Effects of Basis Set Choice upon the Atomization Energy of the Second-Row Compounds SO_2, CCl, and ClO_2 for B3LYP and B3PW91

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Received: May 19, 2003; In Final Form: June 16, 2003

The atomization energies of the species SO_2, ClO_2, and CCl have been calculated using the hybrid density functional approaches B3LYP and B3PW91. These functionals have been used in combination with the correlation-consistent basis sets cc-pVxZ and aug-cc-pVxZ (where x = D(2), T(3), Q(4), or 5). The impact of the newly revised correlation-consistent basis sets for second-row atoms (cc-pV(x+d)Z, aug-cc-pV(x+d)Z) upon the description of these systems has been assessed. Smooth convergence toward the Kohn−Sham limit is observed. The impact of the tight d function is particularly significant in the description of atomization energies for ClO_2 and SO_2 at the double-ζ and triple-ζ levels of basis sets, improving the energies by 13−17 and 9−10 kcal/mol, respectively.

I. Introduction

Density functional theory (DFT) provides a powerful means to account for electron correlation at a much reduced computational cost as compared with conventional advanced ab initio methods. The use of DFT has become widespread due not only to this low cost, but also to its utility in a large realm of chemical problems, ranging from surface studies of periodic systems to atmospheric chemistry.[1−4] In the present work, we focus on three species of importance in atmospheric modeling. All three systems have been difficult to describe theoretically as demonstrated in a study by Martell et. al. of the impact of functional and basis set choice upon atomization energies of a series of 44 molecules.[5] Of this set, the errors, as compared with results from experiment, were most severe for SO_2, ClO_2, and CCl, with errors in the dissociation energies at the B3LYP/cc-pVTZ//cc-pVDZ level of −19.4, −11.9, and 14.4 kcal/mol, respectively. It must be noted that the largest basis sets used in this study were of triple-ζ quality. In general, it has been assumed that the basis set requirements for density functional theory are less than for advanced ab initio (post-HF) approaches, and that convergence has been reached, or nearly reached, at the triple-ζ level.

In previous studies, it has been found that advanced ab initio methods such as CCSD(T) in combination with high-level basis sets such as 6-311+G(3df) and correlation-consistent basis sets (cc-pV5Z) result in significant errors in the atomization energy of SO_2 (∼14 and ∼4 kcal/mol, respectively).[6] Using CCSD(T), the correlation-consistent basis set series (cc-pVTZ, cc-pVQZ, and cc-pV5Z) and a three-point extrapolation scheme to estimate a complete basis set (CBS) limit, Bauschlicher and Partridge obtained an underestimation of the dissociation energy of 6.2 kcal/mol.[6] They found that the addition of a high-exponent d function in the sulfur basis set reduced the error significantly in CBS-TQ5 (three-point CBS limit extrapolation using results at the triple-, quadruple-, and quintuple-ζ level basis sets) limit to −1.9 kcal/mol. The study by Bauschlicher and Partridge was the first indication of a potential deficiency in the correlation-consistent basis sets. Martin noted that the same problem existed in SO and suggested a systematic series of improvements comprised of higher angular momentum functions (d, f, g) should occur in the correlation-consistent basis sets for sulfur, as he found that these functions enabled dramatic improvements in the extrapolated binding energies.[7] He prescribed that the correlation-consistent basis sets should be revised as follows: add a 1d set to the cc-pVTZ set, add a 2d1f set to the cc-pVQZ set, and add a 3d2f1g set to the cc-pV5Z set. Martin and Uzan noted this deficiency occurred not only for sulfur systems such as SO but also for other systems containing second-row atoms.[8] In a study of SO and SO_2, Bauschlicher and Ricca examined the impact of additional higher angular momentum functions upon convergence to the CBS limit. They noted that the best agreement was obtained by adding a 2d set to each level of the correlation-consistent basis set.[9]

Dunning, Peterson, and Wilson investigated the noted basis set deficiencies.[10] One of the challenges in examining the basis set deficiencies is that the addition of any function to the basis set will improve the total energy and likely the dissociation energy. The key to any improvements in basis sets is to preserve systematic behavior needed to provide accurate extrapolations to the CBS limit. Dunning et al. developed a strategy for improving the standard correlation-consistent basis sets for second-row atoms, providing an improved family of basis functions, noted cc-pV(x+d)Z, where x = D(2), T(3), Q(4), or 5.[10] They found that the lower level basis sets simply required the addition of an optimized tight d function, but that the cc-pVQZ and higher basis sets required reexamination of the basis set coverage. To date, these revised basis sets have been used in a number of ab initio studies of sulfur systems, and significant improvements in energies have been observed.[10,11]

