Comment on “Revised electron affinity of SF6 from kinetic data” [J. Chem. Phys. 136, 121102 (2012)]

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(Received 6 April 2012; accepted 3 May 2012; published online 21 May 2012)

The adiabatic electron affinity (AEA) of SF6 has been the subject of considerable theoretical and experimental study over the years (see Brinkmann and Schaefer1 for an overview of early work). The previously best established experimental value2 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 Eisfeld3 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 Eisfeld.

Earlier best computational estimates include: (a) the 1998 Bauschlicher and Ricca6 value of 0.90 eV obtained from CCSD(T)/AVTZ calculations scaled up by the MP2/AVTZ:MP2/AVDZ ratio; (b) in the same year, the Gutsev and Bartlett7 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 Schaefer1 considered a variety of density functional theory (DFT) exchange-correlation functionals, and found the following AEA0 values: KMLYP (Ref. 10) 0.77, B3LYP (Refs. 11 and 12) 2.20, B3P86 (Refs. 11 and 13) 2.33, BHLYP (Refs. 12 and 14) 1.06, BLYP (Refs. 12 and 15) 2.81, and BP86 (Refs. 13 and 15) 2.55 eV.

Another bone of contention they addressed was the symmetry of the anion: while they found an octahedral (Oh) anion at the B3LYP, B3P86, BLYP, and BP86 levels, a C4v geometry resembling SF5− · · · F was found at the KMLYP and BHLYP levels. As reported by Miller et al.,10 the self-consistent field (SCF) level geometry is C4v deformed while the MP2 geometry is symmetric; the finding of a C4v structure at the CCSD(T)/AV(Q+d)Z C4v geometry by Eisfeld would appear to definitively indicate a deformed (pseudo Jahn–Teller) geometry.

In recent years, we developed the Wn (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 C4v anion, as well as W4lite to both neutral and anionic Oh species.

W4lite theory17 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 modification19 of Jensen’s extrapolation formula.20 The shorthand notation AVnZ indicates the combination of aug-cc-pVnZ on fluorine,21 and aug-cc-pV(n+d)Z on sulfur.22 The valence coupled-cluster with singles and doubles (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, T3−(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–Hess25 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.

In the present work, the equilibrium geometry of SF6 (in Oh symmetry) and the Oh-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 C4v symmetry) was taken from reference;3 we re-optimized the geometry reported there at the RHF-UCCSD(T) level and found30 discrepancies of 0.001 Å or less, which translate into thermochemically insignificant total energy differences on the order of 1 microhartree. Table I (given as Supplemental Material30) summarizes the component breakdown of the AEA0 of SF6. Our best valence, nonrelativistic, clamped-nuclei, CCSD(T) at the bottom of the well (AEA0) amounts to 0.6935 eV. Adding the anharmonic zero-point vibrational energy (ZPVE) correction from reference,3 we obtain AEA0 = 0.9058 eV. 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 co-workers\(^6\) at the SCF level and by de Oliveira et al.\(^6\) near the full CI limit. The two remaining W4lite terms are the inner-shell correction 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\(D\) = 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 parentethetical connected triple excitations, \(\%\text{TAE}_[(T)]\), has been shown to be a reliable indicator for the thermochemical importance of such effects.\(^17, 18\) The \(\%\text{TAE}_[(T)]\) values of 4.3\% for SF\(_6\) and 5.5\% for SF\(_{6}^{−}\) (both obtained from W1w theory relative to the neutral atoms) indicate that such contributions might be thermochemically significant, albeit perhaps not so on the eV scale. In the period between the publications of Refs. 3 and 4, we engaged in many fruitless attempts to carry out CCSDT/cc-pVTZ and CCSDT/Q/cc-pVQZ calculations on the \(C_{4v}\) structure. However, in light of the comparatively small \(\Delta_{v}E_{\text{oh}}\) deformation energy of the anion (just 0.0417 eV at the CCSD(T) level obtained from W4-lite theory), we believe that even the \(\Delta_{v}E_{\text{oh}}\) result might be useful. For the SF\(_6\) (\(O_{h}\) → SF\(_6\)(\(O_{h}\)) reaction, the effect of higher-order connected triple excitations, \(T_{3}\) (\(T_{2}\)), 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-pVQD 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\(D\) 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\(D\) 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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\(^26\) MRCC, a string-based general coupled cluster program suite written by M. Källay; see also M. Källay and P. R. Surján, J. Chem. Phys. 115, 2945 (2001), see http://www.mrcc.hu.


\(^30\) See supplementary material at http://dx.doi.org/10.1063/1.4719180 for Table 1, Software used, Acknowledgements, the RHF-UCCSD(T)/AV(Q+d)Z optimized geometries of SF\(_6\) and SF\(_{6}^{−}\) (in \(O_{h}\) symmetry), and, for the sake of completeness, the RHF-UCCSD(T)/AV(Q+d)Z optimized geometry SF\(_{6}^{−}\) (in \(C_{4v}\) symmetry), which differs very slightly from the ROCCSD(T)/AV(Q+d)Z geometry actually used, see ibid.

