

Comment on: “Revised electron affinity of SF₆ from kinetic data”
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Abstract

The adiabatic electron affinity (AEA) of SF₆ has been calculated near the relativistic CCSDT(Q) basis set limit. Our best theoretical value (1.0340±0.03 eV) is in excellent agreement with the recently revised experimental value of 1.03±0.05 eV reported by Troe *et al.* [J. Chem. Phys. 136, 121102 (2012)]. While our best nonrelativistic, clamped-nuclei, valence CCSD(T) basis set limit value of 0.9058 eV is in good accord with the previously reported CCSD(T)/CBS values, to obtain an accurate AEA several additional contributions need to be taken into account. The most important one is scalar-relativistic effects (0.0839 eV), followed by inner-shell correlation (0.0216 eV) and post-CCSD(T) correlation effects (0.0248 eV), the latter almost entirely due to connected quadruple excitations. The diagonal Born-Oppenheimer correction is an order of magnitude less important at -0.0022 eV.

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The adiabatic electron affinity (AEA) of SF₆ has been the subject of considerable theoretical and experimental study over the years (see Brinkmann and Schaefer[1] for an overview of early work). The previously best established experimental value[2] of 1.07±0.01 eV has been a rather elusive computational target (see below); most recently, a large basis set coupled cluster study by Einfeld[3] inspired a reanalysis by Troe *et al.* [4, 5] of previously measured attachment/detachment equilibrium constants leading to 1.03±0.05 eV. Still, this value is considerably higher than the 0.94 eV obtained by Einfeld.

Earlier best computational estimates include (a) the 1998 Bauschlicher and Ricca[6] value of 0.90 eV obtained from CCSD(T)/AVTZ calculations scaled up by the $\frac{MP2/AV\{T,Q\}Z}{MP2/AVTZ}$ ratio; (b) in the same year, the Gutsev and Bartlett[7] CCSD(T)/6-311+G(3df) value AEA₀=0.92 eV; (c) using the G3 composite thermochemistry method[8], Miller et al.[9] obtained 1.21 eV. Brinkmann and Schaefer[1] considered a variety of DFT exchange-correlation functionals, and found the following AEA₀ values: KMLYP[10] 0.77, B3LYP[11, 12] 2.20, B3P86[11, 13] 2.33, BHLYP[12, 14] 1.06, BLYP[12, 15] 2.81, and BP86[13, 15] 2.55 eV.

Another bone of contention they addressed was the symmetry of the anion: while they found an octahedral (*O_h*) anion at the B3LYP, B3P86, BLYP, and BP86 levels, a *C_{4v}* geometry resembling SF₅⁻ ··· F was found at the KMLYP and BHLYP levels. As reported by Miller et al., the SCF level geometry is *C_{4v}* deformed while the MP2 geometry is symmetric; the finding of a *C_{4v}* structure at the CCSD(T)/AV(Q+d)Z *C_{4v}* geometry by Einfeld would appear to definitively indicate a deformed (pseudo Jahn-Teller) geometry.

In recent years, we developed the *W_n* (*n* = 1–4) series of computational thermochemistry methods[16–18], aiming at better-than-chemical accuracy. While W1, W2, and W2.2 represent layered extrapolations to the relativistic CCSD(T) basis set limit, W3, W3.2, W4lite, and W4 also include higher order correlation contributions. With the computational resources available to us at the Weizmann Institute and at the University of North Texas, we were able to apply W3.2 to the neutral species and the *C_{4v}* anion, as well as W4lite to both neutral and anionic *O_h* species.

W4lite theory[17] represents a layered extrapolation to the all-electron, relativistic CCSDT(Q) basis set limit energy. The computational protocol of W4lite has been specified in detail previously[17, 18]. In brief, the Hartree–Fock component is extrapolated from the AV5Z and AV6Z basis sets using the Karton–Martin modification[19] of Jensen’s extrapolation formula[20]. The shorthand notation AV*n*Z indicates the combination of aug-