In this study, two widely used density functional approaches, B3LYP and B3PW91,[12−15] are paired with the standard and revised correlation-consistent basis sets and augmented correlation-consistent basis sets to examine the impact of the additional tight d function and higher angular momentum functions upon the structures and energetics of SO_2, ClO_2, and CCl. B3LYP and B3PW91 are known to be among the more reliable functions in the prediction of atomization energies. B3LYP has been a

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10.1021/jp0353791 CCC: $25.00

primary approach used in earlier studies of SO_2,[6] and both functionals have been shown to be among the more reliable functionals in the study of systems of atmospheric importance.[5,16]

Widespread use of the correlation-consistent basis sets is due in part to their systematic construction, which has resulted in convergent behavior toward the CBS limit for ab initio methods for a range of properties. This systematic behavior has enabled the development of schemes to estimate CBS limits, thus enabling a better understanding of the performance of computational methods due to elimination of the basis set error. In this study, two schemes commonly used to estimate CBS limits were used to determine estimates of Kohn−Sham limits for each DFT approach.

II. Computational Methods

All calculations were performed using the Gaussian 98 program package.[17] The default numerical grid (75, 302) in Gaussian 98 was used to evaluate the density functional theory integrals. This grid includes 75 radial shells and 302 angular points per shell, resulting in approximately 7000 quadrature points per atom. In general, this grid is known to provide energies accurate to five places past the decimal.[18]

Four series of the correlation-consistent basis sets were used in the calculations: the standard sets, cc-pV*x*Z,[19] the revised sets, cc-pV(*x*+*d*)Z,[10] the augmented sets, aug-cc-pV*x*Z,[20] which include diffuse functions, and the revised augmented sets, aug-cc-pV(*x*+*d*)Z[10] (where x = D(2), T(3), Q(4), or 5). These sets were used in combination with the B3LYP and B3PW91 functionals.

Geometry optimizations and frequency calculations were done for each level of basis set. Contributions from the zero-point corrections were taken directly from the frequency calculations without scaling and were included in the final energies reported.

Due to the construction of correlation-consistent basis sets, convergent behavior toward the CBS limit can be observed for a wide range of properties and energetics. In numerous previous ab initio studies, this convergence has been well represented by the exponential equation[21]

$$\mathrm{E(x)} = \mathrm{E}_\infty + \mathrm{A}e^{-\mathrm{B}x} \tag{1}$$

where x is the cardinal number of the basis set (i.e., for cc-pVDZ, $x = 2$ and, for cc-pVTZ, $x = 3$), $E(x)$ represents the energy at the xth level, and E_∞ represents the extrapolated CBS limit. A and B are parameters that are determined in the fit. To obtain the extrapolation values, at least three points are used in the nonlinear fitting scheme.

A more recent, but also successful, extrapolation scheme is the two-parameter extrapolation scheme developed by Halkier et al. given below:[22]

$$\mathrm{E(x)} = \mathrm{E}_\infty + \mathrm{A}l_{\max}^{\;-3} \tag{2}$$

where $l_{\max}$ is the highest l value in the basis set and is also equal to x. A is a parameter determined in the fit.

Though there are a number of approaches to obtain extrapolated CBS limits, the above two schemes are used to extrapolate to Kohn−Sham limits in this study. A more in-depth study of extrapolation schemes to Kohn−Sham limits for a large set of molecules will be presented in a forthcoming paper.[16]

III. Results and Discussion

SO_2. Optimized bond lengths and bond angles for B3LYP and B3PW91 functionals and the full series of basis functions are given in Table 1. The S−O bond distance and O−S−O bond angle given by experiment are 1.432 Å and 119.5°, respectively. For both functionals, there is improvement in the bond length as the cardinal number of the basis set is increased, with a difference of ∼0.05 Å between the double-ζ and quintuple-ζ levels of the standard correlation-consistent basis sets (cc-pV*x*Z and aug-cc-pV*x*Z). This difference is reduced to ∼0.02 Å for both the cc-pV(*x*+*d*)Z and aug-cc-pV(*x*+*d*)Z sets. For the bond angle, there is a slight lowering (<0.20°) with increasing basis set size from double-ζ to quintuple-ζ for the tight d sets, whereas for the standard and standard augmented sets, this difference is as large as 1.5°.

