

# A New Database and Benchmark of the Bond Energies of Noble-Gas Containing Molecules

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## Abstract

We have developed a new database of structures and bond energies of 45 noble-gas containing molecules. The structures were calculated by CCSD(T)/aug-cc-pVTZ methods and the bond energies were obtained using CCSD(T)/CBS (complete basis set) method. Many wavefunction-based and density functional theory methods have been benchmarked against the 45 accurate bond energies. Our result showed that the MPW1B95, B2GP-PLYP, and DSD-BLYP functionals with the aug-cc-pVTZ basis set excel on predicting the bond energies of the noble-gas molecules with MUEs (mean unsigned errors) of 1.5-1.9 kcal/mol. When combinations of Dunning's basis sets are used, the MPW1B95, MPW1PW91, and B2GP-PLYP functional give significantly lower MUEs of 1.1-1.3 kcal/mol. Doubly hybrid methods using B2GP-PLYP and DSD-BLYP functionals and MP2 calculation also provide satisfactory accuracy with MUEs of 1.3-1.4 kcal/mol. If the noble-gas 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 functional with combinations of basis sets (MUEs = 1.8 kcal/mol) give the overall best result.

## Introduction

The noble gases have been thought to be inert in forming compounds or in participating chemical reactions since their surprising discovery in the 1890s.<sup>[1,2]</sup> The reactivity of Xe has been suggested in the 1930s<sup>[3]</sup> but the first noble-gas containing molecules, XePtF<sub>6</sub>, has not been synthesized until 1962.<sup>[4]</sup> A few Xe- and Kr- containing molecules were synthesized soon after.<sup>[5]</sup> By using method of matrix isolation, many noble gas molecules have been prepared and observed by IR spectroscopy in the 1990s and 2000s.<sup>[6-13]</sup> In particular, the first Ar containing molecules HArF has been observed in 2000.<sup>[10]</sup> 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.<sup>[14-34]</sup> Computational study has played an integral role in noble gas chemistry. The predictions on the stabilities and spectral properties of noble-gas molecules have not only provided directions for the experimental synthesis but also helped to confirm the identities of new noble-gas molecules.<sup>[14,18,20,21,24,25,27,29,35-38]</sup> 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 serious hinder the progress of this field.<sup>[35,37,38]</sup> For example, the bond-energy prediction by the popular MP2 and some hybrid density functional methods would give average errors as large as 5-10 kcal/mol for several types noble-gas molecules.<sup>[14,18,23,25,35,37,38]</sup> We have benchmarked many commonly used theoretical methods on the bond energies of noble-gas molecules based on a database of 31 noble-gas molecules.<sup>[37]</sup> The database values were obtained by very high-level electronic structure calculation, which gave standard bond energies for simple noble-gas containing molecules observed in experiments or predicted by theoretical calculation. 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 the current study, we have increased the size of the database to 45 noble-gas molecules. In addition to test 15 frequently used wavefunction-based and density functional theories with different basis sets, we have also developed new multi-coefficient density functional theory (MC-DFT, DFT methods using more than one basis sets)<sup>[39-41]</sup> and the doubly hybrid (DFT+MP2) methods<sup>[41,42]</sup> for predicting the bond

energies of noble-gas containing molecules and other main-group molecules. The new database and the benchmark results would benefit future theoretical prediction and experimental exploration in the field of noble-gas chemistry.

## Methods

### (1) Noble gas molecules

In addition to the 31 molecules we previously studied,<sup>[37]</sup> we have added FNgNBH (Ng = Kr, Xe), HNgNBH (Ng = Kr, Xe), FNgCC<sup>-</sup> (Ng = He, Ar, Kr, Xe),<sup>[23]</sup> FNgO<sup>-</sup> (He, Ar, Kr, Xe),<sup>[14]</sup> and HBNNgO<sup>-</sup> (Kr, Xe). Some of the new molecules contain Ng–N bonding which was not included in previous studies. Three 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.<sup>[14,23,43]</sup> The noble gas molecules in the current study are listed in Table 1.

### (2) Basis sets

The current study used Dunning's correlation consistent polarization basis sets, including cc-pVnZ and aug-cc-pVnZ ( $n = D, T, Q$ ).<sup>[44,45]</sup> For Ar, the cc-pV( $n+d$ )Z and aug-cc-pV( $n+d$ )Z basis sets were used for better performance in basis set extrapolation.<sup>[46]</sup> For Au and Xe, the cc-pVnZ-pp and aug-cc-pVnZ-pp<sup>[47]</sup> 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)<sup>[48]</sup> energy calculation, is abbreviated as apqz.

### (3) Geometry Optimization

The molecular geometries were fully optimized at the CCSD(T)/aug-cc-pVTZ level. Vibrational frequency calculation has been performed at the same level of theory to ensure that the molecular structures obtained are true energy minima. All the subsequent electronic structure calculation is based on the molecular structures obtained at this level.

