

Systematic Coupled Cluster, Brueckner Coupled Cluster, G3, CBS-QB3, and DFT Investigation of SX Diatomics; X = First- or Second-Row Atom

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The SX diatomics, X = first- or second-row atom, have been studied employing coupled cluster theory and the aug-cc-pV(X+d)Z basis sets. To estimate $\Delta_f H^\circ_{298}$, we have included a correction for core–valence (CV) correlation, spin–orbit splitting, and scalar-relativistic (SR) effects. For SO and SC, the estimated $\Delta_f H^\circ_{298}$ values are 0.5 kcal/mol within the experiment. However, for the remaining molecules, a revision of their $\Delta_f H^\circ_{298}$ are required. Deviations as large as 10 kcal/mol have been found between our best estimates and the values adopted by the NIST-JANAF tables. The proposed $\Delta_f H^\circ_{298}$ (± 0.5 kcal/mol) are 67.6 (SB), 66.7 (SN), 0.8 (SF), 47.4 (SAI), 27.9 (SSi), 38.1 (SP), 29.4 (S₂), and 27.1 (SCl) kcal/mol. For comparative purposes we performed BD(T), G3, CBS-QB3, B3LYP, and B3PW91 calculations. The mean absolute error (MAE) of the G3 and CBS-QB3 $\Delta_f H^\circ_{298}$ with respect to our best results is 1.0 kcal/mol for both methodologies, whereas for B3LYP/6-311+G(3df) and B3PW91/6-311+G(3df), the MAE is 1.6 and 2.0 kcal/mol, respectively. At the coupled cluster level of theory, with respect to the experiment, the MAE of the equilibrium bond lengths is 0.0013 and 0.0012 Å for the first- and second-row SX, respectively. This result involves extrapolation to the CBS limit, a correction for CV and SR effects, and also a correction for complete triple excitations. Two molecules presented an unstable HF wave function, SN and SP. In both cases, the use of the CCSDT and BD(T) methods outperformed CCSD(T). Our spin–orbit corrected coupled cluster adiabatic electron affinities (EA_{ad}) are ± 0.7 kcal/mol within the experiment for SN, SO, SF, and S₂. However, some discrepancies were found for SC and SAI. Our best estimates are EA_{ad}(SC) = 2.3 kcal/mol and EA_{ad}(SAI) = 62.5 kcal/mol, 2.4 and 1.6 kcal/mol larger than the experimental EA_{ad}, respectively. For SB, SSi, SP, and SCl, we propose new EA_{ad} of 53.7, 12.4, 36.5, and 59.0 kcal/mol, respectively. The MAE of the CBS-QB3 and G3 EA_{ad} with respect to our estimated EA_{ad} is 0.9 kcal/mol for both methodologies, whereas for B3LYP/6-311+G(3df) and B3PW91/6-311+G(3df), the MAE are 1.9 and 2.7 kcal/mol, respectively, but 50% of the error is provided only by SC and SN.

Introduction

The SX molecules, X = first- or second-row atom, constitute a very attractive set of molecules for experimental and theoretical chemists because of the importance that they have in modern chemistry.^{1–28} Among the various areas in which the SX are important, combustion chemistry, the semiconductor industry, and astrochemistry can be highlighted. For example, the SF radical and SSi are important in the semiconductor industry,^{2,7} SO, SC, and S₂ are key intermediates in combustion chemistry^{3,25–27} and atmospheric chemistry,⁴ and very recently, SB has been used in new propellants.⁵ SN is also important in combustion chemistry as well as in solid-state chemistry since the (SN)_x polymers have metallic conductivity properties.⁶ In the past decades, several experimental and theoretical studies have been performed to characterize the SX.^{2–28} However, the difficulties in studying these species experimentally and the lack of an adequate treatment of the dynamical correlation in the ab initio calculations^{2,5,7,8,12,20,70–71} have made that characterization incomplete. Regarding thermochemistry, only the $\Delta_f H^\circ_{298}$ of SO and SC have been determined properly. As proof of this, there is the inclusion of only three SX (SO, SC, and S₂) in the G2 test set.⁴² For the remaining molecules, their thermochemical

properties are not well established. Thus, they cannot be used to construct model chemistries such as G3 and the CBS-QB3 methodologies, and they also cannot be used to determine new parametrizations at the DFT level of theory. Some examples about the recent discrepancies between the theoretical and experimental determinations of the enthalpies of formation of the SX are SN, SF, and SB. For SF, the JANAF thermochemical tables propose $\Delta_f H^\circ_{298}(\text{SF}) = 2.9 \pm 1.5$ kcal/mol, whereas it has been determined theoretically to be 0.72 kcal/mol by Bauschlicher and Ricca¹¹ and 1.7 kcal/mol by Irikura.¹² The situation is similar for SN, where the difference between the coupled cluster estimation of Peebles and Marshall¹³ and the JANAF recommendation is 3 kcal/mol. Quite recently, Chin et al.⁵ reported a difference of 10 kcal/mol for SB between their G3 estimation and the JANAF value. The problems in the characterization of the SX molecules are not only limited to thermochemistry but also to adiabatic electron affinities (EA_{ad}). The EA_{ad} of SC, SN, SO, SF, SAI, and S₂ have been reported. However, there are some discrepancies in the estimated EA_{ad}. For example, in the case of S₂, Jones et al.²⁷ determined EA_{ad}(S₂) = 36.1 \pm 1.2 kcal/mol, whereas Moran and Ellison²⁵ determined EA_{ad}(S₂) = 38.5 \pm 0.4 kcal/mol by employing photoelectron spectroscopy. For this reason, we decided to perform an extensive study of the SX molecules, X = first- or second-row atom. The properties determined were enthalpies

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TABLE 1: Calculated Bond Distances for the SX Molecules, X = First-Row Atom at the CCSD(T), CCSDT, BD(T), B3LYP, and B3PW91 Levels of Theory (Results in Å)

		SB	SC	SN	SO	SF	ma-error	
CCSD(T)	aug-cc-pV(D+d)Z	1.6389	1.5620	1.5245	1.5197	1.6498	0.0359	
	aug-cc-pV(T+d)Z	1.6206	1.5460	1.5062	1.4924	1.6083	0.0116	
	aug-cc-pV(Q+d)Z	1.6157	1.5414	1.5000	1.4858	1.6014	0.0058	
	aug-cc-pV(5+d)Z	1.6142	1.5398	1.4976	1.4831	1.5983	0.0035	
	cc-pwCVTZ, fc	1.6170	1.5434	1.5035	1.4872	1.6005	0.0072	
	cc-pwCVTZ, full	1.6126	1.5397	1.5005	1.4844	1.5980	0.0040	
	Δ_{core}	0.0044	0.0037	0.0030	0.0028	0.0025		
CCSDT	cc-pwCVTZ, fc	1.6187	1.5434	1.5031	1.4872	1.6015		
	ΔT^c	0.0017	0.0000	-0.0004	0.0000	0.0010		
	$\infty(\text{T},\text{D})$	1.6129	1.5393	1.4985	1.4809	1.5908	0.0036	
	$\infty(\text{Q},\text{T})$	1.6121	1.5380	1.4955	1.4810	1.5964	0.0016	
	$\infty(5,\text{Q})$	1.6126	1.5381	1.4951	1.4803	1.5951	0.0012	
	$\infty(5,\text{Q}) + \Delta_{\text{core}}$	1.6082	1.5344	1.4921	1.4775	1.5926	0.0020	
	$\infty(5,\text{Q}) + \Delta_{\text{core}} + \Delta T$	1.6099	1.5344	1.4942	1.4775	1.5936	0.0015	
	$\infty(5,\text{Q}) + \Delta_{\text{core}} + \Delta T + \Delta R^d$	1.6095	1.5340	1.4940	1.4778	1.5943	0.0013	
	BD(T)	cc-pwCVTZ, fc	1.6170	1.5424	1.5020	1.4867	1.5999	0.0065
	BD(T)	cc-pwCVQZ, fc	1.6144	1.5396	1.4969	1.4831	1.5983	0.0034
BD(T)	$\infty(\text{wCQ},\text{wCT})$	1.6125	1.5376	1.4931	1.4803	1.5971	0.0013	
B3LYP	6-311+G(3df)	1.6101	1.5320	1.4903	1.4883	1.6145	0.0066	
B3PW91	6-311+G(3df)	1.6084	1.5310	1.4872	1.4826	1.6055	0.0045	
B3PW91	cc-pV6Z	1.6070	1.5296	1.4847	1.4800	1.5987	0.0040	
xpt		1.6092 ^a	1.5349 ^a	1.4940 ^a	1.48109 ^a	1.5962 ^b		