In Table 1, B3LYP and B3PW91 atomization energies approach results from experiment with increasing basis set size. The B3LYP/cc-pVQZ energy improves upon the B3LYP/cc-pVTZ energy by 6.61 kcal/mol. This series convergences very slowly for DFT, as B3LYP/cc-pV5Z still results in a significant increase in energy, 5.23 kcal/mol greater than that of cc-pVQZ. The behavior of the B3LYP/aug-cc-pV*x*Z, B3PW91/cc-pV*x*Z, and B3PW91/aug-cc-pV*x*Z series results in similar convergence. The energies are dramatically affected by the tight d functions as shown in changes between the cc-pV*x*Z and cc-pV(*x*+*d*)Z results. At the B3LYP/cc-pVDZ level, the +*d* basis set improves

TABLE 1: Atomization Energy of SO_2 (kcal/mol) Using B3LYP and B3PW91 with the Correlation-Consistent Basis Sets

method	basis set	D_0	r (Å)	A (deg)
experiment^a		254.0	1.4321	119.50
B3LYP	cc-pVDZ	210.02	1.4808	117.71
	cc-pVTZ	235.69	1.4505	118.25
	cc-pVQZ	242.30	1.4419	118.65
	cc-pV5Z	247.53	1.4355	119.13
	cc-pV∞Z^b	248.32		
	cc-pV(D+*d*)Z	227.32	1.4525	119.33
	cc-pV(T+*d*)Z	245.93	1.4370	119.23
	cc-pV(Q+*d*)Z	248.09	1.4349	119.18
	cc-pV(5+*d*)Z	248.61	1.4340	119.20
	cc-pV∞+Z^b	248.55		
	aug-cc-pVDZ	215.69	1.4842	117.46
	aug-cc-pVTZ	235.98	1.4514	118.15
	aug-cc-pVQZ	242.33	1.4420	118.63
	aug-cc-pV5Z	247.64	1.4355	119.14
	aug-cc-pV∞Z^b	249.50		
	aug-cc-pV(D+*d*)Z	232.52	1.4567	119.17
	aug-cc-pV(T+*d*)Z	246.13	1.4381	119.12
	aug-cc-pV(Q+*d*)Z	248.05	1.4350	119.15
	aug-cc-pV(5+*d*)Z	248.71	1.434	119.20
	aug-cc-pV∞+Z^b	248.64		
B3PW91	cc-pVDZ	212.02	1.4758	117.80
	cc-pVTZ	238.00	1.4468	118.28
	cc-pVQZ	244.46	1.4385	118.68
	cc-pV5Z	249.41	1.4322	119.10
	cc-pV∞Z^b	250.01		
	cc-pV(D+*d*)Z	229.48	1.4483	119.39
	cc-pV(T+*d*)Z	248.26	1.4337	119.23
	cc-pV(Q+*d*)Z	250.30	1.4317	119.16
	cc-pV(5+*d*)Z	250.88	1.4308	119.19
	cc-pV∞+Z^b	250.78		
	aug-cc-pVDZ	218.27	1.4796	117.53
	aug-cc-pVTZ	238.34	1.4475	118.20
	aug-cc-pVQZ	244.45	1.4385	118.67
	aug-cc-pV5Z	249.84	1.4320	119.13
	aug-cc-pV∞Z^b	251.63		
	aug-cc-pV(D+*d*)Z	235.28	1.4527	119.21
	aug-cc-pV(T+*d*)Z	248.53	1.4347	119.15
	aug-cc-pV(Q+*d*)Z	250.23	1.4317	119.15
	aug-cc-pV(5+*d*)Z	250.93	1.4309	119.20
	aug-cc-pV∞+Z^b	250.81		

^{a} Experimental data were obtained from ref 24. ^{b} Kohn−Sham limits were obtained using the exponential extrapolation scheme (eq 1).