### (4) Noble-Gas Bond Energies (NGBE)

The NGBE has been defined as in the previous study.<sup>[37]</sup> If the molecules are of the type XNgY where X and Y are atoms or chemical groups, the NGBE are the energy changes of XNgY  $\rightarrow$  X + Ng + Y. If the molecules are of the type NgZ where

Z are BeO or AuF, the NGBE are defined as the energy changes of  $\text{NgZ} \rightarrow \text{Ng} + \text{Z}$ . For the anions of the type  $\text{XNgY}^-$ , the NGBE are defined as the energy changes of  $\text{XNgY}^- \rightarrow \text{X} + \text{Ng} + \text{Y}^-$  where Y has larger electron affinity than X. All energies in the current study are Born-Oppenheimer energies.

#### (5) Complete Basis Set (CBS) Energies

The CCSD(T)/CBS energies for all species were obtained using the formula:<sup>[49]</sup>

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

$$E_{\text{CBS}} = E_4 - \left( \frac{E_3 - E_4}{3^{-3} - 4^{-3}} \right) 4^{-3} \quad (2)$$

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

#### (6) Theoretical Methods Tested

The wavefunction-based theory MP2<sup>[50]</sup> and CCSD(T), and the density functionals theory (DFT) MPW1B95,<sup>[51]</sup> MPW1PW9,<sup>[52,53]</sup> B98,<sup>[54]</sup> B3LYP,<sup>[55]</sup> BMK,<sup>[56]</sup> B3P86,<sup>[57,58]</sup> M05-2X,<sup>[59]</sup> M06-2X,<sup>[60]</sup> BLYP,<sup>[58,61]</sup> MPWB95,<sup>[52,62]</sup> MPWPW91,<sup>[52,53]</sup> B2GP-PLYP,<sup>[63]</sup> DSD-BLYP<sup>[64]</sup> have been benchmarked for the prediction of the NGBE against the CCSD(T)/CBS values described above.

#### (7) Main-Group Total Atomization Energies

Some of the methods in the current study have also been benchmarked against a standard main-group total atomization energy database MGAE109<sup>[65]</sup> to check if they give balanced performance in predicting both the bond energies of “non-noble” main-group molecules and noble-gas containing molecules.

#### (8) Multi-coefficient DFT (MC-DFT)

The MC-DFT method<sup>[39-41]</sup> uses more than one basis set (B1, B2, B3, etc.) to extrapolate the Born-Oppenheimer energies according to the formula:

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

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

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

#### (9) *Doubly Hybrid (DH) Methods*

The doubly hybrid method<sup>[41,42]</sup> combines the Hartree-Fock (HF), MP2 and DFT energies according to the formula:

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

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

All the electronic structure calculation was performed using the Gaussian 16 programs, revision A03.<sup>[66]</sup>

## Results and Discussion

### (1) *Molecular Structures*

The calculated geometry parameters of the 45 noble-gas containing molecules at the CCSD(T)/aptz level are listed in Table 2. The schematic molecular structures are shown in Figure 1. Except for FNgCH<sub>3</sub> which is in the point group  $C_{3v}$ , all other structures are linear with  $C_{\infty v}$  symmetry. Thirty one of the structures have been included in our previous study,<sup>[37]</sup> and 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 are found not to be energy minima at the CCSD(T)/aptz level. To our knowledge, FNgNBH, HNgNBH, and HBNNgO<sup>-</sup> 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 bond lengths in HNgNBH are 0.2 ~ 0.3 Å longer, which reflects the significantly larger NGBE of FNgNBH (See Table 3). The HBNNgO<sup>-</sup> molecules can also be viewed as ion-induced dipole complexes as HBN<sup>-</sup>...NgO, similar to F<sup>-</sup>...NgO.<sup>[14]</sup> The N...Ng bond distances in HBNKrO<sup>-</sup> and HBNXeO<sup>-</sup> are 2.457 and

2.497 Å, respectively. They are  $\sim 0.2$  Å larger than the F...Ng distances in FNgO<sup>-</sup>. The Ng–O distances in both types of molecules are very similar. The previous study<sup>[37]</sup> 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.

## (2) Noble-Gas Bond Energies

Table 3 shows the calculated NGBE at CCSD(T)/CBS level. As expected, all the NGBE for molecules containing He, Ne, and Ar are very low. To our knowledge, there are still no known stable neutral or anionic Ne-containing molecules either by experiments or theoretical prediction. The FKrNBH which has a NGBE of 22.3 kcal/mol is expected to be stable at cryogenic conditions. The HKrNBH has a similar NGBE to that of HKrCCH. Since HKrCCH has been observed in Kr matrix,<sup>[13]</sup> there is a good chance that HKrNBH can also be observed at similar conditions. The calculated NGBE for FKrCN is  $\sim 7$  kcal/mol higher than those obtained by Zhu et al.<sup>[26]</sup> because of the larger basis sets and the CBS extrapolation used in the current study. All the anions included in the current database, except for FHeCC<sup>-</sup>, should also be stable at cryogenic conditions. For XNgY<sup>-</sup>, there is another three-body dissociation pathway, i.e., to X<sup>-</sup> + 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 NGBE obtained in the current study are almost identical to the previous results. The NGBE of some of the Xe-containing molecules are slightly different due to the different program defaults on the definition of core electrons.