^a From ref 28. ^b From ref 22. ^c Estimated as the difference between the CCSD(T)/cc-pwCVTZ and CCSDT/cc-pwCVTZ calculations. ^d Estimated as the difference between the DKCCSD(T)/cc-pVTZ_DK and CCSD(T)/cc-pVTZ calculations.

of formation, electron affinities, bond distances, and harmonic vibrational frequencies. The selected methodology was coupled cluster theory, more specifically, the CCSD(T) method with the correlation consistent basis sets of Dunning and co-workers that were employed to extrapolate to the complete basis set limit. A correction for core–valence correlation and relativistic effects has also been considered. At this level of theory, it is possible to obtain highly accurate results that on several occasions have proved to be more accurate than the experimental estimations.^{11,51,61–64} This allowed us to compare the performance of lower levels of theory such as G3, CBS-QB3, and the density functionals B3LYP and B3PW91, which have been employed to study the SX.

Theoretical Methods

Three coupled cluster formulations have been employed: CCSD(T),²⁹ CCSDT,³⁰ and BD(T).³¹ The basis sets selected were the aug-cc-pV(X+d)Z and cc-pwCVXZ correlation consistent basis sets,^{32–35} X = D, T, Q, 5. For neutral molecules, we optimized geometries with all the basis sets and methods considered, except the CCSD(T)/cc-pwCVQZ full and DKCCSD(T)/cc-pVQZ_DK calculations for which we used the CCSD(T)/cc-pwCVTZ full and DKCCSD(T)/cc-pVTZ_DK geometries, respectively. For anions, we optimized with basis sets up to aug-cc-pV(T+d)Z. However, for the aug-cc-pV(X+d)Z, X = Q, 5, calculations for anions were performed at the aug-cc-pV(T+d)Z geometry. Core–valence (CV) correlation effects were estimated as the difference between the full- and frozen-core CCSD(T) results employing the cc-pwCVXZ basis sets, X = T, Q. The CV and CCSDT corrections to bond lengths were determined by employing the cc-pwCVTZ basis set. The frozen-core approximation was used for the coupled cluster calculations. The extrapolations to the complete basis set limit were performed with the two–parameter extrapolation $E = B + C/L^3$ suggested by Wilson et al.³⁷ We performed a separated extrapolation of the correlation binding energies from the HF binding energies. The latter were determined with the aug-cc-

pV(5+d)Z basis set. The scalar relativistic (SR) effects were estimated at the DKCCSD(T)/cc-pVQZ_DK level of theory,^{65–67} where the cc-pVQZ_DK basis set is a recontraction for relativistic calculations³³ of the cc-pVQZ basis set. The T1 diagnostic of Lee and Taylor⁵⁰ was used to assess the quality of the reference HF wave function.

The spin–orbit splitting for atoms was taken from Moore⁶⁰ and for molecules from the compilation of Huber and Herzberg,²⁸ except for that of SCl, SO-, SC- S₂-, for which we used Yamada,¹⁴ Lineberger,^{15–16} and Moran²⁵ determinations, respectively. Zero-point energies (ZPE) were taken from the experiment, except for that of SCl. The ZPE of SCl was estimated as one-half of the sum of the theoretical harmonic and experimental fundamental values, following the advice of Grev and Schaefer.³⁶ Theoretical harmonics were determined at the CCSD(T)/aug-cc-pV(T+d)Z level of theory.

For comparative purposes, we employed the B3LYP^{38,39} and B3PW91^{38,40} functionals. For the DFT calculations, the 6-311+G-(3df)⁴¹ and cc-pV6Z basis sets were employed. We also determined the $\Delta_f H^\circ_{298}$ and EA_{ad} of the SX molecules with the aid of G3⁴² and CBS-QB3 methodologies.⁴³

The bulk of the coupled cluster calculations were performed with ACESII^{44,45} and Gaussian 03.⁴⁶ The Brueckner, DFT, G3, and CBS-QB3 calculations were carried out with Gaussian 03. The CCSD(T) calculations for SP and SN presented some spin contamination, $S^2 = 1.08$. We were able to lower spin contamination to $S^2 = 0.80$ employing the same procedure that we used for the XO radicals X = F, Cl, Br.^{47,48} We first performed a ROHF calculation, and with this density, we started a UHF calculation; finally, we performed a UCCSD(T) calculation.

Results and Discussion

Bond Distances. In Tables 1 and 2, we report the coupled cluster, DFT bond distances, and mean absolute errors (MAE) with respect to the experimental bond lengths. We excluded SP when we estimated the MAE for two reasons. First, the

TABLE 2: Calculated Bond Distances for the SX Molecules, X = Second-Row Atom at the CCSD(T), CCSDT, BD(T), B3LYP, and B3PW91 Levels of Theory (Results in Å)

		SAI	SSi	SP	SS	SCI	ma-error	
CCSD(T)	aug-cc-pV(D+d)Z	2.0821	1.9643	1.9375 ^a	1.9250	2.0249	0.0435	
	aug-cc-pV(T+d)Z	2.0501	1.9475	1.9181 ^a	1.9060	1.9955	0.0192	
	aug-cc-pV(Q+d)Z	2.0394	1.9394	1.9126 ^a	1.8970	1.9837	0.0093	
	aug-cc-pV(5+d)Z	2.0365	1.9368	1.9117 ^a	1.8940	1.9803	0.0063	
	cc-pwCVTZ, fc	2.0447	1.9432	1.9164 ^a	1.9028	1.9925	0.0153	
	cc-pwCVTZ, fc			1.9007 ^b				
	cc-pwCVTZ, full	2.0391	1.9380	1.9144 ^a	1.8987	1.9884	0.0105	
	Δ core	0.0056	0.0052	0.0024	0.0041	0.0039		
	CCSDT	cc-pwCVTZ, fc	2.0470	1.9433	1.9127	1.9031	1.9944	
		ΔT^f	0.0023	0.0001	-0.0037	0.0003	0.0019	
∞ (T,D)		2.0366	1.9404	1.9099 ^a	1.8928	1.9831	0.0077	
∞ (Q,T)		2.0316	1.9335	1.9086 ^a	1.8904	1.9751	0.0021	
∞ (5,Q)		2.0335	1.9341	1.9108 ^a	1.8909	1.9767	0.0033	
∞ (5,Q) + Δ core		2.0256	1.9280	1.9083 ^a	1.8857	1.9712	0.0029	
∞ (5,Q) + Δ core + ΔT		2.0279	1.9290	1.9047 ^a	1.8871	1.9747	0.0009	
∞ (5,Q) + Δ core + ΔT + ΔR^g		2.0276	1.9286	1.9045 ^a	1.8873	1.9753	0.0012	
BD(T)		cc-pwCVTZ, fc	2.0449	1.9420	1.9108	1.9023	1.9922	0.0148
		cc-pwCVQZ, fc	2.0370	1.9363		1.8949	1.9816	0.0069
	∞ (wCQ,wCT)	2.0312	1.9321		1.8895	1.9739	0.0015	
B3LYP	6-311+G(3df)	2.0451	1.9384	1.9018	1.9026	1.9939	0.0145	
B3PW91	6-311+G(3df)	2.0342	1.9332	1.8946	1.8913	1.9761	0.0032	
B3PW91	cc-pV6Z	2.0307	1.9308	1.8929	1.8894	1.9747	0.0009	
expt		2.029 ^g	1.9293 ^g	1.9009 ^c	1.8892 ^c	1.97465 ^f		
expt ¹				1.899 ^d				
expt ¹¹				1.897404 ^e				