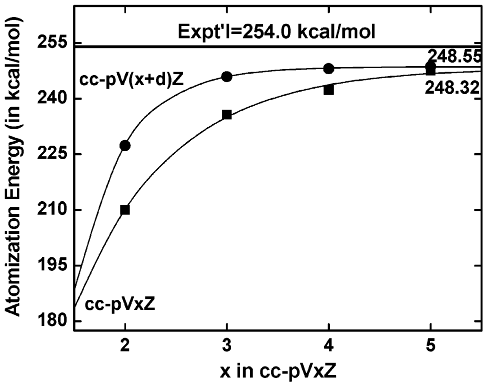

Figure 1. Atomization energy of SO_2 using B3LYP/cc-pV*x*Z.

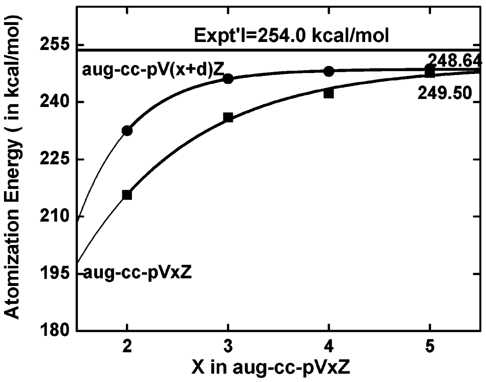

Figure 2. Atomization energy of SO_2 using B3LYP/aug-cc-pV*x*Z.

the atomization energy by 17.30 kcal/mol. For the higher level sets (cc-pVTZ, cc-pVQZ, cc-pV5Z), the +*d* basis sets result in improvements of 10.24, 5.79, and 1.08 kcal/mol, respectively. The cc-pV(*x*+*d*)Z series converges more quickly than the cc-pV*x*Z basis set, as demonstrated by the small difference (0.52 kcal/mol) between the cc-pV(Q+*d*)Z and cc-pV(5+*d*)Z results. These improvements are similar for B3LYP/aug-cc-pV(*x*+*d*)Z, B3PW91/cc-pV(*x*+*d*)Z, and B3PW91/aug-cc-pV(*x*+*d*)Z.

The augmented sets provide an improvement over the standard valence sets. However, the effect is not as dramatic as the effect of the tight *d* sets. At the double-ζ level for B3LYP, the diffuse basis set results in an increase of 5.67 kcal/mol in atomization energy, whereas the tight d results in an increase of 17.30 kcal/mol.

Figure 1 better illustrates the convergence of cc-pV(*x*+*d*)Z as compared to that of cc-pV*x*Z. Though the new sets significantly improve the B3LYP energies at the lower levels of basis set and the series converges more quickly, both series converge to nearly the same limit. Figure 2 shows the same behavior for the augmented series comparison. Similar behavior is exhibited for the B3PW91 calculations.

Table 1 also includes extrapolated Kohn−Sham limits obtained using eq 1. For all of the basis set series, B3PW91 provides Kohn−Sham limits that are nearer experiment than B3LYP. The B3PW91/aug-cc-pVxZ Kohn−Sham limit provided the best agreement with experiment, with an error of 2.37 kcal/mol. Although the tight *d* sets have a dramatic impact upon the accuracy of calculations using small basis sets, the sets have little effect upon the Kohn−Sham limit, with differences in the limit of no more than 1 kcal/mol from results obtained using the corresponding standard or augmented valence basis sets.

Table 2 lists the atomization energies calculated using the two-parameter extrapolation scheme (eq 2). All possible fits of eq 2 using two levels of basis sets were considered. As shown, the B3LYP/cc-pV*x*Z and B3LYP/aug-cc-pV*x*Z extrapolated limits using only results at the quadruple and quintuple basis sets (Q5) are in good agreement with experiment, with errors of 0.98 and 0.79 kcal/mol, respectively. The B3LYP/DT and B3PW91/DQ extrapolation for cc-pV(*x*+*d*)Z also provide reasonable agreement with experiment, with errors of 0.23 and 0.73 kcal/mol, respectively, though increasing levels of basis sets actually result in a lowering in the extrapolated limits.

