···NgO, similar to F$^-$···NgO.[14] The N···Ng bond distances in HBNKrO$^-$ and HBNXeO$^-$ are 2.457 and 2.497 Å, respectively. They are ~0.2 Å larger than the F···Ng distances in FNgO$^-$. The Ng–O distances in both types of molecules are very similar. A previous study[37] has shown that the MP2, MPW1B95, MPW1PW91, BMK, B3P86, B2GP-PLYP, and DSD-BLYP theories with 6-311+G(2df,2pd) and apdz basis sets predicted reasonably accurate bond lengths.

3.2 | Noble-gas bond energies

Table 3 shows the calculated NGBEs at the CCSD(T)/CBS level. The values cover a large range from −15 to 83 kcal/mol. This makes the theoretical prediction on these NGBEs challenging. As expected, most of the NGBEs for molecules containing He and Ne are relatively low. FHeBN$^-$ and FNeBN$^-$ were predicted with unusually high NGBEs, which is consistent with a previous study.[16] However, their two-body dissociation (FNgBN$^-$ → Ng + FBN) barriers are still too low to be stable. FKrNBH, which has an NGBE of 22.3 kcal/mol, is expected to be stable at cryogenic conditions. HKrNBH has a similar NGBE

TABLE 2 Calculated structures (in angstroms and degrees) of the noble-gas-containing molecules at the CCSD(T)/aptz level

	He	Ne	Ar	Kr	Xe
HNgF					
H–Ng	0.811		1.329	1.477	1.663
Ng–F	1.415		1.979	2.042	2.116
FNgCCH					
F–Ng			1.923	1.978	2.064
Ng–C			1.826	1.923	2.084
C–C			1.211	1.212	1.215
C–H			1.065	1.065	1.065
HNgCCH					
H–Ng				1.614	1.754
Ng–C				2.271	2.354
C–C				1.226	1.226
C–H				1.066	1.066
FNgBO					
F–Ng			1.987	2.031	2.098
Ng–B			1.827	1.971	2.162
B–O			1.207	1.209	1.211
FNgCN					
F–Ng			1.915	1.940	2.031
Ng–C			1.956	1.975	2.123
C–N			1.169	1.167	1.167
FNgCH$_3$[a]					
F–Ng			2.024	2.076	2.135
Ng–C			1.951	2.047	2.195
Ng–C–H			103.1	105.3	106.9
FNgBNH					
F–Ng			2.033	2.064	2.128
Ng–B			1.799	1.953	2.148
B–N			1.234	1.238	1.242
N–H			0.995	0.995	0.994
FNgNBH					
F–Ng				1.932	2.031
Ng–N				1.898	2.035
N–B				1.253	1.255
B–H				1.171	1.171
HNgNBH					
H–Ng				2.064	2.128
Ng–N				1.953	2.148
N–B				1.238	1.242
B–H				0.995	0.994
HNgH					
H–Ng					1.922
HNgCl					
H–Ng				1.523	1.692
Ng–Cl				2.525	2.622
HNgCN					
H–Ng			1.422	1.546	1.716

TABLE 2 (Continued)

	He	Ne	Ar	Kr	Xe
Ng–C			2.271	2.333	2.421
C–N			1.173	1.173	1.172
HNgNC					
H–Ng			1.315	1.469	1.664
Ng–N			2.225	2.271	2.341
N–C			1.185	1.185	1.185
NgBeO					
Ng–Be	1.524	1.799	2.073	2.201	2.370
Be–O	1.338	1.340	1.341	1.342	1.344
NgAuF					
Au–F	1.908	1.921	1.918	1.924	1.930
Ng–Au	1.842	2.451	2.401	2.473	2.565
FNgO⁻					
F–Ng	1.625		2.226	2.259	2.309
Ng–O	1.110		1.766	1.854	1.956
FNgCC⁻					
F–Ng	1.625		2.176	2.224	2.233
Ng–C	1.137		1.782	1.935	2.044
C–C			1.264	1.282	1.257
HBNNgO⁻					
H–B				0.995	0.995
B–N				1.238	1.242
N–Ng				1.954	2.148
Ng–O				2.064	2.128
FNgBN⁻					
F–Ng	1.724	2.234	2.278	2.305	2.338
Ng–B	1.202	1.571	1.813	1.960	2.144
B–N	1.266	1.272	1.270	1.271	1.274

^{a}Structures in C_{3v} point group.