cc-pVnZ on fluorine[21], and aug-cc-pV($n+d$)Z on sulfur[22]. The valence CCSD correlation energy is extrapolated using the same basis sets (where the singlet-coupled and triplet-coupled pair energies are extrapolated separately to the basis set limit). The (T) valence correlation energy is extrapolated from the AVQZ and AV5Z basis sets. The higher-order connected triples, \hat{T}_3 -(T), valence correlation contribution is extrapolated from the cc-pVDZ and cc-pVTZ basis sets[23]. The (Q) valence correlation energy is calculated with the cc-pVDZ basis set. The CCSD(T) inner-shell correlation contribution is extrapolated from the APWCVTZ and APWCVQZ core-valence basis sets[24]. The scalar relativistic contribution is obtained from second-order Douglas–Kroll–Hess[25] CCSD(T) calculations using the AVQZ-DK basis set[26]. Finally, a diagonal Born–Oppenheimer correction (DBOC) is obtained at the HF/AVTZ level of theory. W2.2 theory is obtained by omitting the post-CCSD(T) steps. All calculations reported here were carried out using MOLPRO 2010.1[27], except for the post-CCSD(T) steps for which the MRCC general coupled cluster code[28] was employed, and the diagonal Born–Oppenheimer correction which was obtained using CFOUR[29].

In the present work the equilibrium geometry of SF₆ (in O_h symmetry) and the O_h -symmetrized geometry of SF₆⁻ were optimized at the RHF-UCCSD(T)/AV(Q+d)Z level of theory[30]. The RCCSD(T)/AV(Q+d)Z equilibrium geometry of SF₆⁻ (in C_{4v} symmetry) was taken from reference [3]: we reoptimized the geometry reported there at the RHF-UCCSD(T) level and found[30]. discrepancies of 0.001 Å or less, which translate into thermochemically insignificant total energy differences on the order of 1 microhartree. Table I summarizes the component breakdown of the AEA₀ of SF₆. Our best valence, nonrelativistic, clamped-nuclei, CCSD(T) at the bottom of the well (AEA_e) amounts to 0.6935 eV. Adding the anharmonic ZPVE correction from reference [3] we obtain AEA₀ = 0.9058. This result is in reasonably good to excellent agreement with the previously reported CCSD(T) values of: 0.90 (ref. [6]), 0.92 (ref. [7]), and 0.94 eV (ref. [3]). However, it underestimates the revised experimental value of Troe *et al.* [4] by as much as 0.1242 eV.

In fact, we find that the gap in all of the above is mostly due to scalar relativistic effects, which we find to stabilize the anion by 0.0839 eV. The impact of scalar relativistic corrections on electron affinities — by favoring the neutral species over the electronically more diffuse anion — was originally documented for atoms by de la Vega and coworkers[31] at the SCF level and by de Oliveira *et al.*[32] near the full CI limit. The two remaining

W4lite terms are the inner-shell correlation contribution of 0.0216 eV and the diagonal Born-Oppenheimer correction of -0.0022 eV. Adding these, we obtain an all-electron, relativistic, DBOC-inclusive CCSD(T)/CBS value of $AEA_0 = 1.0092$ eV, within the uncertainty of the revised experimental value.

This still leaves the issue of post-CCSD(T) contributions unaddressed. The percentage of the atomization energy accounted for by parenthetical connected triple excitations, $\%TAE_e[(T)]$, has been shown to be a reliable indicator for the thermochemical importance of such effects[17, 18]. The $\%TAE_e[(T)]$ values for 4.3 % for SF_6 and 5.5% for SF_6^- (both obtained from W1w theory relative to the neutral atoms) indicate such contributions might be thermochemically significant, albeit perhaps not so on the eV scale. In the period between the publications of Refs.[3, 4] we engaged in many fruitless attempts to carry out CCSDT/cc-pVTZ and CCSDT(Q)/cc-pVDZ calculations on the C_{4v} structure. However, in light of the comparatively small $O_h \rightarrow C_{4v}$ deformation energy of the anion (just 0.0417 eV at the CCSD(T) level obtained from W4lite theory) we believe that even the O_h result might be useful. For the $SF_6^-(O_h) \rightarrow SF_6(O_h)$ reaction, the effect of higher-order connected triple excitations, $T_3-(T)$, is essentially negligible at just 0.0016 eV. The effect of connected quadruple excitation is found to be somewhat more significant, namely 0.0232 eV at the CCSDT(Q)/cc-pVDZ level. Ideally we should be using an augmented basis set in light of the anionic character; however, despite numerous attempts, these calculations likewise proved beyond our computational resources.