TABLE 2: Extrapolation of the Calculated Atomization Energy of SO_2 to the Kohn−Sham Limit Using Several Two-Parameter Extrapolation Schemes and the Exponential Scheme[a]

method	extrapolation scheme[b]	cc-pV*x*Z	cc-pV(*x*+*d*)Z	aug-cc-pV*x*Z	aug-cc-pV(*x*+*d*)Z
B3LYP	DT	246.50	253.77	244.52	251.86
	DQ	246.91	251.06	246.14	250.27
	D5	250.09	250.07	249.82	249.82
	TQ	247.12	249.67	246.96	249.45
	T5	250.79	249.35	250.85	249.42
	Q5	253.02	249.16	253.21	249.40
	∞	248.32	248.55	249.50	248.64
B3PW91	DT	248.94	256.17	246.79	254.11
	DQ	249.09	253.27	248.19	252.37
	D5	251.97	252.34	252.00	252.00
	TQ	249.17	251.79	248.91	251.47
	T5	252.55	251.60	253.01	251.59
	Q5	254.60	251.49	255.50	251.66
	∞	250.01	250.78	251.63	250.81

[a] The atomization energy from experiment is 254.0 kcal/mol.[24] [b] DT represents extrapolation using cc-pVDZ and cc-pVTZ, TQ represents extrapolation using cc-pVTZ and cc-pVQZ, and ∞ represents the extrapolated Kohn−Sham limit.

CCl. CCl geometries and energies are presented in Table 3. The bond lengths are in good agreement (0.01 Å) with experiment. The tight *d* basis functions enable a slightly faster convergence to experiment as do the augmented sets over the standard valence sets. Basically, these additional functions result in bond length convergence for B3LYP at the quadruple-ζ level as opposed to the quintuple-ζ level (which is the case for the standard sets).

Until recently, previous theoretical studies resulted in large deviations in atomization energy from experiment for CCl. The G2 scheme, which usually gives atomization energies accurate to within 2−3 kcal/mol, predicted an atomization energy of 95.9 kcal/mol for CCl,[23] whereas the value from experiment was 80 ± 5 kcal/mol.[24] However, combining a recent experimental determination of the heat of formation of CCl of 105.0 ± 3.1 kcal/mol by Jesinger et al.[25] with the known heats of formation of C (170.14 ± 0.11 kcal/mol) and Cl (28.617 ± 0.001 kcal/mol) leads to a derived atomization energy of 93.8 kcal/mol. NIST reports a value of 94.4 kcal/mol for the atomization energy. These results provide much better agreement with previous theory, such as the G2 result of 95.9 kcal/mol[23] and a recent high-level ab initio study by Dixon and Peterson,[26] who obtained an atomization energy of 95.5 ± 0.3 kcal/mol using a CBS limit extrapolation of CCSD(T)/aug-cc-pV*x*Z and including the effects of core valence (0.37 kcal/mol), scalar relativity (−0.19 kcal/mol), and spin−orbit (−0.73 kcal/mol) corrections.

Atomization energy results for CCl are shown in Table 3. The atomization energy increases by including diffuse functions, and increases even further by using the tight *d* basis sets. As was the case for SO_2, the most significant effects are observed at the double-ζ level, where the augmented set increases the energy by 0.48 kcal/mol over those of the standard valence sets, and the tight *d* set increases the energy by 1.72 kcal/mol for B3LYP. The tight d sets also result in faster convergence toward a Kohn−Sham limit. However, it must be noted that B3LYP

TABLE 3: Atomization Energy of CCl (kcal/mol) Using B3LYP and B3PW91 with the Correlation-Consistent Basis Sets