as that of HKrCCH. Since HKrCCH has been observed in Kr matrix,[13] there is a good chance that HKrNBH can also be observed at similar conditions. The calculated NGBE for FKrCN is ~7 kcal/mol higher than that obtained by Zhu et al[26] because of the larger basis sets and the CBS extrapolation used in the current study. For the same reason, the calculated NGBEs for FNgBN⁻ are also 5 to 7 kcal/mol higher than those previously reported by Grandinetti and coworkers. [16] All the anions included in the current database except FHeCC⁻, FHeBN⁻, and FNeBN⁻ should also be stable at cryogenic conditions. For XNgY⁻, there is another three-body dissociation pathway, that is, to X⁻ + Ng + Y. Since the energy of reaction for this channel is related to the NGBE by the difference of the electron affinity of X and Y, only the NGBE defined in the Method section are considered. For the 31 molecules studied previously, the NGBEs obtained in the current study are almost identical to the previous results. The NGBEs of some of the Xe-containing molecules are slightly different because of the different program defaults on the definition of core electrons. We have also calculated the %TAE$_e$[(T)][75] for all the Ng-containing molecules, and the results are shown in Table S4. Most of the molecules belong to the types of mild nondynamical correlation (2%-5%) and moderate nondynamical correlation (5%-10%). Only for the molecules HKrF, HXeF, HXeH, HKrCl, HXeCl, and FArCN the %TAE$_e$[(T)] values exceed 10%. The nondynamical correlation contribution for these molecules should be analyzed in future studies.

3.3 | Benchmark on NGBE

Table 4 shows the MUE and root-mean-square deviation (RMSD) values obtained by various theoretical methods on the 59 NGBEs. The HF theory seriously underestimates the NGBE by more than 50 kcal/mol, on average. For all theories, except for the non-hybrid DFT: BLYP, MPWB95, and MPWPW91, the MUEs obtained using the ptz basis set are significantly lower than those using the pdz basis set. The size of the basis set is

	He	Ne	Ar	Kr	Xe
HNgF	−15.0		9.4	28.5	52.3
HNgH					5.3
HNgCl				8.3	34.2
HNgCCH				9.3	31.5
FNgCCH			7.6	35.1	67.5
FNgBO			5.1	26.8	53.8
FNgCN			−2.9	25.7	59.4
HNgCN			−6.7	11.4	32.9
HNgNC			−11.8	5.8	28.0
FNgCH$_3$			0.04	19.2	43.2
FNgBNH			12.5	32.5	57.9
FNgNBH				22.3	59.3
HNgNBH				8.7	33.0
NgBeO	5.2	5.5	11.7	14.5	17.8
NgAuF	6.5	2.5	13.3	19.0	26.7
FNgCC$^-$	2.1		22.6	41.6	66.6
FNgO$^-$	17.1		36.0	55.9	83.1
FNgBN$^-$	40.4	22.5	53.3	65.5	82.2
HBNNgO$^-$				39.4	66.0

TABLE 3 Calculated noble-gas bond energy (in kcal/mol) at CCSD(T)/complete basis set level

	pdz	apdz	ptz	aptz
HF	64.8 (71.3) [105.8]	57.0 (62.9) [93.6]	58.1 (63.8) [94.8]	56.4 (61.6) [88.1]
MP2	15.9 (19.0) [20.6]	6.6 (8.9) [20.6]	8.1 (10.3) [22.6]	10.3 (13.8) [30.3]
B3LYP	10.9 (12.9) [23.6]	4.0 (5.3) [17.5]	4.2 (5.4) [11.2]	3.3 (4.3) [12.8]
MPW1B95	11.0 (12.7) [22.4]	2.8 (3.7) [12.1]	3.9 (4.9) [11.5]	2.1 (2.6) [7.4]
MPW1PW91	12.3 (14.4) [26.5]	4.0 (5.1) [15.1]	5.0 (6.2) [16.0]	2.8 (3.6) [10.4]
B98	10.2 (12.1) [22.5]	3.3 (4.4) [13.4]	3.9 (5.0) [11.2]	3.0 (3.7) [8.7]
BMK	13.3 (15.7) [27.8]	4.8 (5.9) [14.8]	4.7 (5.7) [12.9]	2.5 (3.3) [9.2]
B3P86	8.3 (10.1) [20.8]	3.7 (4.7) [11.2]	4.1 (5.4) [14.0]	4.5 (5.5) [11.4]
M05-2X	16.6 (19.2) [32.7]	8.1 (10.2) [28.2]	6.5 (7.7) [15.6]	4.7 (6.1) [15.5]
M06-2X	16.4 (18.8) [29.3]	7.8 (9.1) [16.5]	7.6 (8.8) [15.1]	5.2 (6.2) [12.1]
B2GP-PLYP	17.6 (20.2) [31.4]	5.3 (6.3) [13.5]	6.3 (7.6) [14.4]	2.1 (2.8) [9.0]
DSD-BLYP	17.3 (19.9) [30.7]	4.5 (5.6) [14.1]	5.5 (6.8) [12.5]	2.0 (2.6) [8.4]
DSD-PBEP86	16.3 (18.8) [31.1]	3.8 (4.8) [11.9]	5.0 (6.4) [13.2]	2.5 (3.7) [11.5]
BLYP	7.4 (9.6) [28.0]	6.7 (8.5) [19.9]	6.6 (8.7) [24.4]	7.7 (9.4) [20.3]
MPWB95	10.0 (14.5) [39.7]	12.9 (15.0) [27.8]	12.5 (15.3) [34.7]	14.3 (16.4) [29.2]
MPWPW91	6.4 (9.3) [31.9]	8.6 (10.4) [22.1]	8.5 (11.0) [27.4]	9.9 (11.7) [23.3]