Inclusion of the post-CCSD(T) contributions leads to our best AEA_0 value of 1.0340 ± 0.03 eV, to which we have attached a conservative uncertainty estimate in light of the imponderabilia described in the previous paragraph. This value is, of course, in excellent agreement with the Troe *et al.* re-evaluation.

Summarizing, we calculated the AEA_0 of SF_6 near the relativistic CCSDT(Q) basis set limit. Our best theoretical value (1.0340 ± 0.03 eV) is in excellent agreement with the recently revised experimental value of 1.03 ± 0.05 eV of Troe *et al.* [4]. Our best nonrelativistic, clamped-nuclei, valence CCSD(T) basis set limit value of 0.9058 eV is in good accord with the previously reported CCSD(T)/CBS values. However, to obtain an accurate AEA the following contributions have to be taken into account: scalar-relativistic (0.0839), inner-shell (0.0216), and post-CCSD(T) contributions (0.0248 eV), while the diagonal Born-Oppenheimer correction (-0.0022 eV) is an order of magnitude smaller.

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TABLE I: Component breakdown of the adiabatic electron affinity (AEA) of SF₆ (in eV).

comp.	basis sets	extrap. ^a	AEA[SF ₆ ,O _h] ^b	C _{4v} →O _h ^c	AEA[SF ₆] ^d
SCF	AV{T,Q}Z	<i>e</i>	-1.4482	0.4464	-1.0017
SCF	AV{Q,5}Z	<i>f</i>	-1.4615	0.4485	-1.0130
SCF	AV{5,6}Z	<i>g</i>	-1.4674	0.4490	-1.0184
val. CCSD	AV{T,Q}Z	<i>e</i>	1.7171	-0.2934	1.4236
val. CCSD	AV{Q,5}Z	<i>f</i>	1.7068	-0.2908	1.4160
val. CCSD	AV{5,6}Z	<i>g</i>	1.7039	-0.2904	1.4135
val. (T)	AV{T,Q}Z	<i>f</i>	0.3859	-0.0884	0.2975
val. (T)	AV{Q,5}Z	<i>g</i>	0.3874	-0.0889	0.2984
val. T-(T)	cc-pV{D,T}Z	<i>f,g</i>	0.0016	N/A	0.0016 ^h
val. (Q)	cc-pVDZ		0.0232	N/A	0.0232 ^h
inner-shell	APWCVTZ		0.0309	-0.0097	0.0212
inner-shell	APWCV{T,Q}Z	<i>f</i>	0.0301	-0.0085	0.0216
scalar rel.	AVQZ-DK		0.1012	-0.0173	0.0839
DBOC	HF/AVTZ		-0.0031	N/A	-0.0031 ^h
DBOC	ΔCCSD/AVDZ		0.0009	N/A	0.0009 ^{h,k}
ZPVE					0.2123 ⁱ
AEA ₀	CCSD(T) _{val,nonrel,BO} ^g				0.9058
AEA ₀	CCSD(T) ^g				1.0092
AEA ₀	CCSDT(Q) ^f				1.0409
AEA ₀	CCSDT(Q) ^g				1.0340±0.03
AEA ₀	Expt. ^j				1.03±0.05

^aExtrapolation used in the two-point extrapolations.

^bEnergy of the SF₆⁻(O_h)→SF₆(O_h) reaction.

^cEnergy of the SF₆⁻(C_{4v})→SF₆⁻(O_h) reaction.

^dEnergy of the SF₆⁻(C_{4v})→SF₆(O_h) reaction.

^eFrom W1w theory[16, 17].

^fFrom W3.2 theory[17].

^gFrom W4lite theory[17].

^hTaken from AEA[SF₆,O_h], see text.

ⁱFrom reference [3].

^jFrom reference [4].

^k CCSD DBOC obtained using CFOUR[29] using the algorithm described in Ref.[33]

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- [30] See supplementary material at <http://dx.doi.org/10.1063/-----> for the RHF-UCCSD(T)/AV(Q+d)Z optimized geometries of SF₆ and SF₆⁻ (in *O_h* symmetry), and, for the sake of completeness, the RHF-UCCSD(T)/AV(Q+d)Z optimized geometry SF₆⁻ (in *C_{4v}* symmetry) which differs very slightly from the ROCCSD(T)/AV(Q+d)Z geometry actually used, see text.
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