## (3) Benchmark on NGBE

Table 4 shows the MUE by various theoretical methods on the 45 NGBE. The Hartree Fock theory seriously underestimates the NGBE by more than 50 kcal/mol on average. For all the 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 basis set is certainly important in NGBE prediction. By comparing the results obtained using apdz and pdz, or aptz with ptz, except for the HF theory and the non-hybrid DFTs, the diffuse functions are also

crucial for obtaining accurate NGBE. For the non-hybrid functionals, the accuracy is relatively insensitive to the choice of basis sets, and the MUEs are in the range of 6-15 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 1.9, 1.9 and 1.5 kcal/mol, respectively. This is consistent with our previous benchmark.<sup>[37]</sup> In comparison, the commonly used MP2, B3LYP, M06-2X theories with aptz basis sets give MUEs of 7.4, 3.3, and 5.6 kcal/mol, respectively. It is well-known that MP2 theory usually overestimates the NGBE.<sup>[14,15,35,37,38]</sup> The MP2/apdz method gives an MUE of 4.4 kcal/mol, significantly smaller than those of MP2/aptz and MP2/pdz methods. It is worth mentioning that the MPW1PW91, B98, and BMK functionals also give reasonably accurate results (MUEs  $\leq$  3.0 kcal/mol). The CCSD(T) theory with aptz and apqz basis sets gives MUEs of 1.8 and 0.8 kcal/mol, respectively.

#### (4) Development of MC-DFT Methods

We have shown in previous work that the MC-DFT methods can provide accurate prediction on the thermochemical kinetics data at relatively low computational cost.<sup>[39-41]</sup> In the current study, we have tested the basis set combinations of apdz/aptz and pdz/apdz/aptz using the functionals MPW1B95, MPW1PW91, B98, B3LYP, B2GP-PLYP, and DSD-BLYP. The energies were computed according to Eqs.(3) and (4). The MC-DFT performance on the NGBE as compared to the result using a single aptz basis set is shown in Table 5. For the MPW1PW91 and B2GP-PLYP functionals, the apdz/aptz combination significantly reduces the MUEs by 35-40%. Using this combination, the lowest MUE of 1.3 kcal/mol was obtained by the B2GP-PLYP functional with only one empirical coefficient( $c_1 \sim 1.459$ ). For all functionals except DSD-BLYP, the pdz/apdz/aptz combination significantly reduces the MUEs by 37-50%. Using this combination, the lowest MUE of 1.1 kcal/mol was obtained by the B2GP-PLYP functional, followed very closely by MPW1B95 and MPW1PW91 with MUEs of 1.2 and 1.3 kcal/mol, respectively. Two empirical coefficients were used for this basis set combination. The empirical coefficients of the most accurate methods are listed in the Supporting Information (Table S2).

## (5) Development of Doubly Hybrid Method

The doubly hybrid method combines the hybrid-DFT and the MP2 calculation. It has been shown to be a very economical way to achieve good accuracy on thermochemical kinetics.<sup>[41,42]</sup> In the current study, we have combined the hybrid functionals MPW1B95, MPW1PW91, B98, B3LYP, B2GP-PLYP, and DSD-BLYP using the aptz basis set with MP2 calculation using the pdz, apdz, ptz, and aptz basis sets. The energies were computed according to Eq.(5), and the performance of the doubly hybrid methods on the NGBE as compared to the pure DFT calculation are listed in Table 6. As seen in the Table, the MPW1PW91 and B2GP-PLYP functionals show significant improvement in accuracy when combining with the additional MP2 calculation. It is noted that in the MP2 part of calculation, using aptz basis set does not significantly improve the accuracy over that of using apdz basis set. Since the computational cost of MP2/aptz is significantly higher, using MP2/apdz in the doubly hybrid methods is preferred. The lowest MUEs, 1.3 and 1.4 kcal/mol, were obtained using the DSD-BLYP and B2GP-PLYP functionals, respectively, with the MP2/apdz calculation. These MUEs are only slightly higher than those of the best MC-DFT methods mentioned above, and the computational costs of the MC-DFT and the Doubly Hybrid 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 the Supporting Information (Table S3) that for MPW1B95, B2GP-PLYP, and DSD-BLYP functionals, the DFT/apdz + MP2/apdz combinations give MUEs of 2.3, 2.1, and 2.0 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 doubly hybrid methods may also be good choices. The B2GP-PLYP and DSD-BLYP functionals are themselves so called “double hybrid” functionals which include second-order correlation energy calculated from the density orbitals.<sup>[63,64,67-70]</sup> In a sense, the doubly hybrid methods based on these functionals can also be called the “triply hybrid” methods.