TABLE 4 Mean unsigned error (in kcal/mol) of various theoretical methods on the 59 noble-gas bond energies

Note: The root-mean-square deviations and maximum absolute errors are shown in parentheses and brackets.

certainly important in NGBE prediction. By comparing the results obtained using apdz and pdz, or aptz with ptz, except for the HF theory, B3P86, and the non-hybrid DFTs, the diffuse functions are also crucial for obtaining accurate NGBEs. For the non-hybrid functionals, the accuracy is relatively insensitive to the choice of the basis sets, and the MUEs are in the range 7 to 14 kcal/mol. The methods that stand out in the benchmark include the MPW1B95, B2GP-PLYP, and DSD-BLYP functionals with aptz basis set, which give MUEs of 2.1, 2.1, and 2.0 kcal/mol, respectively. This is consistent with our previous benchmark.[37] In comparison, the commonly used MP2, B3LYP, M06-2X theories with aptz basis sets give MUEs of 10.3, 3.3, and 5.2 kcal/mol, respectively. It is well known that MP2 theory usually overestimates the NGBE.[14,15,35,37,38] The MP2/apdz method gives an MUE of 6.6 kcal/mol, which is significantly smaller than those of MP2/aptz and MP2/pdz methods. It is worth mentioning that the MPW1PW91, B98, BMK, and DSD-PBEP86 functionals with the aptz basis set also give reasonably accurate results (MUEs ≤3.0 kcal/mol),

and the MPW1B95/apdz method also gives a low MUE of 2.8 kcal/mol. The CCSD(T) theory with aptz and apqz basis sets gives MUE, RMSD, and maximum error of 2.0, 2.8, 14.2 kcal/mol and 0.8, 1.2, 6.0 kcal/mol, respectively.

3.4 | Development of MC-DFT methods

We have shown in our previous work that MC-DFT methods can provide accurate prediction on the thermochemical kinetics data at relatively low computational cost.[47–49] In the current study, we have tested the basis set combinations apdz/aptz and pdz/apdz/aptz using the functionals MPW1B95, MPW1PW91, B98, B3LYP, B2GP-PLYP, DSD-BLYP, and BMK. The energies were computed according to Equations (3) and (4). The performance of MC-DFT on NGBE as compared to that using a single aptz basis set is shown in Table 5. For the MPW1PW91, B2GP-PLYP, and BMK functionals, the apdz/aptz combination significantly reduces the MUEs by 12% to 21%. Using this combination, the lowest MUE of 1.7 kcal/mol was obtained by the B2GP-PLYP functional with only one empirical coefficient ($c_1 \approx 1.349$). For all functionals except DSD-BLYP, the pdz/apdz/aptz combination significantly reduces the MUEs by 13% to 25%. Using this combination, the lowest MUE of 1.6 kcal/mol was obtained by the B2GP-PLYP functional, followed very closely by MPW1B95, DSD-BLYP, and BMK with MUEs of 1.7, 1.8 and 1.9 kcal/mol, respectively. Two empirical coefficients were used for this basis set combination. The empirical coefficients of the most accurate methods are listed in Table S2.