method	basis set	D_0	r (Å)
experiment[a]		94.4	1.65
B3LYP	cc-pVDZ	92.42	1.6897
	cc-pVTZ	94.56	1.6666
	cc-pVQZ	95.44	1.6594
	cc-pV5Z	96.06	1.6541
	cc-pV∞Z[b]	96.49	
	cc-pV(D+*d*)Z	94.14	1.6760
	cc-pV(T+*d*)Z	95.66	1.6577
	cc-pV(Q+*d*)Z	96.14	1.6542
	cc-pV(5+*d*)Z	96.20	1.6531
	cc-pV∞+Z[b]	96.27	
	aug-cc-pVDZ	92.90	1.6832
	aug-cc-pVTZ	94.77	1.6638
	aug-cc-pVQZ	95.60	1.6581
	aug-cc-pV5Z	96.42	1.6533
	aug-cc-pV∞Z[b]	97.30	
	aug-cc-pV(D+*d*)Z	94.76	1.6686
	aug-cc-pV(T+*d*)Z	95.88	1.6549
	aug-cc-pV(Q+*d*)Z	96.30	1.6530
	aug-cc-pV(5+*d*)Z	96.55	1.6523
	aug-cc-pV∞+Z[b]	96.68	
B3PW91	cc-pVDZ	94.76	1.6795
	cc-pVTZ	97.39	1.6577
	cc-pVQZ	98.26	1.6521
	cc-pV5Z	98.90	1.6471
	cc-pV∞Z[b]	99.15	
	cc-pV(D+*d*)Z	96.53	1.6661
	cc-pV(T+*d*)Z	98.53	1.6498
	cc-pV(Q+*d*)Z	98.97	1.6471
	cc-pV(5+*d*)Z	99.05	1.6460
	cc-pV∞+Z[b]	99.08	
	aug-cc-pVDZ	95.62	1.6740
	aug-cc-pVTZ	97.64	1.6556
	aug-cc-pVQZ	98.55	1.6510
	aug-cc-pV5Z	99.18	1.6464
	aug-cc-pV∞Z[b]	99.72	
	aug-cc-pV(D+*d*)Z	97.54	1.6593
	aug-cc-pV(T+*d*)Z	98.78	1.6476
	aug-cc-pV(Q+*d*)Z	99.25	1.6461
	aug-cc-pV(5+*d*)Z	99.32	1.6453
	aug-cc-pV∞+Z[b]	99.41	

[a] Experimental data were obtained from ref 24. [b] Kohn−Sham limits were obtained using the exponential extrapolation scheme (eq 1).

and B3PW91 both overshoot results from experiment as the basis set approaches convergence. B3LYP is approximately 2 kcal/mol greater than experiment, whereas B3PW91 is approximately 5 kcal/mol larger than experiment.

Estimated Kohn−Sham limits obtained from the three-point extrapolation scheme given by eq 1 are also included in the table. These limits are very near (0.1−0.6 kcal/mol) the quintuple-ζ calculated energies. An investigation of the two-point extrapolation scheme (eq 2) is given in Table 4. Regardless of the two points selected in the extrapolation, there is very little fluctuation in the estimated limit.

TABLE 4: Extrapolation of the Calculated Atomization Energy of CCl to the Kohn−Sham Limit Using Several Two-Parameter Extrapolation Schemes and the Exponential Scheme[a]

method	extrapolation scheme[b]	cc-pV*x*Z	cc-pV(*x*+*d*)Z	aug-cc-pV*x*Z	aug-cc-pV(*x*+*d*)Z
B3LYP	DT	95.46	96.30	95.56	96.35
	DQ	95.87	96.43	95.99	96.52
	D5	96.31	96.34	96.66	96.67
	TQ	96.08	96.49	96.21	96.61
	T5	96.47	96.35	96.87	96.73
	Q5	96.71	96.26	97.28	96.81
	∞	96.49	96.27	97.30	96.68
B3PW91	DT	98.50	99.37	98.49	99.30
	DQ	98.76	99.32	98.97	99.49
	D5	99.18	99.22	99.42	99.44
	TQ	98.89	99.29	99.21	99.59
	T5	99.32	99.19	99.60	99.47
	Q5	99.57	99.13	99.84	99.30
	∞	99.15	99.08	99.72	99.41

[a] The atomization energy from experiment is 94.4 kcal/mol.[24] [b] DT represents extrapolation using cc-pVDZ and cc-pVTZ, TQ represents extrapolation using cc-pVTZ and cc-pVQZ, and ∞ represents the extrapolated Kohn−Sham limit.