## (6) Benchmark on both MGAE109 and NGBE44 Database

The benchmark on MGAE109 has been performed using various theoretical methods previously.<sup>[39,41,59,60,71-73]</sup> We applied the methods developed in the current

study to test their performance against MGAE109, and the results are shown in the Supporting Information (Tables S1-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/[apdz/aptz] with MUEs of 1.9, 1.7, and 2.2 kcal/mol, respectively. All of them are significantly better than corresponding single-basis-set results. The M06-2X benchmark is consistent with previous studies.<sup>[40,41,60,74,75]</sup> We then benchmarked the various methods against both the MGAE109 and NGBE45 (total 154 energies), and selected results are shown in Table 7. Full test results are included in the Supporting Information (Table S2 and Table 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 MUE for B3LYP and M06-2X with single aptz basis set are 4.9 and 3.6 respectively. The best MC-DFT methods include B2GP-PLYP/[apdz/aptz], and DSD-PLYP/[apdz/aptz] with overall MUEs of 1.8 and 2.0 kcal/mol, respectively. For the overall performance of the doubly hybrid methods, the most accurate ones are B2GP-PLYP/aptz + MP2/apdz and DSD-BLYP/aptz + MP2/apdz with MUE of 2.0 and 2.1 kcal/mol, respectively. These methods, as shown in Table 7, are almost as accurate as the MC-DFT methods, and they are significantly more accurate than their DFT components are (with MUE of 5.2 and 3.7 kcal/mol). The empirical coefficients of the best methods mentioned above are listed in the Supporting Information (Tables S2 and S3).

## Summary

We have expanded the noble-gas bond energies (NGBE) database from 31 to 45 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 multi-coefficient DFT (MC-DFT) and doubly hybrid (DH) methods which give significantly more accurate NGBE at only small additional cost. The database, the benchmark, and the new methods are important for future theoretical study in the field of the 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.

### **Funding Information**

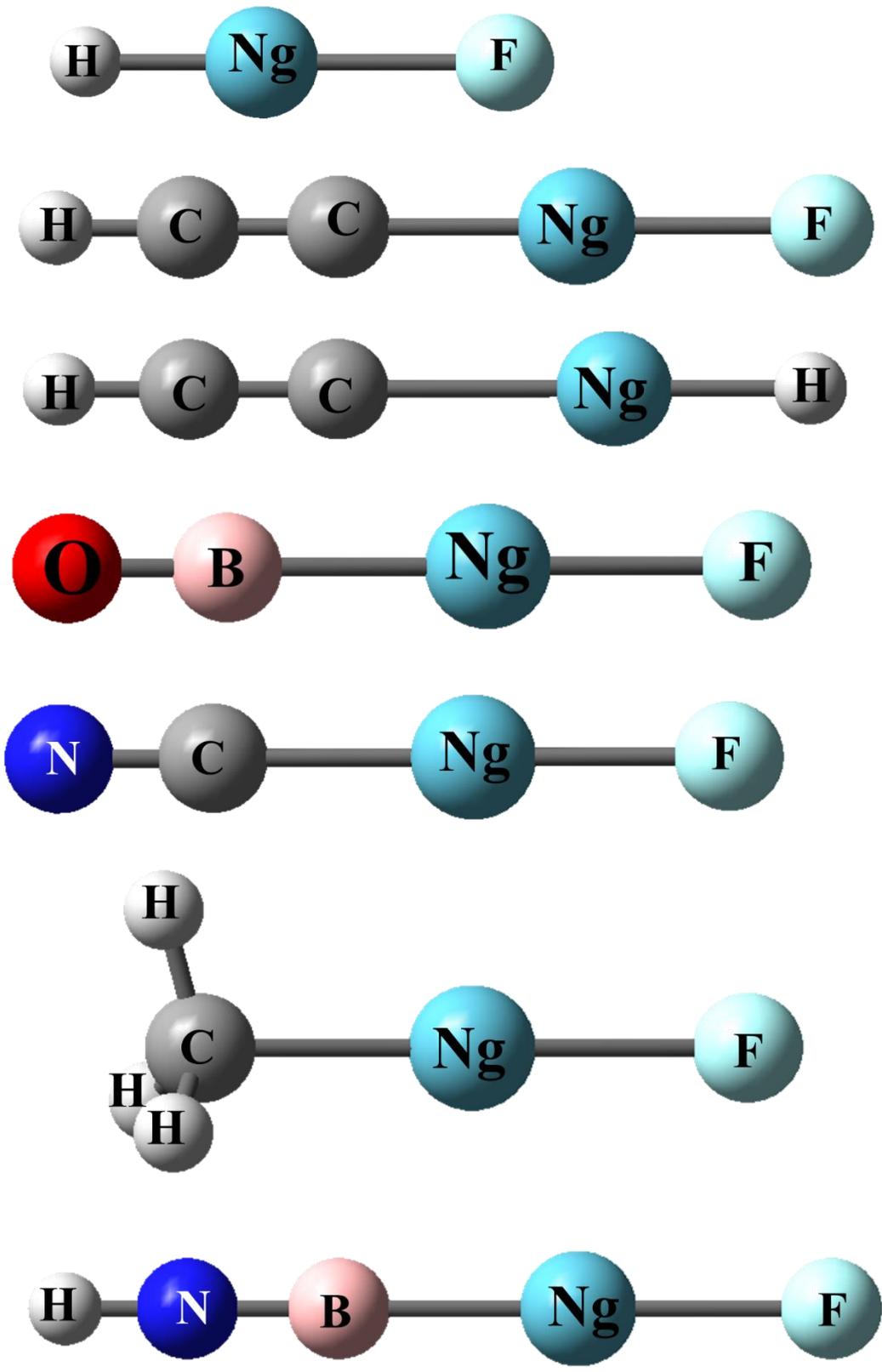
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### **Research Resources**

We are grateful to the National Center for High-Performance Computing (NCHC) for providing part of the computational resources.