3.5 | Development of DH method

The DH method combines the hybrid-DFT and MP2 calculation. It has been shown to be a very economical way to achieve good accuracy on thermochemical kinetics.[49,50] In the current study, we have combined the hybrid functionals MPW1B95, MPW1PW91, B98, B3LYP, B2GP-PLYP, DSD-BLYP, and BMK using the aptz basis set with MP2 calculation using the pdz, apdz, ptz, and aptz basis sets. The energies were computed according to Equation (5). The performance of the DH methods on the NGBE as compared to that of pure DFT calculation is shown in Table 6. As can be seen in the table, most functionals show significant improvement in accuracy when combining with the additional MP2 calculation. It is to be noted that in the MP2 part of the calculation, using the aptz basis set does not significantly improve the accuracy over that using

TABLE 5 MC-DFT performance (MUE in kcal/mol) on the 59 NGBEs

	aptz	apdz/aptz	pdz/apdz/aptz
MPW1B95	2.1	2.0 (2.5) [5.9]	1.7 (2.2) [5.9]
MPW1PW91	2.8	2.2 (2.7) [6.9]	2.1 (2.8) [7.2]
B98	3.0	3.0 (3.7) [8.2]	2.6 (3.2) [6.9]
B3LYP	3.3	3.2 (4.1) [11.2]	2.7 (3.3) [7.5]
B2GP-PLYP	2.1	1.7 (2.3) [8.7]	1.6 (2.3) [9.3]
DSD-BLYP	2.0	2.0 (2.6) [8.2]	1.8 (2.4) [7.9]
BMK	2.5	2.2 (2.8) [7.9]	1.9 (2.5) [7.3]

Note: The root-mean-square deviations and maximum absolute errors are shown in parentheses and brackets.
Abbreviations: MC-DFT, multi-coefficient density functional theory; MUE, mean unsigned error; NGBE, noble-gas bond energy.

TABLE 6 Performance (MUE in kcal/mol) of doubly hybrid methods on the 59 NGBEs using different basis sets in the MP2 calculation

	DFT/aptz[a]	pdz	apdz	ptz	aptz
MPW1B95	2.1	2.0 (2.5) [5.6]	2.1 (2.6) [7.5]	2.0 (2.5) [6.0]	1.7 (2.2) [6.1]
MPW1PW91	2.8	2.0 (2.5) [5.6]	2.4 (3.0) [7.5]	2.3 (3.1) [7.4]	2.4 (3.0) [6.9]
B98	3.0	2.8 (3.4) [7.2]	2.8 (3.6) [9.9]	2.7 (3.3) [7.1]	2.7 (3.5) [9.4]
B3LYP	3.3	3.1 (3.9) [9.3]	3.2 (4.1) [12.2]	3.0 (3.7) [9.0]	3.1 (3.9) [11.5]
B2GP-PLYP	2.1	1.9 (2.4) [7.6]	1.5 (2.0) [6.7]	1.8 (2.4) [7.4]	1.7 (2.2) [7.0]
DSD-BLYP	2.0	1.8 (2.4) [7.7]	1.4 (1.9) [6.7]	1.8 (2.4) [7.9]	1.5 (2.1) [7.1]
BMK	2.5	2.3 (3.0) [7.8]	2.2 (3.0) [7.8]	2.3 (3.1) [9.3]	2.2 (2.9) [8.1]

Note: The root-mean-square deviations and maximum absolute errors are shown in parentheses and brackets.
Abbreviations: MUE, mean unsigned error; NGBE, noble-gas bond energy.
[a]Pure DFT results using aptz basis set for comparison.

Methods	MUE
MPW1B95/aptz	2.7 (4.0) [19.4]
BMK/aptz	3.0 (4.1) [20.0]
B3LYP/aptz	4.8 (7.2) [31.6]
M06-2X/aptz	3.6 (4.9) [18.6]
B2GP-PLYP/aptz	4.9 (6.2) [19.2]
DSD-BLYP/aptz	3.7 (4.9) [21.5]
MPW1PW91/aptz	4.4 (6.3) [34.0]
BMK/apdz/aptz	2.6 (3.8) [22.1]
B2GP-PLYP/apdz/aptz	1.9 (2.6) [9.6]
DSD-BLYP/apdz/aptz	2.2 (3.3) [17.5]
MPW1PW91/apdz/aptz	3.2 (4.3) [18.4]
B2GP-PLYP/aptz + MP2/apdz	2.0 (3.2) [14.1]
DSD-PLYP/aptz + MP2/apdz	2.1 (3.6) [19.6]

TABLE 7 Performance (MUE in kcal/mol) of selected DFT, MC-DFT and doubly hybrid methods on both MGAE109 and NGBE 59

