

Atomization Energies of SO and SO₂: Basis Set Extrapolation Revisited

Charles W. Bauschlicher, Jr.*

STC-230-3, NASA Ames Research Center, Moffett Field, California 94035

Alessandra Ricca

STC-230-3, Thermosciences Institute, NASA Ames Research Center, Moffett Field, California 94035

Received: April 23, 1998

The addition of tight functions to sulfur and extrapolation to the complete basis set limit are required to obtain accurate atomization energies. Six different extrapolation procedures are tried. The best atomization energies come from the series of basis sets that yield the most consistent results for all extrapolation techniques. In the variable α approach, α values larger than 4.5 or smaller than 3 appear to suggest that the extrapolation may not be reliable. It does not appear possible to determine a reliable basis set series using only the triple and quadruple- ζ based sets. The scalar relativistic effects reduce the atomization of SO and SO₂ by 0.34 and 0.81 kcal/mol, respectively, and clearly must be accounted for if a highly accurate atomization energy is to be computed. The magnitude of the core-valence (CV) contribution to the atomization is affected by missing diffuse valence functions. The CV contribution is much more stable if basis set superposition errors are accounted for. A similar study of SF, SF⁺, and SF₆ shows that the best family of basis sets varies with the nature of the S bonding.

1. Introduction

The calculation of accurate bond energies or atomization energies has many important applications. While there are several approaches to this problem, the common thread is the determination of the equilibrium geometries and calculation of the zero-point energies at a modest level of theory (such as density functional theory, DFT), the calculation of the bond energies using an accurate treatment of the electron correlation problem (such as the coupled cluster singles and doubles approach¹ with a perturbational estimate of the connected triples,² CCSD(T)), and a correction to reach the basis set limit. The inclusion of relativistic effects and core-valence (CV) correlation are also required for some systems. The largest uncertainty in these procedures probably comes from the correction for basis set incompleteness, whether the G2 additive type correction³ is used or an extrapolation^{4–6} approach is used. No approach appears to be fail proof. The usually reliable G2 approach does not work well for SiF_n, whereas basis set extrapolation works well for these systems,⁷ while we have shown⁸ that basis set extrapolation, using the standard basis sets, does not work well for SO₂.

The (augmented-) correlation-consistent polarized-valence ((aug-) cc-pV) sets, which were developed by Dunning and co-workers,^{9–12} have been used extensively in studies that include basis set extrapolation. Extrapolation using the triple- ζ (TZ), quadruple- ζ (QZ), and quintuple- ζ (5Z) sets has proven to yield accurate bond energies in most cases. However, Bauschlicher and Partridge⁸ showed that missing tight functions on sulfur resulted in an inaccurate extrapolation for the atomization energy of SO₂. That is, if a family of basis sets is deficient in some systematic way, extrapolation will not overcome the deficiency and will therefore not yield reliable results. This problem is not unique to SO₂, we have recently found this also applies to

SF_n¹³ and Martin^{14,15} found it for several additional second-row compounds.

In their study, Bauschlicher and Partridge⁸ showed that adding a tight d function to the cc-pV basis sets significantly improved the atomization energy of SO₂. They suggested that adding two tight d functions to the cc-pV sets would yield an accurate value; in this work we denote such a series of basis sets as cc-pV+2d. More recently, Martin¹⁵ showed that the addition of diffuse functions was also required. However, Martin did not use two tight d functions, but instead used a series where a tight d was added to aug-cc-pVTZ, a 2d1f set of tight functions was added to aug-cc-pVQZ, and a 3d2f1g set was added to the aug-cc-pV5Z set; we denote this series as aug-cc-pV+d,2df,3d2fg. Using this series of basis sets in conjunction with a variable α extrapolation approach, Martin found excellent agreement with experiment for the atomization energies of SO and SO₂. The geometries and anharmonic force fields were also quite accurate. Martin optimized the geometries at the CCSD(T) level, which would be impractical for larger systems using such large basis sets. Martin did not include scalar relativistic effects nor correct the core-valence contribution for basis set superposition error (BSSE). In addition, Martin did not note that other extrapolation approaches did not agree well with the value obtained using the variable α approach.

In our very recent study¹³ of SF_n, we used an aug-cc-pV+d,-df,dfg series since this family of basis sets yielded very similar results for two-point n^{-3} , two-point n^{-4} , three-point ($n^{-4} + n^{-6}$), and variable α approaches. In addition to a consistent extrapolation, this series yielded an SF₆ atomization energy in good agreement with experiment. This basis set series is similar to the one used by Martin in his SO and SO₂ study.