TABLE 5: Atomization Energy of ClO_2 (kcal/mol) Using B3LYP and B3PW91 in Combination with the Correlation-Consistent Basis Sets

method	basis set	D_0	r (Å)	A (deg)
experiment[a]		122.9	1.47	117.6
B3LYP	cc-pVDZ	88.10	1.5405	117.79
	cc-pVTZ	110.74	1.4992	116.97
	cc-pVQZ	116.87	1.4880	117.08
	cc-pV5Z	122.05	1.4780	117.35
	cc-pV∞Z[b]	123.10		
	cc-pV(D+*d*)Z	101.36	1.5036	118.89
	cc-pV(T+*d*)Z	119.64	1.4797	117.54
	cc-pV(Q+*d*)Z	122.39	1.4767	117.42
	cc-pV(5+*d*)Z	123.19	1.4757	117.36
	cc-pV∞+Z[b]	123.15		
	aug-cc-pVDZ	97.26	1.5407	116.80
	aug-cc-pVTZ	112.32	1.4998	116.77
	aug-cc-pVQZ	117.36	1.4881	116.98
	aug-cc-pV5Z	122.55	1.4778	117.31
	aug-cc-pV∞Z[b]	125.23		
	aug-cc-pV(D+*d*)Z	110.52	1.5058	117.85
	aug-cc-pV(T+*d*)Z	121.11	1.4803	117.36
	aug-cc-pV(Q+*d*)Z	122.79	1.4768	117.33
	aug-cc-pV(5+*d*)Z	123.63	1.4757	117.36
	aug-cc-pV∞+Z[b]	123.53		
B3PW91	cc-pVDZ	91.15	1.5272	117.82
	cc-pVTZ	115.37	1.4892	116.99
	cc-pVQZ	121.50	1.4788	117.11
	cc-pV5Z	126.84	1.4692	117.41
	cc-pV∞Z[b]	127.63		
	cc-pV(D+*d*)Z	105.11	1.4922	118.85
	cc-pV(T+*d*)Z	124.61	1.4707	117.54
	cc-pV(Q+*d*)Z	127.24	1.4679	117.45
	cc-pV(5+*d*)Z	128.03	1.4668	117.41
	cc-pV∞+Z[b]	127.95		
	aug-cc-pVDZ	101.29	1.5286	116.89
	aug-cc-pVTZ	116.91	1.4898	116.83
	aug-cc-pVQZ	122.07	1.4788	117.04
	aug-cc-pV5Z	127.22	1.4689	117.36
	aug-cc-pV∞Z[b]	129.70		
	aug-cc-pV(D+*d*)Z	115.23	1.4952	117.89
	aug-cc-pV(T+*d*)Z	126.05	1.4712	117.40
	aug-cc-pV(Q+*d*)Z	127.72	1.4679	117.39
	aug-cc-pV(5+*d*)Z	128.37	1.4668	117.41
	aug-cc-pV∞+Z[b]	128.31		

[a] Experimental data were obtained from ref 24. [b] Kohn−Sham limits were obtained using the exponential extrapolation scheme (eq 1).

ClO_2. Table 5 provides optimized structures and atomization energies for ClO_2. As the cardinal number of the basis set increases, the Cl−O bond length comes within 0.01−0.02 Å of experiment for all method/basis set combinations. For the atomization energies, the impact of augmented and tight *d* basis sets is quite significant, as was the case for SO_2. At the B3LYP/cc-pVDZ level, the augmented set increases the atomization energy by 9.16 kcal/mol whereas the tight d sets increase the atomization energy by 13.26 kcal/mol. The addition of augmenting functions to the tight *d* set is particularly dramatic, with an increase in energy of 22.42 kcal/mol. B3PW91 overestimates the atomization energy by 4.0−6.0 kcal/mol at the quintuple-ζ level.

The three-point extrapolation scheme provides Kohn−Sham limits within 0.6 kcal/mol for B3LYP with the cc-pV*x*Z, cc-

TABLE 6: Extrapolation of the Calculated Atomization Energy of ClO_2 to the Kohn−Sham Limit Using Several Two-Parameter Extrapolation Schemes and the Exponential Scheme[a]

method	extrapolation scheme[b]	cc-pV*x*Z	cc-pV(*x*+*d*)Z	aug-cc-pV*x*Z	aug-cc-pV(*x*+*d*)Z
B3LYP	DT	120.27	127.34	118.66	125.57
	DQ	120.98	125.39	120.23	124.54
	D5	124.37	124.68	124.28	124.53
	DQ	121.34	124.40	121.04	124.02
	T5	125.17	124.17	125.37	124.32
	Q5	127.48	124.03	128.00	124.51
	∞	123.10	123.15	125.23	123.53
B3PW91	DT	125.57	132.82	123.49	130.61
	DQ	125.84	130.40	125.04	129.50
	D5	129.28	129.60	128.99	129.27
	DQ	125.97	129.16	125.84	128.94
	T5	130.00	128.97	130.06	129.01
	Q5	132.44	128.86	132.62	129.05
	∞	127.63	127.95	129.70	128.31