Note: The root-mean-square deviations and maximum absolute errors are shown in parentheses and brackets.
Abbreviations: MC-DFT, multi-coefficient density functional theory; MUE, mean unsigned error; NGBE, noble-gas bond energy.

the apdz basis set in most cases. Since the computational cost of MP2/aptz is considerably higher, using MP2/apdz in the DH methods is preferred. The lowest MUEs, 1.4 and 1.5 kcal/mol, were obtained using the DSD-BLYP and B2GP-PLYP functionals, respectively, with the MP2/apdz calculation. These MUEs are similar to those of the best MC-DFT methods mentioned above, and the computational costs of the MC-DFT and the DH methods are comparable. It is also interesting to know whether the large aptz basis set is really necessary for the DFT part. We show in Table S3 that for MPW1B95, B2GP-PLYP, and DSD-BLYP functionals, the DFT/apdz + MP2/apdz combinations give MUEs of 2.4, 2.1, and 2.1 kcal/mol, respectively. While they are not as accurate as the DFT/aptz-based methods mentioned above, they are significantly more accurate than both the single-level DFT/apdz and MP2/apdz calculation. For large molecules, the DFT/apdz + MP2/apdz DH methods may also be good choices. The B2GP-PLYP and DSD-BLYP functionals are themselves the so-called double-hybrid functionals, which include the second-order correlation energy calculated from the density orbitals.[70–72,76–78] In a sense, the DH methods based on these functionals can also be called the "triply hybrid" methods.

3.6 | Benchmark on both MGAE109 and NGBE59 databases

The benchmark on MGAE109 has been performed using various theoretical methods previously.[47,49,66,67,79–81] We applied the methods developed in the current study to test their performance against MGAE109, and the results are shown in Table S1 to S3. The best single-level methods are M06-2X/aptz, MPW1B95/aptz, and BMK/aptz with MUEs of 2.8, 3.0, and 3.2, respectively. The best MC-DFT methods tested in the current study are M06-2X/[pdz/apdz/aptz], B2GP-PLYP/[pdz/apdz/aptz], and DSD-BLYP/[pdz/apdz/aptz] with MUEs of 1.9, 1.7, and 2.1 kcal/mol, respectively. All of them are significantly better than the corresponding single basis sets. The M06-2X benchmark is consistent with previous studies.[48,49,67,75,82] We then benchmarked the various methods against both MGAE109 and NGBE59 (total 168 energies), and selected results are shown in Table 7. Full test results are included in Tables S2 and S3. The best single-level methods are MPW1B95/aptz and BMK/aptz with MUEs of 2.7 and 3.0 kcal/mol, respectively. In comparison, the MUEs for B3LYP and M06-2X with a single aptz basis set are 4.8 and 3.6 kcal/mol, respectively. The best MC-DFT methods include B2GP-PLYP/[apdz/aptz] and DSD-BLYP/[apdz/aptz] with overall MUEs of 1.9 and 2.2 kcal/mol, respectively. The most accurate DH methods are B2GP-PLYP/aptz + MP2/apdz and DSD-BLYP/aptz + MP2/apdz with MUEs of 2.0 and 2.1 kcal/mol, respectively. These methods, as shown in Table 7, are as accurate as the MC-DFT methods and are significantly more accurate than their DFT counterparts (with MUE of 4.9 and 3.7 kcal/mol). The empirical coefficients of the best methods mentioned above are listed in Tables S2 and S3.

SUMMARY

We have expanded the NGBE database from 31 to 59 molecules and have included molecules with noble gas-nitrogen bonding and noble-gas-containing anions. Based on these accurate structures and bond energies, we have benchmarked the performance of various wavefunction-based methods and density functionals. We have also developed a series of MC-DFT and DH methods, which give significantly more accurate NGBEs at only a small additional cost. The database, the benchmark, and the new methods are important for future theoretical studies in the field of noble gas chemistry. In addition, the new methods have also been tested on the atomization energies of main-group molecules (MGAE) that do not

contain noble-gas atoms. Recommendations on the choices of theoretical methods have been made for the NGBE and the overall (NGBE + MGAE) thermochemical prediction.

AUTHOR CONTRIBUTIONS

Cheng-Cheng Tsai: Data curation; investigation; methodology; writing-original draft. **Zhi-Yao Tsai:** Data curation; methodology. **Ming-Yu Tseng:** Data curation. **Wei-Ping Hu:** Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; resources; supervision; writing-original draft; writing-review and editing.

ORCID

Wei-Ping Hu 🄳 https://orcid.org/0000-0001-9404-9988

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