In this manuscript we reinvestigate SO and SO₂. We consider different families of basis sets using several different extrapolation techniques. Our goals being to determine if one can judge a family of basis sets to be reliable based on the consistency of

TABLE 2: The Effect of Core-Valence on the Atomization Energy of SO₂, in kcal/mol

	BSSE				D_e			
	S		O		without BSSE		with BSSE correction	
	SCF	CCSD(T)	SCF	CCSD(T)	SCF	CCSD(T)	SCF	CCSD(T)
	cc-pVTZ+1p3d2f ^a							
valence						245.99		
CV						246.76		
Δ						0.77		
	aug-cc-pVTZ+3d2f							
valence	0.13	2.66	0.38	1.38	115.55	248.85	115.04	244.81
CV	0.13	2.85	0.38	1.40	115.55	249.58	115.04	245.33
Δ						0.73		0.52

^a From Martin.¹⁵**TABLE 3: The Dissociation Energy of SO ³ Σ^- , in kcal/mol**

	BSSE				D_e			
	S		O		no BSSE correction		with BSSE correction	
	SCF	(T) ^a	SCF	(T)	SCF	(T)	SCF	(T)
cc-pVTZ	0.04	0.71	0.21	1.21	45.54	114.35	45.29	112.42
cc-pVQZ	0.01	0.27	0.07	0.49	48.08	120.02	48.01	119.26
cc-pV5Z	0.00	0.18	0.01	0.17	49.68	123.02	49.67	122.67
aug-cc-pVTZ	0.06	1.02	0.12	0.64	46.65	116.96	46.47	115.30
aug-cc-pVQZ	0.01	0.37	0.05	0.34	48.46	121.32	48.41	120.61
aug-cc-pV5Z	0.00	0.22	0.01	0.12	49.82	123.59	49.81	123.26
aug-cc-pVTZ+d	0.06	1.04	0.12	0.65	48.92	119.07	48.74	117.37
aug-cc-pVTZ+2d	0.06	1.04	0.12	0.66	49.50	119.59	49.32	117.90
aug-cc-pVTZ+2df	0.06	1.01	0.13	0.67	49.75	119.99	49.56	118.31
aug-cc-pVQZ+d	0.01	0.36	0.05	0.34	49.72	122.47	49.66	121.76
aug-cc-pVQZ+2d	0.01	0.36	0.05	0.34	50.09	122.81	50.03	122.11
aug-cc-pVQZ+df	0.01	0.35	0.05	0.35	49.74	122.50	49.68	121.80
aug-cc-pVQZ+2df	0.01	0.35	0.05	0.35	50.11	122.85	50.05	122.15
aug-cc-pV5Z+d	0.00	0.21	0.01	0.12	50.16	123.90	50.15	123.57
aug-cc-pV5Z+2d	0.00	0.21	0.01	0.12	50.20	123.94	50.19	123.61
aug-cc-pV5Z+2df	0.00	0.21	0.01	0.12	50.20	123.96	50.19	123.63
aug-cc-pV5Z+dfg	0.00	0.21	0.01	0.12	50.16	123.94	50.15	123.61

^a Signifies CCSD(T).

function. Since Bauschlicher and Partridge²⁵ found the tight p function to have a very small effect, it is not included. To ensure saturation of the tight d space, three tight d functions ($\beta = 2.5$) are added to the S and O basis set. Two tight f ($\beta = 3.0$) are also added to S and O. These sets are denoted aug-cc-pVTZ+3d2f and aug-cc-pVQZ+3d2f. The aug-cc-pVTZ+3d2f and aug-cc-pVQZ+3d2f sets yield the same CV effect once BSSE has been accounted for. These results differ by only 0.02 kcal/mol from that obtained using the aug-cc-pVTZ+1p2d2f set.

The results for SO₂ are given in Table 2. The cc-pVTZ+1p3d2f results are taken from Martin;¹⁵ note that Martin added a third tight d function using a β of 3.0. The aug-cc-pVTZ+3d2f basis set yields a larger atomization energy, but a smaller CV effect, as found for SO. The aug-cc-pVTZ+3d2f CV value is further reduced if BSSE is accounted for. Thus the SO₂ results are consistent with those found for SO, with our values being slightly smaller than those reported by Martin, as a result of our including the diffuse functions and accounting for BSSE.