**Keywords:** Multi-coefficient density functional theory · Doubly hybrid method · Noble gas molecule · Noble gas chemistry · Noble-gas bond energies

Additional Supporting Information may be found in the online version of this article.



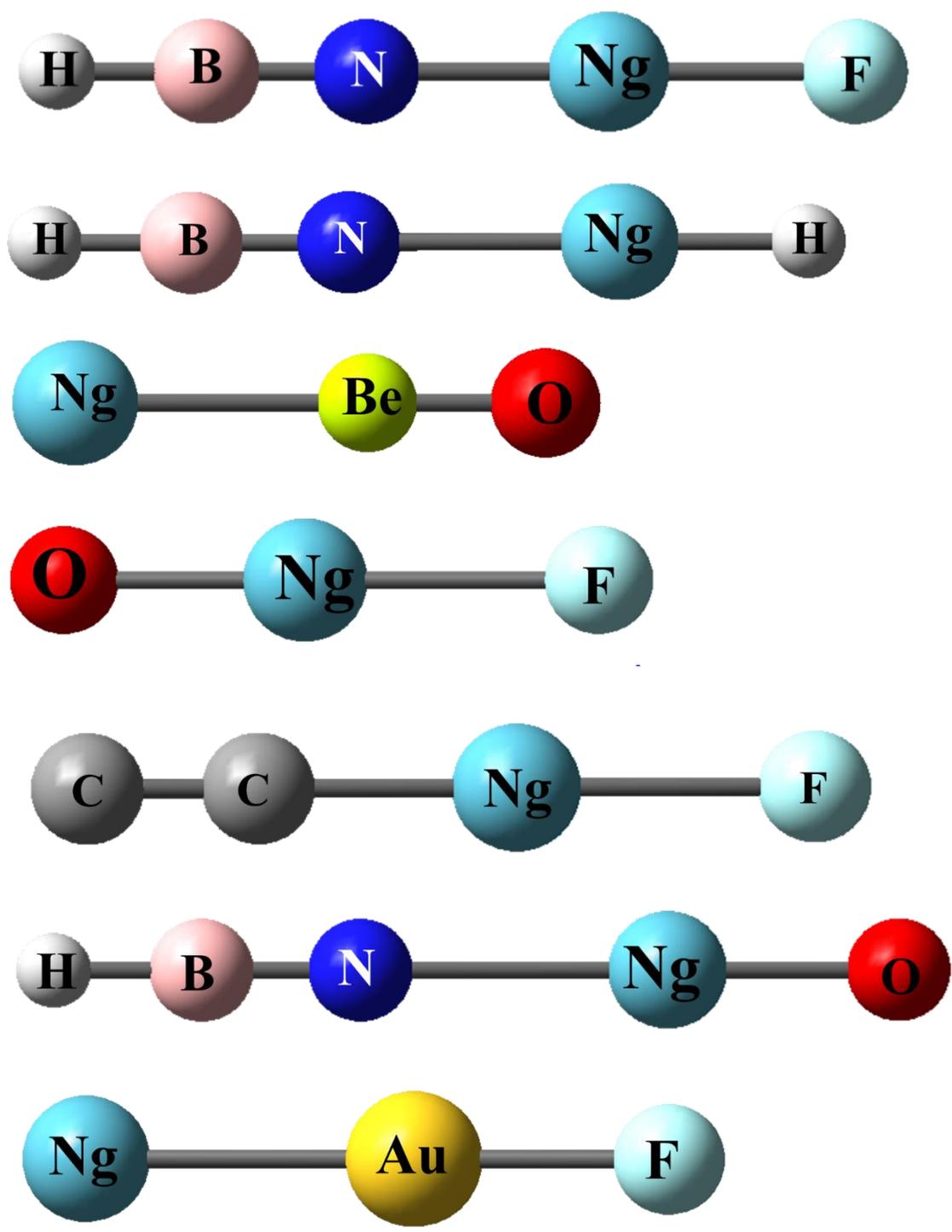


Figure 1. Schematic plot of molecular structures of the noble gas (Ng)-containing molecules in the current study.

Table 1. List of the 45 noble gas-containing molecules in the current study.