^a Low-spin contamination ($S^2 = 0.81$). ^b High-spin contamination ($S^2 = 1.11$). ^c From ref 28. ^d From ref 17. ^e From ref 18. ^f Estimated as the difference between the CCSD(T)/cc-pwCVTZ and CCSDT/cc-pwCVTZ calculations. ^g Estimated as the difference between the DKCCSD(T)/cc-pVTZ_DK and CCSD(T)/cc-pVTZ calculations.

experimental determinations^{17,18,28} differ too much to allow us to estimate the MAE. For example, the difference between the Herzberg²⁸ and Kawaguchi¹⁸ results is 0.003 Å, more than the MAE that can be obtained with CCSD(T), as we will show later. The second reason to exclude SP is that it presents some methodological problems that we will explain in detail later. It is important to note that the bond length of SCl was not determined from direct observation because Yamada et al.¹⁴ were unable to identify spectral lines from the $^2\Pi_{1/2}$ state; therefore, they could not determine the internuclear distance. They estimated it approximately with the aid of the relation of Dixon and Kroto.⁵⁴ By assuming that the spin densities in SCl are very similar to that of SF, they obtained the spin-orbit coupling constant of SCl, $A_0 = -402 \text{ cm}^{-1}$; therefore, they predicted the internuclear distance as 1.97465 Å. The assumption of similar spin densities in SCl and SF is supported by our CCSD(T) calculations.

The MAE determined with each aug-cc-pV(X+d)Z basis set follows an exponential decay, showing that it is very difficult to reduce the MAE to less than 0.003 Å by systematically increasing the size of the basis set. Indeed, the differences between the MAE determined for the aug-cc-pV(Q+d)Z and that of the aug-cc-pV(5+d)Z basis sets are only 0.0023 and 0.0020 Å for the first- and second-row SX, respectively. This is a little disappointing if we consider that the former basis set has 169 basis functions and the aug-cc-pV(5+d)Z has 263. The extrapolation to the CBS limit tremendously improves the results for the smaller basis sets. For example, if we use the double- and triple- ζ basis set, ∞ (T,D), to extrapolate to the CBS limit, then the MAE obtained is almost the same as that determined with the aug-cc-pV(5+d)Z basis set. The ∞ (Q,T) and ∞ (5,Q) extrapolations gave very similar MAE for the first-row SX. However, for the second-row SX, the MAE is smaller with the aug-cc-pV(Q+d)Z basis set.

The CV effects on the estimated bond distances are surprisingly important.⁶⁸ They were evaluated at the CCSD(T)/cc-pwCVTZ level of theory. According to the results of Peterson and Dunning,³⁵ this basis set recovers at least 70% percent of the total effect for first-/second-row compounds (SiO 70%, PN 72%, BCl 79%). It is important to comment on the quality of the results obtained with the CCSD(T) frozen-core cc-pwCVTZ calculations. Despite having nearly the same number of basis functions as the aug-cc-pV(T+d)Z basis set, the MAE obtained with the cc-pwCVTZ basis set is 40% lower than with the former basis set, showing that the cc-pwCVXZ family of basis sets can be an excellent choice over the aug-cc-pV(X+d)Z. On average, the inclusion of CV effects reduces the bond lengths by 0.003 and 0.005 Å for the first- and second-row SX, respectively. If we consider the CV effects on the ∞ (5,Q) bond distances, the MAE becomes 0.0019 and 0.0029 Å for the first- and second-row SX, respectively. In all cases (except SP), the ∞ (5,Q) + Δ core bond distances are smaller than the experimental results, an indication that CCSD(T) systematically underestimates bond distances as noted previously by Dixon and Feller.⁵¹ Performing some expensive FCI or estimated FCI calculations, they were able to appreciate the underestimation of bond lengths at the CCSD(T) level of theory. For the SX compounds, an FCI calculation with a TZ basis set is very expensive. However, we performed CCSDT/cc-pwCVTZ optimizations to explore the differences between CCSD(T) and CCSDT. For the molecules with singlet (SC, SSi) and triplet (SO, S₂) ground states, there is almost no difference between the bond distances predicted by both coupled cluster formulations. However, there is an important elongation of the bond lengths for the doublet states of SB, SF, SAI, and SCl. Finally, for two molecules, SN and SP, CCSDT reduces the bond distances obtained with CCSD(T). This is related to the instability of the HF wave function of SN and SP, as we will

TABLE 3: Calculated Harmonic Vibrational Frequencies for the SX Molecules, X = First-Row Atom with Different Methodologies (Results in cm^{-1})

		SB	SC	SN	SO	SF	ma-error
CCSD(T)	aug-cc-pV(D+d)Z	1157.9	1259.7	1179.9	1082.5	804.6	49.1
	aug-cc-pV(T+d)Z	1172.6	1270.4	1217.4	1146.7	829.0	6.9
	∞ (T,D)	1178.8	1275.0	1233.2	1173.7	839.3	10.4
	cc-pwCVTZ	1179.2	1274.4	1224.1	1154.6	840.7	5.1
	cc-pwCVTZ,full	1187.7	1282.1	1236.7	1166.6	851.4	11.9
	Δ core	8.5	7.7	12.6	12.0	10.7	
BD(T)	cc-pwCVTZ	1178.2	1280.0	1216.8	1156.6	843.1	4.4
B3LYP	6-311+G(3df)	1183.6	1311.0	1260.4	1156.4	814	20.4
B3PW91	6-311+G(3df)	1198.9	1321.0	1277.8	1180.5	835	29.5
expt		1180.2 ^a	1285.08 ^a	1218.7 ^a	1149.2 ^a	837.6 ^b	

^a From ref 28. ^b From ref 22.

TABLE 4: Calculated Harmonic Vibrational Frequencies for the SX Molecules, X = Second-Row Atom with Different Methodologies (Results in cm^{-1})

		SAI	SSi	SP	SS	SCI	ma-error
CCSD(T)	aug-cc-pV(D+d)Z	570.6	722.6	783.2	697.6	537.0	33.9
	aug-cc-pV(T+d)Z	609.2	738.2	852.2	715.7	566.3	9.8
	∞ (T,D)	625.5	744.8		723.3	578.6	5.2
	cc-pwCVTZ-fc	614.3	741.7	784.9 ^a	718.2	571.5	6.1
	cc-pwCVTZ-fc			753.9 ^b			
	cc-pwCVTZ-fu	613.3	744.6		721.1	572.1	4.5
	Δ core		2.9		2.9		
BD(T)	cc-pwCVTZ-fc	608.9	745.2		719.8	571.0	6.2
BD(T)	aug-cc-pVTZ			730.9			
B3LYP	6-311+G(3df)	596.7	745.5	747.2	718.0	561.6	10.8
B3PW91	6-311+G(3df)	616.2	757.0	763.9	737.8	585.0	6.8
expt		617.1 ^c	749.64 ^c	739.1 ^d	725.7 ^c		
expt ^f				739.5 ^e			
expt ^g				733.6 ^f			

^a Low-spin contamination ($S^2 = 0.81$). ^b High-spin contamination ($S^2 = 1.11$). ^c From ref 10. ^d From ref 28. ^e From ref 17. ^f From ref 18.

discuss later. If we correct $\infty(5,Q) + \Delta$ core bond distances for complete triple excitations and SR effects, the MAE is reduced to 0.0013 and 0.0012 Å for first- and second-row SX, respectively. The maximum absolute deviation (MAD) is obtained for SO. The r_{S-O} is underestimated by 0.0033 Å, probably because of problems in the extrapolation scheme employed and convergence problems of the properties of SO.³²

The use of BD(T) has minor advantages for all the molecules considered, except SP and SN; again, this is related to the instability of the wave function as we will discuss later. Employing the cc-pwCVTZ basis set, BD(T) improves the MAE over CCSD(T) only by 0.0007 and 0.0005 Å in the first- and second-row SX, respectively.