The computed dissociation energies of the X³ Σ^- state of SO are summarized in Table 3 as a function of basis set. The cc-pV and aug-cc-pV sets are those given by Dunning and co-workers. The number and type of tight functions added to S are added to the end of the basis set label. The β for these functions is the lesser of 3 and the β determined using the two tightest functions in the original basis set.

An inspection of the results yields several obvious conclusions. The BSSE decreases and the D_e increases as the basis

sets are improved from TZ to 5Z. The D_e increases even if the BSSE correction is included. Adding the diffuse functions increases the S(O) BSSE, but decreases the O(S) BSSE; it also increases the D_e values. Adding the tight functions has little effect on the BSSE and increases the D_e . The increase in D_e with the tight functions is very large at the TZ level and drops off quickly with improvement in the basis set, such that the effect of the tight functions is small at the 5Z level. The first d function has the largest effect. The second d has a larger effect than the first tight f function. It should also be noted that much of the effect of the tight functions is observed at the SCF level.

The extrapolated results for the SO D_e are summarized in Table 4. The first line is derived from the results reported by Martin¹⁵ using the aug-cc-pV+d,2df,3d2fg series. We first note the large α and the similar results for the variable α and $n^{-4} + n^{-6}$ extrapolation techniques. The two-point approaches using the TZ and QZ basis sets yield results that are larger than three-point values. The cc-pV results show a large variation with extrapolation approach; correcting for BSSE or adding the diffuse functions does not significantly improve the results. Adding the tight functions significantly improves the agreement between the different extrapolation methods. The aug-cc-pV+d and aug-cc-pV+d,df,dfg results are very similar. The variation with extrapolation technique is very small for the aug-cc-pV+2d and aug-cc-pV+2df sets and even the two-point approaches, based on the TZ and QZ sets, are in good agreement with the three-point approaches. Our $n^{-4} + n^{-6}$ and variable α extrapolated aug-cc-pV+2d values are smaller than those

TABLE 4: Extrapolation of SO Dissociation Energy, in kcal/mol

basis ^b	method ^a					
	3 TZ,QZ	3 QZ,5Z	4 TZ,QZ	4 QZ,5Z	4+6 TZ,QZ,5Z	α^c TZ,QZ,5Z
Martin ^d	126.78	126.07	126.12	125.78	125.67	125.60(4.615)
cc-pV	124.16	126.17	123.30	125.46	126.22	129.86(1.813)
cc-pV-BSSE	124.24	126.24	123.20	125.43	126.22	129.32(2.063)
aug-cc-pV	124.50	125.98	123.84	125.44	126.01	128.58(1.872)
aug-cc-pV-BSSE	124.49	126.04	123.68	125.41	126.02	128.41(2.068)
aug-cc-pV+d	124.95	125.41	124.43	125.07	125.30	125.83(2.778)
aug-cc-pV+d-BSSE	124.97	125.47	124.30	125.04	125.31	125.88(2.892)
aug-cc-pV+2d	125.16	125.12	124.67	124.86	124.92	125.01(3.585)
aug-cc-pV+2d-BSSE	125.18	125.19	124.54	124.83	124.93	125.08(3.511)
aug-cc-pV+2df	124.93	125.13	124.50	124.87	125.00	125.24(3.128)
aug-cc-pV+2df-BSSE	124.94	125.19	124.36	124.84	125.01	125.31(3.155)
aug-cc-pV+d,df,dfg	125.01	125.44	124.48	125.10	125.32	125.82(2.829)
			At $r = 1.49 \text{ \AA}$			
aug-cc-pV+2d	125.80	125.77	125.28	125.49	125.57	125.67(3.559)

^a The value signifies the type of extrapolation, for example “3” indicates an n^{-3} extrapolation, “4+6” indicates an $n^{-4} + n^{-6}$ extrapolation, and “ α ” indicates the variable α extrapolation. The second line shows which basis sets are used in the extrapolation. ^b The basis sets are described in detail in the text. ^c The α is given in parentheses. ^d At the CCSD(T) optimized distance using the aug-pV+d,2df,3d2fg set.¹⁵

