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

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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 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 Einfeld³ 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 Ricca⁶ 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 Bartlett⁷ CCSD(T)/6-311+G(3df) value $AEA_0 = 0.92$ 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 AEA_0 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 (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 self-consistent field (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 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 AV n Z indicates the combination of aug-cc-pV n Z 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, \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-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 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 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 AEA_0 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 zero-point vibrational energy (ZPVE) correction from reference,³ we obtain $AEA_0 = 0.9058$. 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 co-workers³¹ 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 of 4.3% for SF₆ and 5.5% for SF₆⁻ (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-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 SF₆⁻(O_h) \rightarrow SF₆(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 SF₆ 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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- ³⁰See 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 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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