The DFT functionals considered gave excellent results. For the first-row SX, B3PW91 performs a little better than B3LYP. However, for the second-row SX, the differences are quite appreciable, and the MAE obtained with B3PW91 is 5 times lower than that obtained with B3LYP. One important question is what is the CBS limit in these sulfur compounds for the functionals considered. We have addressed this topic in previous articles^{52,53} where we studied the molecules SO, SO₂, SO₃, and HSO₂ with the correlation consistent basis sets up to cc-pV6Z. We concluded that the 6-311+G(3df) basis set gave results that are better than those obtained with the cc-pVQZ basis set, but slightly worse than the cc-pV5Z results. Therefore, we optimized the geometries of the SX compounds with the cc-pV6Z basis set. For the first-row SX, the MAE changes only 0.0005 Å. However, the variation in bond distances with respect to the results obtained by employing the 6-311+G(3df) basis set are quite appreciable, especially for SF, 0.006 Å. The optimizations performed with the cc-pV6Z basis set for the second-row SX lower the MAE of B3PW91 to 0.0009 Å, but even with this basis set the B3PW91 results are not converged (to 0.0001 Å),

showing that the basis set dependence is very strong, not only for the ab initio methodologies, but also for the density functionals considered.

Vibrational Frequencies. The harmonic vibrational frequencies of first-row and second-row SX are presented in Tables 3 and 4, respectively. We found experimental harmonics for all the molecules considered except SCI. Only the fundamental ν was determined by Yamada¹⁴ et al., $\nu = 574.6 \text{ cm}^{-1}$, and by Willner¹⁹ et al., $\nu = 574.2 \text{ cm}^{-1}$. We cannot compare our ω_e results with the fundamental experimental results, but from a qualitative stand point, we conclude that the agreement is reasonable. To estimate the MAE, we have excluded SP, as we did in the discussion of the bond distances.

The aug-cc-pV(D+d)Z basis set considered gives a reasonable approach to the experimental results. The MAE with this basis set is 49.1 and 33 cm^{-1} for first- and second-row SX, respectively; the MAE is improved 1 order of magnitude with the use of the aug-cc-pV(T+d)Z basis set. The performance of the cc-pwCVTZ basis set is superb, with an MAE of 5.1 cm^{-1} . Again, the cc-pwCVTZ basis set seems to be a smart choice when second-row atoms are involved. The extrapolation to the CBS limit worsens the agreement with the experiment for first-row SX. Indeed, the CCSD(T)/ $\infty(6,5)$ stretch obtained for SO by Dunning et al.³² is 1163.89 cm^{-1} , 10 cm^{-1} smaller than our CBS limit but 13 cm^{-1} larger than the experimental results. When we performed an extrapolation to the CBS limit with the frequencies obtained for second-row SX employing the double- and triple- ζ basis set, the MAE is reduced to 5.1 cm^{-1} . This result is fortuitous because our extrapolation underestimates the correct CBS limit. For example, in the case of S₂, the CCSD(T)/CBS limit determined by Peterson and Dunning³⁵ is 733.9 cm^{-1} , 10.6 cm^{-1} larger than our best estimation. This error explains the smaller MAE observed for SX2. The SR

effects have very little effect on the estimated vibrational frequencies as demonstrated by Visscher et al. in the study of dihalogen⁵⁶ and halogen hydrides.⁴⁹ The inclusion of CV effects increases the harmonics, deviating more the theoretical results from the experimental estimations. It is quite interesting that the CV effects on the harmonics of the second-row SX are significantly lower than those determined for first-row SX. As expected, the behavior of BD(T) in the prediction of vibrational frequencies is similar to that observed for bond distances, showing almost no improvement over CCSD(T).

The performance of the functionals considered is quite different for the first- and second-row SX. For second-row SX, the MAE is smaller than that obtained for first-row SX. Indeed, the MAE is reduced by 50% for B3LYP and by 80% for B3PW91 when we move to the second row. We do not expect serious improvement of the vibrational frequencies if larger basis set are used in the DFT calculations. In previous articles,^{52,53} we estimated the S–O stretch in SO by employing the cc-pV5Z basis set as 1158 and 1182 cm⁻¹ with the B3LYP and B3PW91 functionals, respectively, only 2 cm⁻¹ higher than the results with the 6-311+G(3df) basis set, showing that the basis set dependence for vibrational frequencies is not as strong as those observed for bond distances. This is also true with the ab initio methodologies.

Wave Function Stabilities, SN and SP Instabilities. We performed an analysis of the stability of the HF wave function with the cc-pVTZ basis set. All wave functions are stable, except those of SN and SP. The problem arises in the spin contamination. The unstable wave functions present lower spin contamination, $S^2 = 0.80$, whereas the stable wave functions have large spin contamination, $S^2 = 1.2$. For both molecules, we performed UCCSD(T)/cc-pVTZ calculations over the stable HF wave function. In both cases, the UCCSD(T) energy with a contaminated HF reference is higher than the UCCSD(T) energy of an HF reference with low-spin contamination, 1 and 0.6 kcal/mol for SN and SP, respectively. The spin densities obtained with both wave functions are widely different. For the unstable HF wave function, the spin densities are 0.45 on S and 0.55 on N or P, whereas in a contaminated wave function, they are 0.5 on S and 1.5 on N or P. Thus, the contaminated wave function allocates 1.5 unpaired electrons over N or P in contrast to the experimental evidence. For this reason, we believe that despite employing an unstable HF wave function, we can obtain a reasonable description of the properties of the SN and SP radicals studied at the CCSD(T) level of theory. Indeed, our best estimation of the S–N distance employing the unstable HF reference is identical to the experimental result, whereas the contaminated wave function underestimates the S–N distance by 0.0063 Å. We have faced a similar problem for FOO recently.^{47–48} In this case, we obtained wave functions with $S^2 = 0.76$ and 1.40. The contaminated wave function did not describe properly the F–O distance, ($r_{F-O} = 1.56$ Å), F–O stretch (684 cm⁻¹), and $\Delta_f H^\circ_{298}(\text{FOO}) = 10.5$ kcal/mol. The use of the wave function with low-spin contamination allowed us to obtain results closer to the experimental determinations. The F–O distance was improved to 1.63 Å, the F–O stretch was reduced to 614 cm⁻¹, and $\Delta_f H^\circ_{298}(\text{FOO}) = 7.5$ kcal/mol. To gain further insight in to this problem, we performed CCSDT/cc-pwCVTZ and BD(T) optimizations for SN and SP by employing the unstable HF reference. The inclusion of complete triple excitations reduces the CCSD(T) bond distances, improving the agreement with experiment. This is in contrast to the results obtained for the remaining SX, for which CCSDT also improved the CCSD(T) results but increased the equilibrium

bond lengths. The contraction is very small for SN, 0.0004 Å. However, for SP it is more noticeable, 0.0037 Å, showing that CCSDT performs much better than CCSD(T) in the prediction of structural parameters of molecules with stability problems in the HF reference. Overall, the closest agreement with experiment is obtained employing BD(T), especially for the S–P stretch. The S–P bond distance predicted by BD(T) is shorter than that determined with CCSD(T), and even than that estimated with the CCSDT method. The contraction of the bond distances at the BD(T)/cc-pwCVTZ level are 0.0015 and 0.0056 Å for SN and SP, respectively, both with respect to the results obtained from the unstable HF reference. The spin densities determined using BD(T) are very reasonable, 0.27 and 0.73 for S and P, respectively.