TABLE 5: Extrapolation of SO₂ Atomization Energy, in kcal/mol

basis ^b	method ^a					
	3 TZ,QZ	3 QZ,5Z	4 TZ,QZ	4 QZ,5Z	4+6 TZ,QZ,5Z	α^c TZ,QZ,5Z
Martin ^d	262.34	259.93	260.70	259.30	258.81	258.64(5.085)
cc-pV	256.45	262.41	254.34	260.55	262.74	276.32(1.510)
aug-cc-pV	257.10	262.09	255.34	260.54	262.37	273.78(1.507)
aug-cc-pV+d	258.37	260.12	257.17	259.25	259.98	262.26(2.377)
aug-cc-pV+2d	259.16	259.12	258.05	258.51	258.67	258.88(3.559)
aug-cc-pV+2df	258.62	259.13	257.65	258.53	258.84	259.44(3.071)
aug-cc-pV+d,df,dfg	258.60	260.18	257.38	259.32	260.01	261.99(2.484)
ANO	255.28	261.19	253.51	259.52	261.64	278.93(1.229)
			At $r = 1.44 \text{ \AA}$ and $\angle = 119.17^\circ$			
aug-cc-pV+2d	260.49	260.46	259.32	259.82	259.99	260.24(3.541)

^a The value signifies the type of extrapolation, for example “3” indicates an n^{-3} extrapolation, “4+6” indicates an $n^{-4} + n^{-6}$ extrapolation, and “ α ” indicates the variable α extrapolation. The second line shows which basis sets are used in the extrapolation. ^b The basis sets are described in detail in the text. ^c The α is given in parentheses. ^d At the CCSD(T) optimized distance using the aug-pV+d,2df,3d2fg set.¹⁵

obtained by Martin, but most of this difference arises from using the B3LYP/6-31+G* geometry ($r = 1.5156 \text{ \AA}$), which is longer than the CCSD(T) optimized values. The final line in Table 4 is the aug-cc-pV+2d extrapolation using $r = 1.49 \text{ \AA}$, which is close to the average of Martin’s aug-cc-pVTZ+d and aug-cc-pVQZ+2df results. At this geometry, the aug-cc-pV+2d three-point extrapolation values are in excellent agreement with Martin, but the agreement of the two-point methods with the three-point methods for the aug-cc-pV+2d series is much better than for the series proposed by Martin.

Martin²⁶ has noted that using a cc-pVTZ+d basis set yields a B3LYP geometry of 1.489 \AA , which is in much better agreement with the CCSD(T) results. This is also true for the SO₂ geometry discussed below. Hence the problem with the B3LYP/6-31+G* geometry appears to be associated with the basis set.

In Table 5 the extrapolation results for the SO₂ atomization energy are summarized. The results labeled “Martin” are obtained using his results from the aug-cc-pVTZ+d,2df,3d2fg series. For this series, the variable α and $n^{-4} + n^{-6}$ extrapolation techniques yield similar results, but the agreement between these two techniques is not as good as for SO. The difference between the n^{-3} and n^{-4} approaches using the TZ and QZ basis set and the three-point approaches is rather large. Clearly for this choice of tight functions, the 5Z basis set calculation must be performed.

As found for SO, the cc-pV and aug-cc-pV sets do not yield reliable results for SO₂. There is a wide variation in the result depending on the extrapolation technique. Adding one tight d function improves the agreement between the different extrapolation methods significantly, but the variation is still a few kcal/mol. When the second d function is added, the agreement between all of the methods is good. Of special interest is the accuracy of the two-point extrapolation techniques using the TZ and QZ basis sets. Adding the f function hardly changes the $n^{-4} + n^{-6}$ result or the two-point approaches using the QZ and 5Z basis set. The n^{-3} technique using the TZ and QZ basis sets improves, but the variable α technique and the n^{-4} technique using the TZ and QZ basis sets differ by more with the $n^{-4} + n^{-6}$ result. Overall the aug-cc-pV+2d set appears to be the best set. It is somewhat disappointing that the difference between the two-point methods using the TZ and QZ basis sets is about the same for the aug-cc-pV+d, aug-cc-pV+2d, aug-cc-pV+d,df,dfg, and aug-cc-pV+2d1f basis sets. That is the difference between these two approaches does not indicate a reliable extrapolation using only the TZ and QZ sets. Thus suggesting that to obtain very accurate results, it is very difficult to avoid at least some 5Z calculations.