HHeF		HArF	HKrF	HXeF
			HKrCCH	HXeCCH
		FArCCH	FKrCCH	FXeCCH
		FArBO	FKrBO	FXeBO
		FArCN	FKrCN	FXeCN
		FArCH <sub>3</sub>	FKrCH <sub>3</sub>	FXeCH <sub>3</sub>
		FArBNH	FKrBNH	FXeBNH
			FKrNBH	FXeNBH
			HKrNBH	HXeNBH
HeBeO	NeBeO	ArBeO	KrBeO	XeBeO
HeAuF	NeAuF	ArAuF	KrAuF	XeAuF
FHeCC <sup>-</sup>		FArCC <sup>-</sup>	FKrCC <sup>-</sup>	FXeCC <sup>-</sup>
FHeO <sup>-</sup>		FArO <sup>-</sup>	FKrO <sup>-</sup>	FXeO <sup>-</sup>
			HBNKrO <sup>-</sup>	HBNXeO <sup>-</sup>



		FNgCC <sup>-</sup>			
F-Ng	1.625		2.176	2.201	2.252
Ng-C	1.137		1.782	1.904	2.060
		HBNNgO <sup>-</sup>			
N-Ng				2.457	2.497
Ng-O				1.849	1.950
		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

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<sup>a</sup>Structures in C<sub>3v</sub> point group.

Table 3. Calculated NGBE (in kcal/mol) at CCSD(T)/CBS level.

	He	Ne	Ar	Kr	Xe
HN <sub>g</sub> F	-15.0		10.1	28.5	52.3
HN <sub>g</sub> CCH				9.3	31.5
FN <sub>g</sub> CCH			8.3	35.1	67.5
FN <sub>g</sub> BO			5.8	26.8	53.8
FN <sub>g</sub> CN			-2.2	25.7	59.4
FN <sub>g</sub> CH <sub>3</sub>			0.7	19.2	43.2
FN <sub>g</sub> BNH			13.1	32.5	57.9
FN <sub>g</sub> NBH				22.3	59.3
HN <sub>g</sub> NBH				8.7	33.0
NgBeO	5.2	5.5	12.4	14.5	17.8
NgAuF	6.5	2.5	13.9	19.0	26.7
FN <sub>g</sub> CC <sup>-</sup>	2.1		22.1	41.6	66.6
FN <sub>g</sub> O <sup>-</sup>	17.1		35.5	55.9	83.1
HBNN <sub>g</sub> O <sup>-</sup>				39.4	66.0

Table 4. Mean unsigned error (in kcal/mol) of various theoretical methods on the 45 NGBE.

	pdz	apdz	ptz	aptz
HF	64.1	59.1	57.2	57.3
MP2	17.6	4.4	6.9	7.4
B3LYP	11.0	4.3	4.0	3.3
MPW1B95	11.0	3.0	3.8	1.9
MPW1PW91	12.2	4.2	4.7	2.7
B98	10.2	3.6	3.5	3.0
BMK	13.5	5.1	4.6	2.6
B3P86	8.2	3.6	3.4	4.4
M05-2X	16.4	7.9	6.5	4.8
M06-2X	16.5	8.3	7.6	5.6
B2GP-PLYP	17.4	5.7	6.2	1.9
DSD-BLYP	19.2	4.8	8.0	1.5
BLYP	7.3	7.3	7.3	8.4
MPWB95	11.5	13.9	14.3	15.5
MPWPW91	6.4	9.5	10.0	10.9

Table 5. The MC-DFT performance (MUE in kcal/mol) on the 45 NGBEs

	aptz	apdz/aptz	pdz/apdz/aptz
MPW1B95	1.9	1.7	1.2
MPW1PW91	2.7	1.6	1.3
B98	3.0	2.9	2.1
B3LYP	3.3	2.9	2.1
B2GP-PLYP	1.9	1.3	1.1
DSD-BLYP	1.5	1.4	1.4
BMK	2.6	1.9	1.7

Table 6. The performance (MUE in kcal/mol) of doubly hybrid methods on the 45 NGBEs using different basis sets in the MP2 calculation.

	DFT/aptz <sup>a</sup>	pdz	apdz	ptz	aptz
MPW1B95	1.9	1.8	1.9	1.7	1.6
MPW1PW91	2.7	1.8	2.1	1.9	2.0
B98	3.0	2.6	2.6	2.3	2.4
B3LYP	3.3	2.9	2.8	2.5	2.5
B2GP-PLYP	1.9	1.6	1.4	1.5	1.5
DSD-BLYP	1.5	1.5	1.3	1.5	1.4

<sup>a</sup>Pure DFT results using aptz basis set for comparison

Table 7. The performance (MUE in kcal/mol) of selected MC-DFT and doubly hybrid methods on both MGAE109 and NGBE45.