In contrast to the results observed for the ab initio methodologies, we found that the wave functions of SN and SP are stable if we employ the B3PW91 and B3LYP functionals. For both molecules, the errors in the estimated bond lengths are in line with those observed for the remaining molecules. However, B3PW91 presents a particularly huge error in the S–P stretch. The spin densities determined at the DFT level are almost identical to those obtained with BD(T). Thus, in the present work, the description obtained for SN and SP with the functionals considered is very reasonable.

Thermochemistry. In Table 5 we present our best estimations of the $\Delta_f H^\circ_{298}$ for the 10 molecules studied with the inclusion of CV and SR effects and spin–orbit splitting. We also included in Table 5 the values determined by employing the G3, CBS-QB3, B3LYP/6-311+G(3df), and B3PW91/6-311+G(3df) methods and the atomization reaction. We can divide the 10 molecules considered into two groups. On one hand, we have the molecules for which their $\Delta_f H^\circ_{298}$ is known accurately, SC and SO. Thus, they can be used to test the methodology employed in the present article. On the other hand, we have the remaining eight molecules whose $\Delta_f H^\circ_{298}$ are not known accurately.

Test Cases SC and SO. The estimated $\Delta_f H^\circ_{298}$ for SO and SC are in excellent agreement with experiment; our best estimations are 0.35 and 0.44 kcal/mol larger than the experimental results, respectively. Since we have considered SR and CV effects, spin–orbit splitting, and large basis sets up to aug-cc-pV(5+d)Z, the remaining error can be attributed to high-order correlation effects. In a recent article, we investigated the CCSD(T)–CCSDT difference in the estimated $\Delta_f H^\circ_{298}$ of sulfur compounds.⁵⁸ For all the SX considered in the present article, CCSDT was predicted to have a larger $\Delta_f H^\circ_{298}$ than CCSD(T). As explained by Jorgensen et al.,⁵⁹ this is because of an error cancellation between the missing triple and quadruple excitations. However, it is important to notice that some situations have been found for which this empirical rule is not valid. Some examples^{47,48} are the XO and XO radicals, X = F, Cl, Br, the triplet ground state of BN, and also CN as explained by Feller and Sordo.⁶⁹ In these cases, the enthalpies of formation determined by employing CCSDT were lower than those estimated with CCSD(T). Since the rule of Jorgensen et al.⁵⁹ is effective for SX, it is necessary to include quadruple excitations to obtain better estimations for $\Delta_f H^\circ_{298}(\text{SX})$. Indeed, in a recent article, Boese et al.⁵⁵ determined the T₄ effects, i.e., CCSDT–CCSDTQ, on the total atomization energies of SC and SO as 1.0 and 0.82 kcal/mol. With the aid of the T₃ effects, that is, CCSD(T)–CCSDT calculated by us⁵⁸ at 0.60 and 0.39 kcal/mol for SC and SO, respectively, we determine the CCSDTQ contribution to the estimated $\Delta_f H^\circ_{298}$ as 0.40 and 0.43 kcal/mol, respectively. Employing these corrections, the errors in

TABLE 5: Calculated Enthalpies of Formation for the SX Molecules (Results in kcal/mol).

		SB	SC	SN	SO	SF
CCSD(T)/CBS		68.03	67.67	67.00	1.16	0.48
core correlation		-1.27	-1.11	-0.87	-0.63	-0.45
spin-orbit		0.59	0.64	0.32	0.78	0.57
scalar Relativistic		0.26	0.15	0.25	0.33	0.23
proposed value		67.61 ± 0.5	67.35 ± 0.5	66.70 ± 0.5	1.64 ± 0.5	0.83 ± 0.5
T1 diagnostic		0.033	0.025	0.036	0.019	0.018
G3		67.60	65.90		1.70	2.20
CBS-QB3		67.81	66.58	65.05	0.41	2.12
B3LYP	6-311+G(3df)	68.44	72.0	65.0	0.1	0.6
B3PW91	6-311+G(3df)	64.24	70.5	66.6	-0.8	0.8
expt ^a		58.0 ± 4	67.0 ± 0.2	63.0 ± 25	1.2 ± 0.3	3.1 ± 1.5
Benson ^b			67.6 ± 6	68 ± 5	1.2	3 ± 2
		SAI	SSi	SP	S ₂	SCI
CCSD(T)/CBS		46.38	27.40	38.20	28.72	26.75
core correlation		-0.20	-0.78	-0.82	-0.75	-0.41
spin-orbit		0.77	0.99	0.46	1.12	0.57
scalar Relativistic		0.41	0.29	0.30	0.30	0.22
proposed value		47.36 ± 0.5	27.9 ± 0.5	38.14 ± 0.5	29.39 ± 0.5	27.13 ± 0.5
T1 diagnostic		0.027	0.023	0.033	0.017	0.019
G3		46.92	27.44		31.60	29.29
CBS-QB3		44.91	26.22		29.29	27.29
B3LYP	6-311+G(3df)	49.9	32.5	37.4	29.6	28.2
B3PW91	6-311+G(3df)	47.4	31.8	37.7	26.7	25.5
expt ^a		57.0	25.3 ± 3	33.1 ± 25	30.7 ± 0.1	37.4 ± 4
Benson ^b					30.7	36.5 ± 2

^a From ref 10. ^b From ref 21.

the estimated $\Delta_f H^\circ_{298}$ of SC and SO are reduced to 0.1 kcal/mol. Therefore, we confirm that the main source of error in our estimations is because of quadruple excitations. With this evidence we will assume an uncertainty of ± 0.5 kcal/mol in our proposed values.

First-Row SX. For SB, we propose $\Delta_f H^\circ_{298}(\text{SB}) = 67.6 \pm 0.5$ kcal/mol. Our result differs 11 kcal/mol from the JANAF recommended¹⁰ value, 58.1 kcal/mol, but is in reasonable agreement with the G3 and CBS-QB3 results. There is an important difference in the estimated $\Delta_f H^\circ_{298}(\text{SB})$ with B3LYP and B3PW91. The latter functional differs from our results 3.3 kcal/mol. The estimated value for SN is $\Delta_f H^\circ_{298}(\text{SN}) = 66.70 \pm 0.5$ kcal/mol, which is 3.65 kcal/mol larger than the JANAF value, but it is in excellent agreement with the RCCSD(T) result of Peebles and Marshall,¹³ 66.40 ± 0.5 kcal/mol. The small difference between our UCCSD(T) estimation and that of Peebles and Marshall¹³ is attributable to the use of a different HF reference. At the UCCSD(T)/aug-cc-pV(5+d)Z level of theory, the total atomization energy of SN is 110.7 kcal/mol, whereas, by employing the same basis set and the ROCCSD(T) method of ref 13, we find it is 112.2 kcal/mol, 0.5 kcal/mol larger than our estimation. We also note that our estimation is 1.5 kcal/mol lower than the prediction of Benson,²¹ 68 ± 5 kcal/mol, obtained with the group additivity method. With the default procedure, we were not able to obtain the $\Delta_f H^\circ_{298}(\text{SN})$ with G3; however, it would be possible to obtain this result after some manipulation of the wave function. Finally, we propose $\Delta_f H^\circ_{298}(\text{SF}) = 0.83 \pm 0.5$ kcal/mol. This value is nearly the same as suggested by Bauschlicher and Ricca,¹¹ 0.71 kcal/mol, but it is 0.9 kcal/mol lower than the estimation of Irikura,¹² 1.7 kcal/mol. At this point, there is no doubt that the JANAF recommendation¹⁰ of 2.9 ± 1.5 kcal/mol is too high.