The last basis set test for SO₂ involves using an atomic natural orbital²⁷ (ANO) contraction of the cc-pV5Z basis set. We contract the ANO set to the same size as the cc-pVTZ, cc-pVQZ, and cc-pV5Z sets. The extrapolations using these ANO

TABLE 6: Best Estimate for the Dissociation Energy, kcal/mol

	SO			SO ₂		
	PW		Martin	PW		Martin
	B3LYP ^b	CCSD(T)	CCSD(T)	B3LYP	CCSD(T)	CCSD(T)
extrapolated D_e	124.92	125.57	125.62	258.67	259.99	258.64
spin-orbit	-0.78	-0.78	-0.78	-1.01	-1.01	-1.01
scalar relativistic	-0.34	-0.34		-0.81	-0.81	
core-valence	0.27	0.27	0.41	0.52	0.52	0.77
best D_e	124.03	124.68	125.25	257.13	258.69	258.40
Z_{pt}^a	1.64	1.64	1.64	4.38	4.38	4.38
D_0	122.39	123.04	123.61	252.75	254.07	254.02
experimental D_0	123.58 ²⁸	123.24 ²⁹		253.97 ³⁰		

^a The zero-point energy is taken from Martin.¹⁵ The B3LYP values for SO and SO₂ are 1.60 and 4.22 kcal/mol, respectively. ^b Signifies which geometry is used.

contractions are labeled “ANO” in the table. Clearly this is not an improvement over the original cc-pV series. Thus having tighter functions in the primitive set, but contracting to the size of a cc-pVTZ set does not improve the results. This is perhaps not too surprising as most of the effect of the tight d function on the cc-pVTZ set appears at the SCF level.

As for SO, the B3LYP/6-31+G* geometry ($r = 1.4656$ Å and $\angle = 118.63^\circ$) differs from the optimized CCSD(T) values reported by Martin. Using $r = 1.44$ Å and $\angle = 119.17^\circ$, which are close to the average of Martin’s aug-cc-pVTZ+d and aug-cc-pVQZ+2df results, increases the aug-cc-pV+2d atomization energy by about 1 kcal/mol. The agreement between the different extrapolation methods is very good, and much better than found by Martin.

In Table 6 we summarize our best estimate for the atomization energies of SO and SO₂. Our extrapolated D_e values are taken from the $n^{-4} + n^{-6}$ extrapolation using the aug-pV+2d basis set. We pick these values because this basis set yields the best agreement between the various extrapolation methods and the $n^{-4} + n^{-6}$ extrapolation approach shows the smallest variation for the basis sets with tight functions. We report present work (PW) for both the B3LYP/6-31+G* geometry and the geometry derived from Martin’s CCSD(T) results. We first note that our SO extrapolated D_e value for the B3LYP geometry is smaller than Martin’s value, but that our value at the CCSD(T) geometry is in very good agreement with Martin. For SO₂ our B3LYP value is in very good agreement with Martin, but our value at the CCSD(T) geometry is 1.3 kcal/mol larger. The effect of spin-orbit is taken from experiment²⁴ and therefore is the same for both geometries and for the work of Martin. The scalar relativistic effect, which is computed at the B3LYP geometry, reduces the atomization energy. The core-valence correction, also computed at the B3LYP geometry, increases the atomization energy. However, as noted above our values are smaller than those of Martin because we have included diffuse functions and accounted for BSSE. Our zero-point energy (ZPE) is taken from Martin; however, using the B3LYP value would not change our results significantly. Our D_0 values computed using the CCSD(T) geometries are in good agreement with experiment.^{28–30} Our values computed using the B3LYP/6-31+G* geometry are 0.65 and 1.32 kcal/mol smaller than those using the CCSD(T) geometry.

For SO, our best D_0 value is 0.57 kcal/mol smaller than Martin; most (0.48 kcal/mol) of this difference comes from his neglect of the scalar relativistic effect and overestimation of core-valence correlation. For SO₂ our best value and that of Martin only differ by 0.05 kcal/mol; however, this agreement is fortuitous, as Martin neglected the scalar relativistic effect (-0.81 kcal/mol) and overestimated the core-valence effect by neglecting the BSSE and did not include diffuse functions in

the calculation of the CV effect (but did include diffuse functions in the valence treatments). Our best atomization energies for SO and SO₂ suggest that the most reliable extrapolation occurs for the basis set family with the most consistent results for the various extrapolation methods.