Methods	MUE
MPW1B95/aptz	2.7
BMK/aptz	3.0
B3LYP/aptz	4.9
M06-2X/aptz	3.6
B2GP-PLYP/aptz	5.2
DSD-BLYP/aptz	3.7
MPW1PW91/aptz	4.5
MPW1B95/apdz/aptz	2.7
BMK/apdz/aptz	2.7
B2GP-PLYP/apdz/aptz	1.8
DSD-BLYP/apdz/aptz	2.0
MPW1PW91/apdz/aptz	3.1
MPW1B95/pdz/apdz/aptz	2.7
BMK/pdz/apdz/aptz	2.6
B2GP-PLYP/pdz/apdz/aptz	1.8
DSD-BLYP/pdz/apdz/aptz	2.0
MPW1PW91/pdz/apdz/aptz	3.1
B2GP-PLYP/aptz + MP2/apdz	2.0
DSD-PLYP/aptz + MP2/apdz	2.1

## Reference

- [1] L. Rayleigh, W. Ramsay, *Philos. Trans. Royal Soc. A* **1895**, 186, 187.
- [2] E. N. Hiebert In Historical Remarks on the Discovery of Argon: The First Noble Gas; University of Chicago Press, **1963**.
- [3] L. Pauling, *J. Am. Chem. Soc.* **1933**, 55, 1895.
- [4] N. Bartlett, *Proc Chem Soc*, **1962**, 218.
- [5] D. T. Hawkins, W. E. Falconer, N. Bartlett, Noble Gas Compounds: A Bibliography, 1962-1976; Ifi/Plenum, **1978**.
- [6] M. Pettersson, J. Lundell, M. Räsänen, *J. Chem. Phys.* **1995**, 102, 6423.
- [7] M. Pettersson, J. Lundell; M. Räsänen, *J. Chem. Phys.* **1995**, 103, 205.
- [8] M. Pettersson, J. Lundell, L. Khriachtchev, M. Räsänen, *J. Chem. Phys.* **1998**, 109, 618.
- [9] M. Pettersson, J. Lundell, M. Räsänen, *Eur. J. Inorg. Chem.* **1999**, 729.
- [10] L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, M. Räsänen, *Nature* **2000**, 406, 874.
- [11] M. Pettersson, L. Khriachtchev, A. Lignell, M. Räsänen, Z. Bihary, R. Gerber, *J. Chem. Phys.* **2002**, 116, 2508.
- [12] L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen, M. Räsänen, *J. Am. Chem. Soc.* **2003**, 125, 4696.
- [13] L. Khriachtchev, H. Tanskanen, A. Cohen, R. B. Gerber, J. Lundell, M. Pettersson, H. Kiljunen, M. Räsänen, *J. Am. Chem. Soc.* **2003**, 125, 6876.
- [14] T.-H. Li, C.-H. Mou, H.-R. Chen, W.-P. Hu, *J. Am. Chem. Soc.* **2005**, 127, 9241.
- [15] T.-Y. Lin, J.-B. Hsu, W.-P. Hu, *Chem. Phys. Lett.* **2005**, 402, 514.
- [16] P. Antoniotti, S. Borocci, N. Bronzolino, P. Cecchi, F. Grandinetti, *J. Phys. Chem. A* **2007**, 111, 10144.
- [17] W. Grochala, *Chem. Soc. Rev.* **2007**, 36, 1632.
- [18] Y.-L. Liu, Y.-H. Chang, T.-H. Li, H.-R. Chen, W.-P. Hu, *Chem. Phys. Lett.* **2007**, 439, 14.
- [19] L. Khriachtchev, M. Räsänen, R. B. Gerber, *Acc. Chem. Res.* **2008**, 42, 183.
- [20] L. Khriachtchev, A. Domanskaya, J. Lundell, A. Akimov, M. Räsänen, E. Misochko, *J. Phys. Chem. A* **2010**, 114, 4181.
- [21] Y.-L. Sun, J.-T. Hong, W.-P. Hu, *J. Phys. Chem. A* **2010**, 114, 9359.
- [22] T. Arppe, L. Khriachtchev, A. Lignell, A. V. Domanskaya, M. Räsänen, *Inorg. Chem.* **2012**, 51, 4398.
- [23] C.-Y. Peng, C.-Y. Yang, Y.-L. Sun, W.-P. Hu, *J. Chem. Phys.* **2012**, 137, 194303.
- [24] J.-L. Chen, C.-Y. Yang, H.-J. Lin, W.-P. Hu, *Phys. Chem. Chem. Phys.* **2013**, 15,

9701.