Second-Row SX. The $\Delta_f H^\circ_{298}$ of the entire second-row SX are not known accurately. Thus, our estimations will be the most accurate to date.

SAI. For SAI we found only one theoretical determination by Boldyrev et al.⁷⁰ Their estimation of the dissociation energy of SAI was 3.5 kcal/mol larger than the experimental result. However, in the present work we found a larger discrepancy

between experiment and theory. We propose $\Delta_f H^\circ_{298}(\text{SAI}) = 47.4 \pm 0.5$ kcal/mol, which is 10 kcal/mol lower than the JANAF¹⁰ result, 57.0 kcal/mol. Our estimation is supported by G3 and CBS-QB3 calculations.

SSi. There are two previous determinations of the binding energy of SSi, both performed by employing MRCI methodologies by Dunning and Woon²⁰ and Das et al.⁷ In both cases, the binding energy of SSi is underestimated by 5–7 kcal/mol. Since Dunning et al.²⁰ extrapolated to the CBS limit, we can attribute this discrepancy to an incomplete description of the dynamic correlation by the MRCI methodology employed. Our proposed value is $\Delta_f H^\circ_{298}(\text{SSi}) = 27.90 \pm 0.5$ kcal/mol, which is 2.6 kcal/mol larger than the JANAF¹⁰ estimation of 25.325 kcal/mol. Both model chemistries, G3 and CBS-QB3, also indicated that the experimental $\Delta_f H^\circ_{298}(\text{SSi})$ is underestimated. The G3 and CBS-QB3 determinations are 0.5 and 1.7 kcal/mol lower than our best result. As observed for its first-row counterpart SC, both density functionals considered have some problems in estimation of the $\Delta_f H^\circ_{298}(\text{SSi})$. The errors are around 4 kcal/mol, very similar to that observed for SC.

SP. Although SP presented some problems in the prediction of the S–P equilibrium bond distance and the SP stretch, there is no difference between $\Delta_f H^\circ_{298}$ determined by employing BD(T) or CCSD(T). We propose $\Delta_f H^\circ_{298}(\text{SP}) = 38.1 \pm 0.5$ kcal/mol, which is 5 kcal/mol larger than the JANAF¹⁰ value, 33.216 kcal/mol. Dunning and Woon²⁰ predicted the binding energy SP by employing MRCI and correlation consistent basis sets, but again, their result is 3 kcal/mol higher than our estimation. Some problems in the convergence of the SCF made estimations of G3 and CBS-QB3 impossible. However, there are G2 results available from the work of Boldyrev et al.⁷⁰ that support the idea of a larger enthalpy of formation than that recommended by the JANAF tables. Their G2 estimation of the dissociation energy of SP is 5.8 kcal/mol lower than the experimental result, nearly the same difference found in the present work at a higher level of theory.

S₂. We obtained $\Delta_f H^\circ_{298}(\text{S}_2) = 29.39 \pm 0.5$ kcal/mol, which is 1.1 kcal/mol lower than the experimental estimation of 30.736 kcal/mol. Our findings are in line with the W2 results of Partiban

TABLE 6: Calculated Adiabatic Electron Affinities with Different Methodologies for the SX (Results in kcal/mol)

		SB	SC	SN	SO	SF	SAI	SSi	SP	S ₂	SCI	MAE ^h
CCSD(T)	aug-cc-pV(D+d)Z	51.2	-2.1	25.2	21.9	50.8	60.4	8.5	33.0	33.7	56.5	
CCSD(T)	aug-cc-pV(T+d)Z	52.7	0.6	27.0	23.7	51.4	61.4	11.3	35.4	36.6	57.4	
CCSD(T)	aug-cc-pV(Q+d)Z	53.3	1.5	27.8	25.0	52.7	62.1	11.8	35.9	38.0	58.8	
CCSD(T)	aug-cc-pV(5+d)Z	53.5	1.7	27.9	25.3	53.0	62.3	11.9	36.4	38.3	59.2	
CCSD	aug-cc-pV(5+d)Z	52.3	2.3	29.6	24.5	52.0	61.8	11.6	36.9	37.3	57.5	
Δ(T)		1.2	-0.6	-1.7	1.0	1.0	0.5	0.3	-0.5	1.0	1.7	
CCSD(T)	∞(T,D)	53.3	1.7	27.8	24.5	51.7	61.8	12.5	36.4	37.8	57.8	
CCSD(T)	∞(Q,T)	53.7	2.2	28.4	25.9	53.7	62.6	12.2	36.3	39.0	59.8	
CCSD(T)	∞(S,Q)	53.7	1.9	28.0	25.5	53.3	62.5	12.0	36.9	38.6	59.6	
CCSD(T)	∞(S,Q)+S.O.	53.7	2.3	27.7	25.9	52.7	62.5	12.4	36.5	39.2	59.0	
B3LYP	6-311+G(3df,2p)	53.5	7.2	33.0	26.8	53.3	60.7	13.8	38.1	38.3	58.1	1.8
B3PW91	6-311+G(3df,2p)	51.0	6.9	33.0	24.9	51.4	59.7	15.0	38.0	37.1	56.5	2.8
G3		54.7	0.9		27.2	53.5	63.4	11.8		38.5	59.5	0.9
CBS-QB3		54.2	1.3	26.7	27.1	53.6	61.8	10.8		39.0	60.4	0.9
	expt		4.7 ± 0.5 ^a	27.5 ± 0.3 ^a	25.8 ± 0.1 ^b	52.7 ± 0.1 ^c	59.9 ± 0.7 ^d			38.5 ± 0.4 ^e		
										38.2 ± 0.9 ^f		
										36.2 ± 1.2 ^g		

^a From ref 16. ^b From ref 15. ^c From ref 23. ^d From ref 24. ^e From ref 25. ^f From ref 26. ^g From ref 27. ^h MAE estimated with respect to CCSD(T)+SO results.

and Martin.⁵⁷ Their estimated enthalpy of formation for S₂ is 0.9 kcal/mol lower than that of the experiment. We note that for S₂, the difference between the use of RCCSD(T) instead of UCCSD(T) to estimate the $\Delta_f H^\circ_{298}(S_2)$ is 0.3 kcal/mol with the aug-cc-pV(5+d)Z basis set. This result was obtained by comparing our estimations and those of Dunning et al.³² There are some differences between the G3 and CBS-QB3 estimations. G3 is 1 kcal/mol higher than the experimental result, whereas CBS-QB3 is 1.5 kcal/mol lower. The latter supports our estimation. The functionals considered presented some differences between them. The B3LYP estimation is very close to our recommended value, but it is 1 kcal/mol lower if a B3LYP/cc-pV6Z calculation is performed.^{52,53}

SCI. For the last molecule in the group of second-row SX, we propose $\Delta_f H^\circ_{298}(SCI) = 27.1 \pm 0.5$ kcal/mol, again very far from the JANAF¹⁰ value of 37.397 kcal/mol. As previously noted for S₂, G3 presented some problems in the predicted $\Delta_f H^\circ_{298}(SCI)$. The difference between G3 and the $\Delta_f H^\circ_{298}$ recommended by us is 2 kcal/mol. The performance of CBS-QB3 is very good, again supporting our estimations. Among the DFT functionals considered, the B3LYP estimation is better than the result obtained with B3PW91 by about 3 kcal/mol.