B. SF, SF⁺, and SF₆. In a recent study¹³ of the thermochemistry of SF_n and its ions, we found, similar to the cases of SO and SO₂, it was necessary to add tight functions to the S atom. For these systems we used the series aug-cc-pVTZ+d,df,dfg. This series was picked due to the consistency of the extrapolated results. In this manuscript we report on results for the aug-cc-pV+2d sets that worked the best for SO and SO₂. The results of these calculations are given in Table 7.

For SF and SF⁺ at the CCSD(T) level, the various extrapolation methods agree reasonably well, excluding the aug-cc-pV set, which is missing the tight functions. It would be difficult to pick the best basis set among the aug-cc-pV+d, aug-cc-pV+d,df,dfg, and aug-cc-pV+2d series based only on the agreement between the different extrapolation approaches. The aug-cc-pV+2d results are 0.2–0.3 kcal/mol smaller than the other two series, thus suggesting that even after finding a series that yields similar extrapolation results there is some uncertainty in the results.

The MP2 level extrapolation of SF₆ is given in the bottom of the table. The results are very similar to those given for SF and SF⁺, but the differences are magnified by a much larger atomization energy. The aug-cc-pV results clearly vary too much with extrapolation technique to be reliable. While the aug-cc-pV+2d results show the smallest difference between the two three-point approaches, the n^{-3} TZ QZ results are 3.08 kcal/mol larger than the $n^{-4} + n^{-6}$ results. The aug-cc-pV+1d and aug-cc-pV+d,df,dfg results are reasonably consistent with each other. As with SF and SF⁺, the α is larger than 4.5 for the aug-cc-pV+2d series. The results are also similar to those found for SO₂ by Martin, where the two three-point approaches agree very well, but differed from the two-point approaches, and the α was larger than 4.5.

The origin of the difference between the aug-cc-pV+1d, aug-cc-pV+2d, and aug-cc-pV+d,df,dfg series is not in the description of the correlation energy; for each method, the extrapolated correlation contributions to the atomization energies are very similar for all three series of basis sets; for example the $n^{-4} + n^{-6}$ extrapolation method yields 296.50, 296.37, and 296.57 kcal/mol, for the three series of basis sets. In addition, the correlation contribution is very similar for the different extrapolation methods. The difference between the three basis set families comes at the SCF level, where the aug-cc-pVQZ+2d set yields an atomization energy of 226.86 kcal/mol, which is larger than the aug-cc-pV5Z+2d value of 226.68 kcal/mol. The SCF level

TABLE 7: Extrapolation of Atomization Energies, in kcal/mol

basis ^b	method ^a					
	3 TZ,QZ	3 QZ,5Z	4 TZ,QZ	4 QZ,5Z	4+6 TZ,QZ,5Z	α^c TZ,QZ,5Z
CCSD(T)						
SF						
aug-cc-pV	84.34	84.74	83.88	84.44	84.63	85.08(2.808)
aug-cc-pV+d	84.69	84.44	84.27	84.24	84.23	84.22(4.088)
aug-cc-pV+2d	84.76	84.31	84.37	84.14	84.06	84.02(4.698)
aug-cc-pV+d,df,dfg	84.76	84.46	84.34	84.27	84.24	84.22(4.195)
SF ⁺						
aug-cc-pV	87.86	88.69	87.24	88.25	88.61	89.66(2.461)
aug-cc-pV+d	88.39	88.21	87.85	87.94	87.97	88.00(3.828)
aug-cc-pV+2d	88.52	88.00	88.01	87.78	87.70	87.65(4.555)
aug-cc-pV+d,df,dfg	88.50	88.24	87.95	87.97	87.98	87.98(3.961)
MP2						
SF ₆						
aug-cc-pV	522.56	527.89	519.91	525.80	527.88	536.41(2.004)
aug-cc-pV+d	524.62	525.01	522.79	523.96	524.37	525.02(3.331)
aug-cc-pV+2d	525.61	523.59	523.94	522.90	522.53	522.35(4.773)
aug-cc-pV+d,df,dfg	524.86	525.08	523.01	524.04	524.40	524.94(3.414)

^a The value signifies the type of extrapolation, for example "3" indicates an n^{-3} extrapolation, "4+6" indicates an $n^{-4} + n^{-6}$ extrapolation, and " α " indicates the variable α extrapolation. The second line shows which basis sets are used in the extrapolation. ^b The basis sets are described in detail in the text. ^c The optimized α value is given in parentheses.