[a] The atomization energy from experiment is 122.9 kcal/mol.[24] [b] DT represents extrapolation using cc-pVDZ and cc-pVTZ, TQ represents extrapolation using cc-pVTZ and cc-pVQZ, and ∞ represents the extrapolated Kohn−Sham limit.

pV(*x*+*d*)Z, and aug-cc-pV(*x*+*d*)Z basis set series. The estimated limit for the aug-cc-pV*x*Z series is 125.2 kcal/mol, overestimating the value from experiment by 2.3 kcal/mol. Overall, the two-point extrapolation scheme results in overestimation of the atomization energies, as shown in Table 6.

IV. Conclusions

SO_2, ClO_2, and CCl all exhibit smooth convergence toward a limit as the basis set size is increased. Due to this smooth convergence, extrapolation formulas that have been successfully applied to obtain estimates of the CBS limit for ab initio methods have been used here to obtain estimates of Kohn−Sham limits. A further investigation of the interplay of basis sets and functionals, convergence, and extrapolation to Kohn−Sham limits has been investigated in forthcoming work.

The new correlation-consistent basis sets for second-row atoms have a significant impact upon the convergence rate of the structure and energetics of SO_2 and ClO_2 with respect to increasing basis set size for the B3LYP and B3PW91 functionals. Though the rate of convergence is increased, the overall convergence limit undergoes little change. The impact of the tight *d* function is particularly dramatic for the double-ζ (cc-pVDZ and aug-cc-pVDZ) and triple-ζ (cc-pVTZ and aug-cc-pVTZ) basis sets. Thus, in future studies where basis sets no larger than double- or triple-ζ are used, it is essential that these new basis sets be employed.

Acknowledgment. This work was supported by the National Science Foundation (NSF POWRE Grant No. 9973675) and the University of North Texas Faculty Research Grant Program. Computer resources were, in part, provided by the National Computational Science Alliance under Grant No. CHE010021 and utilized the NCSA SGI Origin 2000. We also thank Dr. Tom Cundari and the reviewers for their useful comments.

References and Notes

(1) Kang, J. K.; Musgrave, C. B. *J. Chem. Phys.* **2000**, *113*, 7582.

(2) Fournier, R.; Sinnott, S. B.; DePristo, A. E. *J. Chem. Phys.* **1992**, *97*, 4149.

(3) Wang, G. T.; Mui, C.; Musgrave, C. B.; Bent, S. F. *J. Am. Chem. Soc.* **2002**, *124*, 8990.

(4) Kwon, O.; McKee, M. L. *J. Phys. Chem. A* **2001**, *105*, 478.

(5) Martell, J. M.; Goddard, J. D. *J. Phys. Chem. A* **1997**, *101*, 1927.

(6) Bauschlicher, C. W.; Partridge, H. *Chem. Phys. Lett.* **1995**, *240*, 533.

(7) Martin, J. M. L. *J. Chem. Phys.* **1998**, *108*, 2791.

(8) Martin, J. M. L.; Uzan, O. *Chem. Phys. Lett.* **1998**, *282*, 16.

(9) Bauschlicher, C. W.; Ricca, A. *J. Phys. Chem. A* **1998**, *102*, 8044.

(10) Dunning, T. H..; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.

(11) Wilson, A. K.; Dunning, T. H. To be published.

(12) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(13) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhas, C. *Phys. Rev. B* **1992**, *46*, 6671.

(16) Wang, N. X.; Wilson, A. K. To be published.

(17) Gaussian 98 (Revision A.11): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 2001.

(18) Altmann, J. A.; Handy, N. C.; Ingamells, V. E. *Mol. Phys.* **1997**, *92*, 339.

(19) Dunning, T. H. Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(20) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(21) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.

(22) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

(23) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(24) M. W. Chase, J.; Davies, C. A.; J. R. Downey, J.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. 1).

(25) Jesinger, R. A.; Squires, R. R. *Int. J. Mass Spectrom.* **1999**, *185*, 745.

(26) Dixon, D. A.; Peterson, K. A. *J. Chem. Phys.* **2001**, *115*, 6327.