The MAE of the G3 and CBS-QB3 $\Delta_f H^\circ_{298}$ with respect to our proposed values is 1.0 kcal/mol for both methodologies, although there are deviations larger than 1 kcal/mol. For G3 the most problematic molecules are SF (1.4 kcal/mol), SCI (2.1 kcal/mol), and SC (1.45 kcal/mol), whereas for CBS-QB3 the major problem is SAI. The performance of the B3LYP and B3PW91 functionals is very good, especially if we consider that we are employing atomization reactions and not isodesmic reactions.⁵²⁻⁵³ The MAE of both functionals with respect to our proposed values is 1.8 kcal/mol for both methodologies in the first row, and in the second row it is respectively 1.4 and 2.2 kcal/mol for B3LYP and B3PW91. For six molecules, SC, SN, SF, SAI, SSI, and SP, B3PW91 is closer to our recommended $\Delta_f H^\circ_{298}$ than B3LYP.

Electron Affinities. In Table 6 we report the estimated EA_{ad} with CCSD(T), CCSD, G3, CBS-QB3, and the density functionals considered. The convergence of the SX EA_{ad} with the basis set and correlation treatment is faster than that observed for distances, vibrational frequencies, and $\Delta_f H^\circ_{298}$. We found that the perturbative triple excitations have a minor effect on the estimated EA_{ad}, changing them no more than 1.7 kcal/mol in the worst cases. For some molecules, the estimated EA_{ad} are nearly converged with the basis set employed. The largest

differences between the estimated EA_{ad} with the aug-cc-pV-(Q+d)Z and aug-cc-pV(5+d)Z basis sets are observed for SP and SCI, 0.5 and 0.4 kcal/mol, respectively. As expected, the agreement between extrapolations performed with different basis sets is very good.

For a precise evaluation of EA_{ad}, it is important to consider molecular spin-orbit splitting. However, we will work under the assumption that the SR and CV effects are nearly the same for neutrals and anions. Four anions have molecular spin-orbit splitting, SC⁻, SSI⁻, SO⁻, and S₂⁻. The spin-orbit coupling constant A_o has been determined experimentally for SC⁻ and SO⁻ by Lineberger^{15,16} and for S₂⁻ by Moran and Elliot.²⁵ For SSI⁻, we did not find experimental determinations of the splitting between the Π states. However, because of the similar A_o found for the pairs SN, SP and SF, SCI, we are going to consider the splitting in SSI⁻ to be the same as that in SC⁻. For neutrals, the A_o is the same as that used to estimate the $\Delta_f H^\circ_{298}$. The estimated EA_{ad} for SN, SO, SF, and S₂ are in excellent agreement with experiment; the deviations are 0.2, 0.1, 0.01, and 0.7 kcal/mol, respectively. However, SC and SAI exhibit large discrepancies, 2.4 and 2.6 kcal/mol, respectively. On the basis of the accuracy achieved for SN, SO, SF, and S₂, we believe that a reexamination of the experimental EA_{ad} of SC and SAI is necessary. Our best estimations are EA_{ad}(SC) = 2.3 kcal/mol and EA_{ad}(SAI) = 62.5 kcal/mol. We did not find experimental EA_{ad} for SB, SSI, SP, and SCI. For these molecules, we propose 53.7, 12.4, 36.5, and 59.0 kcal/mol as EA_{ad} values, respectively.

The CBS-QB3 and G3 results are very close to the EA_{ad} proposed by us; the MAE is 0.9 kcal/mol for both methodologies. The most problematic EA_{ad} for G3 is that of SO, which is 1.4 kcal/mol larger than the experimental result. SSI, SCI, and SO represent a problem for CBS-QB3; the EA_{ad} of SSI is underestimated by 1.6 kcal/mol and that of SCI is overestimated by 1.4, both with respect to the values proposed by us. At the B3LYP/6-311+G(3df) and B3PW91/6-311+G(3df) levels of theory, the MAE is 1.9 and 2.7 kcal/mol, respectively, but this result is somewhat tricky because a large percentage of the error is only provided by two molecules, SC and SN. For both functionals predicted, the EA_{ad} of SC and SN are 5 kcal/mol larger than the values proposed by us. If we exclude SC and SN from the set, the MAE is reduced by more than 50%.

Conclusions

We have determined the geometries, harmonic vibrational frequencies, $\Delta_f H^\circ_{298}$, and EA_{ad} for SX molecules where X = first- or second-row atom. The MAE of equilibrium bond lengths found with respect to the experiment was 0.0013 and 0.0012 Å for first- and second-row SX, respectively. This result involves extrapolation to the CBS limit, a correction for CV and SR effects and also for complete triple excitations. The MAE deviations determined for the bond distances and vibrational frequencies support the idea that the cc-pwCVXZ basis sets would be preferred over the aug-cc-pV(X+d)Z basis sets to study molecules composed by second-row atoms.

Two molecules presented an unstable HF wave function, SN and SP. In both cases, the use of the CCSDT method outperformed CCSD(T) and improved agreement with the experiment for bond distances. Overall, the best results for these two molecules were obtained with BD(T).

For SO and SC, the estimated $\Delta_f H^\circ_{298}$ are 0.5 kcal/mol within the experiment. However, for the remaining molecules, a revision of their $\Delta_f H^\circ_{298}$ is required. Deviations as large as 10 kcal/mol have been found between our recommended $\Delta_f H^\circ_{298}$ and the experimental ones. The proposed $\Delta_f H^\circ_{298}$ (± 0.5 kcal/mol) are the following: $\Delta_f H^\circ_{298}(SB) = 67.6$, $\Delta_f H^\circ_{298}(SN) = 66.7$, $\Delta_f H^\circ_{298}(SF) = 0.8$, $\Delta_f H^\circ_{298}(SAI) = 47.4$, $\Delta_f H^\circ_{298}(SSi) = 27.9$, $\Delta_f H^\circ_{298}(SP) = 38.1$, $\Delta_f H^\circ_{298}(S_2) = 29.4$, and $\Delta_f H^\circ_{298}(SCI) = 27.1$ kcal/mol. The MAE of the G3 and CBS-QB3 $\Delta_f H^\circ_{298}$ with respect to our proposed values is 1.0 kcal/mol for both methodologies. Differences larger than 1.5 kcal/mol for G3 have been found for SC, SCI, and S_2 , whereas for CBS-QB3 the major problem is SAI, for which the estimated $\Delta_f H^\circ_{298}$ is 2.5 kcal/mol lower than our proposed value. The MAE of the B3LYP and B3PW91 functionals is 1.8 kcal/mol in the first row, and, in the second row, 1.4 and 2.2 kcal/mol for B3LYP and B3PW91, respectively.

Finally, the spin-orbit corrected CCSD(T) EA_{ad} are within ± 0.7 kcal/mol of the experiment for SN, SO, SF, and S_2 . Some discrepancies were found for SC and SAI, for which the theoretical estimations are 2.4 and 2.6 kcal/mol larger than the experimental EA_{ad} . Our proposed values are 2.3 and 62.5 kcal/mol for SC and SAI, respectively. For SB, SSi, SP, and SCI we propose new EA_{ad} of 53.7, 12.4, 36.5, and 59.0 kcal/mol, respectively. The G3 and CBS-QB3 EA_{ad} are in good agreement with the EA_{ad} proposed by us; the MAE is 0.9 kcal/mol for both methodologies. The B3LYP and B3PW91 functionals presented MAE of 1.9 and 2.7 kcal/mol, respectively, but a large percentage of the error (50%) is provided by two molecules, SC and SN.