BSSE is determined by the quality of the sp valence space. While the basis set incompleteness is determined by the quality of the entire basis set, for a good valence basis set, the incompleteness is mostly determined by the quality of the polarization set. Thus the SCF atomization energies suggest that the QZ polarization set is close to completeness, so that improving the basis set from QZ to 5Z reduces the BSSE associated with the valence functions by more than improving the polarization functions reduces the basis set incompleteness. Extrapolation with BSSE corrected values would probably allow an improved extrapolation, but the 5Z calculations are already very expensive and the need to compute the BSSE just makes the problem worse.

In addition to the missing tight d function, basis set extrapolation problems can arise when the basis set are not being improved as systematically as hoped. Luckily a comparison of the various extrapolation techniques appears to detect various kinds of basis set problems. Our calculations also suggest that an α larger than 4.5 is another indication of such a problem, but that speculation requires additional testing. A very large α suggests a weak dependence of the results on the basis set, which would appear to be a good feature. However a weak basis set dependence could cause problems since even small nonsystematic improvements in the basis set, such as those demonstrated by SF₆, could lead to problems with the extrapolation.

As discussed in detail previously¹³ the aug-cc-pV+d,df,dfg series results in a heat of formation of SF₆ that is in good agreement with experiment. The aug-cc-pV+2d series would reduce the computed value by one kcal/mol, which would improve the agreement with one experiment but worsen the agreement with the other. Thus, unlike SO and SO₂, it is impossible to use experiment to decide on the best extrapolation approach. It is disappointing, however, that the most consistent results for SF₆ and SO₂ occur for different families of basis sets, but it is encouraging that it is possible to find a basis set series where the extrapolation is consistent for all of the methods, and that the result for the most consistent series is in good agreement with the experiment.

4. Conclusions

The extrapolation of the atomization energies to the complete basis set limit has been studied. We have not found a way of

confirming an extrapolation is reliable using only TZ and QZ results. However, we have found that by comparing the results of various extrapolation techniques using the TZ, QZ, and 5Z basis sets, it appears possible to pick the most reliable basis set series. Using the B3LYP/6-31+G* geometry introduces about 0.6 kcal/mol per bond error for SO and SO₂. Accounting for BSSE and adding diffuse functions to the valence basis set reduces the effect of core-valence correlation, but makes the results more consistent for different choices of basis set. The scalar relativistic effects are sufficiently large that they need to be considered for second row atoms if accurate atomization energies are required.

References and Notes

- (1) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, 32, 359.
- (2) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, 157, 479.
- (3) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, 94, 7221.
- (4) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, 106, 9639.
- (5) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, 259, 669.
- (6) Feller, D. *J. Chem. Phys.* **1992**, 96, 6104.
- (7) Ricca, A.; Bauschlicher, C. W. *J. Chem. Phys.* **1998**, 102, 876.
- (8) Bauschlicher, C. W.; Partridge, H. *Chem. Phys. Lett.* **1995**, 240, 533.
- (9) Dunning, T. H. *J. Chem. Phys.* **1989**, 90, 1007.
- (10) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, 96, 6796.
- (11) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, 98, 1358.
- (12) Woon, D. E.; Peterson, K. A.; Dunning, T. H. Unpublished.
- (13) Bauschlicher, C. W.; Ricca, A. *J. Phys. Chem.* **1998**, 102, 4722.
- (14) Martin, J. M. L.; Uzan, O. *Chem. Phys. Lett.* **1998**, 282, 16.
- (15) Martin, J. M. L. *J. Chem. Phys.* **1998**, 108, 2791.
- (16) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.
- (17) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, 98, 11623.
- (18) Frisch, M. J.; Pople, J. A.; Binkley, J. S., *J. Chem. Phys.* **1984**, 80, 3265 and references therein.
- (19) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, 10, 1.
- (20) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, 99, 5219.
- (21) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, 98, 8718.
- (22) MOLPRO 96 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer,

A. J. Stone, and P. R. Taylor. For a description of the closed shell CCSD program, See: Hampel, C.; Peterson, K.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision D.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(24) Moore, C. E. Atomic Energy Levels, National Bureau of Standards, Department of Commerce: Washington, DC, 1949; Vol. 467.

(25) Bauschlicher, C. W.; Partridge, H. *J. Chem. Phys.* **1994**, *100*, 4329.

(26) Martin, J. M. L. Personal communication.

(27) Almlöf, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 4070.

(28) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(29) Clerbaux, G.; Colin, R. *J. Mol. Spectrosc.* **1994**, *165*, 334.

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