- [25] D. Samanta, *J. Phys. Chem. Lett.* **2014**, *5*, 3151.
- [26] C. Zhu, M. Räsänen, L. Khriachtchev, *J. Chem. Phys.* **2015**, *143*, 074306.
- [27] A. Ghosh, S. Dey, D. Manna, T. K. Ghanty, *J. Phys. Chem. A* **2015**, *119*, 5732.
- [28] T. Vent-Schmidt, J. T. Goettel, G. J. Schrobilgen, S. Riedel, *Chem. Eur. J.* **2015**, *21*, 11244.
- [29] A. Ghosh, D. Manna, T. K. Ghanty, *Phys. Chem. Chem. Phys.* **2016**, *18*, 12289.
- [30] J. T. Goettel, V. G. Haensch, G. J. Schrobilgen, *J. Am. Chem. Soc.* **2017**, *139*, 8725.
- [31] A. Ghosh, A. Gupta, R. Gupta, T. K. Ghanty, *Phys. Chem. Chem. Phys.* **2018**, *20*, 20270.
- [32] K. M. Marczenko, H. P. Mercier, G. J. Schrobilgen, *Angew. Chem. Int. Ed.* **2018**, *57*, 12448.
- [33] R. Saha, B. Mandal, P. K. Chattaraj, *Int. J. Quantum Chem.* **2018**, *118*, 25499.
- [34] R. C. Fortenberry, *J. Mol. Spectrosc.* **2019**, *357*, 4.
- [35] T.-H. Li, Y.-L. Liu, R.-J. Lin, T.-Y. Yeh, W.-P. Hu, *Chem. Phys. Lett.* **2007**, *434*, 38.
- [36] S. Borocci, N. Bronzolino, M. Giordani, F. Grandinetti, *J. Phys. Chem. A* **2010**, *114*, 7382.
- [37] T.-Y. Lai, C.-Y. Yang, H.-J. Lin, C.-Y. Yang, W.-P. Hu, *J. Chem. Phys.* **2011**, *134*, 244110.
- [38] A. Lignell, L. Khriachtchev, J. Lundell, H. Tanskanen, M. Räsänen, *J. Chem. Phys.* **2006**, *125*, 184514.
- [39] J.-L. Chen, Y.-L. Sun, K.-J. Wu, W.-P. Hu, *J. Phys. Chem. A* **2008**, *112*, 1064.
- [40] J.-L. Chen, J.-T. Hong, K.-J. Wu, W.-P. Hu, *Chem. Phys. Lett.* **2009**, *468*, 307.
- [41] P. C. Liu, W. P. Hu, *J. Comput. Chem.* **2014**, *35*, 1560.
- [42] Y. Zhao, B. J. Lynch, D. G. Truhlar, *J. Phys. Chem. A* **2004**, *108*, 4786.
- [43] P. Antoniotti, S. Borocci, N. Bronzolino, P. Cecchi, F. Grandinetti, *J. Phys. Chem. A* **2007**, *111*, 10144.
- [44] T. H. Dunning Jr., *J. Chem. Phys.* **1989**, *90*, 1007.
- [45] R. A. Kendall, T. H. Dunning Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.
- [46] T. H. Dunning Jr., K. A. Peterson, A. K. Wilson, *J. Chem. Phys.* **2001**, *114*, 9244.
- [47] K. A. Peterson, D. Figgen, E. Goll, H. Stoll, M. Dolg, *J. Chem. Phys.* **2003**, *119*, 11113.
- [48] J. D. Watts, J. Gauss, R. J. Bartlett, *J. Chem. Phys.* **1993**, *98*, 8718.
- [49] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A. K. Wilson, *Chem. Phys. Lett.* **1998**, *286*, 243.
- [50] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.

- [51] Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2004**, *108*, 6908.
- [52] C. Adamo, V. Barone, *J. Chem. Phys.* **1998**, *108*, 664.
- [53] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **1992**, *46*, 6671.
- [54] H. L. Schmider, A. D. Becke, *J. Chem. Phys.* **1998**, *108*, 9624.
- [55] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [56] A. D. Boese, J. M. Martin, *J. Chem. Phys.* **2004**, *121*, 3405.
- [57] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.
- [58] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
- [59] Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Theory Comput.* **2006**, *2*, 364.
- [60] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
- [61] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [62] A. D. Becke, *J. Chem. Phys.* **1996**, *104*, 1040.
- [63] A. Karton, A. Tarnopolsky, J.-F. Lamere, G. C. Schatz, J. M. Martin, *J. Phys. Chem. A* **2008**, *112*, 12868.
- [64] S. Kozuch, D. Gruzman, J. M. Martin, *J. Phys. Chem. C* **2010**, *114*, 20801.
- [65] R. Peverati, D. G. Truhlar, *J. Chem. Phys.* **2011**, *135*, 191102.
- [66] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin; V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi; M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford, CT, 2016.
- [67] S. Grimme, *J. Chem. Phys.* **2006**, *124*, 034108.
- [68] T. Schwabe, S. Grimme, *Phys. Chem. Chem. Phys.* **2006**, *8*, 4398.
- [69] T. Schwabe, S. Grimme, *Phys. Chem. Chem. Phys.* **2007**, *9*, 3397.
- [70] A. Tarnopolsky, A. Karton, R. Sertchook, D. Vuzman, J. M. Martin, *J. Phys. Chem. A* **2008**, *112*, 3.
- [71] Y. Zhao, B. J. Lynch, D. G. Truhlar, *Phys. Chem. Chem. Phys.* **2005**, *7*, 43.
- [72] Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 5656.

- [73] R. Peverati, D. G. Truhlar, *J. Phys. Chem. Lett.* **2012**, *3*, 117.
- [74] A. Karton, S. Daon, J. M. L. Martin, *Chem. Phys. Lett.* **2011**, *510*, 165.
- [75] L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi, S. Grimme, *Phys. Chem. Chem. Phys.* **2017**, *19*, 32184.