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References and Notes

- (1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley and Son: 1980.
- (2) (a) King, R. A.; Galbraith, J. M.; Schaefer, H. F. *J. Phys. Chem.* **1996**, *100*, 6061. (b) Sparrapan, R.; Mendes, M. A.; Ferreira, I. P. P.; Santos, C.; Nogueira, J. C. *J. Phys. Chem. A* **1998**, *102*, 5189.
- (3) Moltzen, E. K.; Klubunde, K. J.; Sennin, A. *Chem. Rev.* **1988**, *88*, 391.
- (4) Tyndall, G. S.; Ravishankara, A. R. *Int. J. Chem. Kinet.* **1991**, *23*, 483.
- (5) Chin, C.-H.; Mebel, A.; Hwang, D.-Y. *J. Phys. Chem. A* **2004**, *108*, 473.

- (6) Mawhinney, R. C.; Goddard, J. D. *Inorg. Chem.* **2003**, *42*, 6323.
- (7) Chattopadhyay, S.; Chattopadhyay, A.; Das, K. K. *J. Phys. Chem. A* **2002**, *106*, 833.
- (8) (a) Moussaoui, Y.; Ouamerli, O.; De Mare, G. R. *THEOCHEM* **1998**, *45*, 237.
- (9) Einfeld, T. S.; Maul, C.; Gericke, K. H.; Chichinin, A. *J. Chem. Phys.* **2002**, *117*, 4214.
- (10) NIST Chemistry WebBook. <http://webbook.nist.gov>.
- (11) Bauschlicher, C. W.; Ricca, A. *J. Phys. Chem. A* **1998**, *102*, 4722.
- (12) Irikura, K. K. *J. Chem. Phys.* **1995**, *102*, 5357.
- (13) Peebles, L. R.; Marshall, P. *Chem. Phys. Lett.* **2002**, *366*, 520.
- (14) Yamada, C.; Butler, J. E.; Kawaguchi, K.; Kanamori, H.; Hirota, E. *J. Mol. Spectrosc.* **1986**, *116*, 108.
- (15) Polak, M. L.; Fiala, B. L.; Ervin, K. M.; Lineberger, W. C. *J. Chem. Phys.* **1991**, *94*, 6926.
- (16) Burnett, S. M.; Felgerle, C. S.; Stevens, A. E.; Lineberger, W. C. *J. Phys. Chem.* **1982**, *86*, 4486.
- (17) Jenouvrier, A.; Pascat, B. *Can. J. Phys.* **1978**, *56*, 1088.
- (18) Kawaguchi, K.; Hirota, E.; Ohishi, M.; Suzuki, H.; Takano, S.; Yamamoto, S.; Saito, S. *J. Mol. Spectrosc.* **1988**, *130*, 81.
- (19) Willner, H. *Spectrochim. Acta* **1981**, *37A*, 405.
- (20) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *101*, 8877.
- (21) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.
- (22) Endo, Y.; Nagai, K.; Yamada, C.; Hirota, E. *J. Mol. Spectrosc.* **1983**, *97*, 212.
- (23) Polak, M. L.; Gilles, M. K.; Lineberger, W. C. *J. Chem. Phys.* **1991**, *96*, 7191.
- (24) Nakajima, A.; Taguwa, T.; Nakao, K.; Hoshino, K.; Iwata, S.; Kaya, K. *J. Chem. Phys.* **1995**, *102*, 660.
- (25) Moran, S.; Ellison, G. B. *J. Phys. Chem.* **1988**, *92*, 1794.
- (26) Celotta, R. S.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740.
- (27) Hunsicker, S.; Jones, R. O.; Gantefor, G. *J. Chem. Phys.* **1995**, *102*, 5917.
- (28) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Von Nostrand: Reinhold, New York, 1979.
- (29) (a) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (b) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. H. *Chem. Phys. Lett.* **1989**, *157*, 479.
- (30) (a) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041. (b) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1990**, *93*, 6104.
- (31) Stanton, J. F.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 5544.
- (32) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.
- (33) De Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48.
- (34) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (35) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.
- (36) Grev, R. S.; Janssen, C. L.; Schaefer, F. H. *J. Chem. Phys.* **1991**, *95*, 5128.
- (37) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 242.
- (38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (39) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.
- (40) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244.
- (41) Hehre, W.; Radom, L.; Schleyer, P. v. R. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.
- (42) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
- (43) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, J. A., Jr.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 10570.
- (44) Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Kucharski, S. A.; Gwaltney, S. R.; Beck, S.; Balková, A.; Bernholdt, D. E.; Baeck, K. K.; Rozyczko, P.; Sekino, H.; Hober, C.; Bartlett, R. J. (Integral packages included are *VMOL* (Almlöf, J.; Taylor, P. R.); *VPROPS* (Taylor, P. R.); *ABACUS* (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Taylor, P. R.)) *ACESII*, release 3.0, September 13, 1998; a program product of the Quantum Theory Project, University of Florida, Gainesville, FL, 32611.
- (45) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 7/30/02, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352, U.S.A., and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.
- (46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.;

- Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; 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.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (47) Denis, P. A.; Ventura, O. N. *Chem. Phys. Lett.* **2004**, *385*, 292.
(48) Denis, P. A. *Chem. Phys. Lett.* **2004**, *395*, 12.
(49) Visscher, L.; Styszynski, J.; Nieuwpoort, W. C. *J. Chem. Phys.* **1996**, *105*, 1987.
(50) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1989**, *23*, 1989.
(51) Feller, D.; Peterson, K. A.; de Jong, W.; Dixon, D. A. *J. Chem. Phys.* **2003**, *118*, 3510.
(52) Denis, P. A.; Ventura, O. N. *Int. J. Quantum Chem.* **2000**, *80*, 439.
(53) Denis, P. A.; Ventura, O. N. *Chem. Phys. Lett.* **2001**, *344*, 221.
(54) Dixon, R. N.; Kroto, H. W. *Trans. Faraday Soc.* **1963**, *59*, 1484.
(55) Boese, A. D.; Oren, M.; Atasoylu, O.; Martin, J. M. L.; Kallay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120*, 4129.
(56) Visscher, L.; Dyall, K. G. *J. Chem. Phys.* **1996**, *104*, 9040.
(57) Partiban, S.; Martin, J. M. L. *J. Chem. Phys.* **2001**, 114.
(58) Denis, P. A. *Chem. Phys. Lett.* **2003**, *382*, 65.
(59) Bak, K. L.; Jorgensen, P.; Olsen, J.; Helgaker, T.; Gauss, J. *Chem. Phys. Lett.* **2000**, *317*, 116.
(60) Moore, C. E. *Atomic Energy Levels*; U.S. National Bureau of Standards Circular; NBS: Washington D.C., 197; Vol. 37.
(61) Ruscic, B.; Wagner, A. F.; Harding L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X. M.; Ng, C. Y.; Liu, J. B.; Chen, W. W. *J. Phys. Chem. A* **2002**, *106*, 2727
(62) Feller, D.; Dixon D. A.; Francisco, J. S. *J. Phys. Chem. A* **2003**, *107*, 10419.
(63) Bauschlicher, C. W.; Ricca, A. *J. Phys. Chem. A* **2000**, *104*, 4581.
(64) Dunning, T. H. *J. Phys. Chem. A* **2000**, *104*, 9062.
(65) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742.
(66) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89.
(67) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756.
(68) Pettersson, L. G. M.; Persson, B. *J. Chem. Phys.* **1993**, *170*, 149.
(69) Feller, D.; Sordo, J. A. *J. Chem. Phys.* **2000**, *113*, 485.
(70) Boldyrev, A.; Gonzales, N.; Simons, J. *J. Phys. Chem.* **1994**, *98*, 9931.
(71) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.