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International Journal of Mass Spectrometry 227 (2003) 413–420

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

G3 and G2 thermochemistry of sulfur fluoride neutrals and anions

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Received 15 March 2002; accepted 18 June 2002

Abstract

Gaussian-3 (G3) and Gaussian-2 (G2) calculations were performed to obtain total energies, enthalpies, and Gibbs free energies for neutral and anionic SF_n, for $n = 1$–6. Electron affinities and bond enthalpies were derived from these results. The electron affinities agree well with experimental results. Calculated first dissociation bond strengths agree with experimental results except for SF_5, where a discrepancy was known to exist. G3(MP2) and G2(MP2) total energies are also presented for the SF_n and SF_n^-. Results from more economical density functional theory are compared to the G3 ones and found to agree within 0.4 eV, except for EA(SF_6).

Keywords: Electron affinity; Fluoride affinity; Bond strength; G3; G3(MP2); G2; G2(MP2); SF; SF^-; SF_2; SF_2^-; SF_3; SF_3^-; SF_4; SF_4^-; SF_5; SF_5^-; SF_6; SF_6^-

1. Introduction

Gaussian-3 (G3) and Gaussian-2 (G2) formalisms provide methods based on Møller–Plesset perturbation theory and Gaussian basis sets of calculating total energies for molecules, yielding properties such as electron affinities or ionization potentials accurate *on average* at the 41- and 68-meV level, respectively [1–3]. From a database of G3 or G2 energies, one may likewise deduce atomization energies, heats of formation, bond strengths, reaction enthalpies, and acidities. While G3-derived quantities tend to be more accurate than those obtained from G2 energies, the G2 energies remain useful because the database of G2 numbers is greater than that for G3 at present. G3 results were carried out for the present work on the SF_n and SF_n^- primarily because G3 theory does a far better job in calculating EA(F) than does G2, and hence might be expected to perform better in predicting S–F bond strengths for the neutrals and anions. G2 results have earlier been presented for many of the sulfur fluoride neutrals, cations, and anions. Irikura [4] reported G2 calculations on SF_n neutrals and cations, for $n = 1$–5. [Seven years ago, Irikura said “At this time, G2 calculations are not generally feasible for molecules containing more than six non-hydrogen (‘heavy’) atoms.”] Cheung et al. [5] reported G2-type results for SF and SF_2 neutrals, anions, and cations. Though the results of Cheung et al. are labeled “G2,” they actually correspond to a modification of the G2 formalism. Cheung et al. calculated geometries using the frozen-core approximation and zero point energies using scaled MP2 perturbation theory [instead of Hartree–Fock (HF)]. While their results for electron affinities, for example, may be slightly better than those from true G2

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doi:10.1016/S1387-3806(03)00079-4

energies, use of the results in conjunction with literature G2 energies to obtain quantities such as reaction enthalpies could result in slight errors (by a few tens of meV). Furthermore, as discussed below, a different point group was used in the present work for SF_2^- than in the work of Cheung et al. In the present work, we report true G2 and G3 total energies at 0 K for SF_n and SF_n^-, for $n = 1$–6, along with enthalpies and Gibbs free energies at 298 K. The free energies are not often tabulated, but are needed for calculations of gas-phase acidities and in analysis of experiments involving equilibrium. A byproduct of the G2 calculations is total energies at a slightly lower level of theory, G2(MP2). We will present G2(MP2) results as well, for comparison with G2(MP2) energies given by Irikura [4] (and Cheung et al. [5], though again a departure from the strict formalism) for those SF_n too large for application of G2 theory seven years ago with a reasonable allocation of computing time. G2(MP2) energies are also useful in calculating reaction enthalpies involving systems still too large for G2 application. (The largest molecule for which we have G2 results is uracil [6], which has eight non-hydrogen atoms.) We will also present G3(MP2) results. The G3(MP2) total energies are not a simple byproduct of the G3 computations, but are as accurate as the G2 ones on average, and are more economical. We will not address SF_7^-, which has been observed experimentally [7,8] and has been examined theoretically [9,10]. A thorough density functional theory (DFT) study of the SF_n and SF_n^- was carried out by King et al. [10]. More recently, Bauschlicher and Ricca [11] carried out accurate coupled cluster calculations for the SF_n, SF_n^-, and SF_n^+.

The GAUSSIAN-98W program package was used in the present work [12]. Following the G3 and G2 prescriptions [1,2] geometries were calculated at the MP2(Full)/6-31G(d) level of theory. Harmonic frequencies (scaled by an empirical factor of 0.8929) were computed at the HF/6-31G(d) level of theory to obtain zero-point, enthalpy, and free energy adjustments to the equilibrium energies. The zero-point energies were added to the total energies at equilibrium in order to express 0 K results. Total energies were calculated for the MP2 geometries using QCISD(T), MP2, and MP4 perturbation theory with different basis sets to approximate a QCISD(T,Full)/G3Large result for G3 theory and QCISD(T)/6-311+G(3df,2p) result for G2 theory. The basis set denoted by “G3Large” is a modification of the 6-311+G(3df,2p) Gaussian basis set to include core correlation. In addition, G3 theory contains a spin–orbit correction for open-shell atomic species. An empirical correction (“higher level correction”) is included in the G2 and G3 results, and that for G3 is different for atoms and molecules. Molecular symmetries were enforced, primarily so that the rotational symmetry number would be correct in entropy calculations and hence in the free energy. The stability of all wavefunctions was checked, i.e., it was verified that the electron orbital set chosen gave the lowest-energy wavefunction in each case. All these results are given in Tables 1 and 2, which include S and F neutrals and anions in order to derive bond strengths; these atomic energies agree with previous work [1–3]. The G3 and G2 values for EA(F) are 3.401 and 3.477 eV, respectively, results which may be compared with the experimental value of 3.401189 ± 0.000003 eV [13].[1] The G3 and G2 values for EA(S) are 2.065 and 2.003 eV, respectively, results which may be compared with the experimental value of 2.077103 ± 0.000001 eV [14].[2] While G3 theory agrees remarkably with experiment for EA(F) and EA(S), G2 theory yields a value for EA(F) which is 76 meV *higher* than experiment, and a value of EA(S) which is 74 meV *lower* than experiment. However, the better agreement for G3 theory is mostly due to the facts that (a) atomic spin–orbit corrections are included and (b) the empirical correction for atoms is based on a fit solely to atomic data, neither of which will affect the molecular results.

One issue which limits the accuracy of these calculations are the accuracies of the ZPEs, though in evaluating electron affinities or bond strengths, only

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[1] EA(F) given here was converted from the measured cm^{-1} units into eV using the 1998 CODATA value of $e/hc = 8065.5447 \pm 0.00032\ \mathrm{cm}^{-1}\,\mathrm{eV}^{-1}$.

[2] EA(S) given here was converted from the measured cm^{-1} units into eV using the 1998 CODATA value of $e/hc = 8065.5447 \pm 0.00032\ \mathrm{cm}^{-1}\,\mathrm{eV}^{-1}$.

Table 1
G3 and G3(MP2) total energies for F and SF_n neutrals and anions, in hartree units

Species, point group	Zero-point energy	G3			G3(MP2)
		Total energy (0 K)	Enthalpy (298 K)[a]	Free energy (298 K)[a]	Total energy (0 K)
S	0	−397.96111	−397.95875	−397.97704	−397.66376
S^-	0	−398.03701	−398.03465	−398.05256	−397.74005
F	0	−99.68421	−99.68184	−99.69902	−99.64094
F^-	0	−99.80919	−99.80683	−99.82335	−99.76629
SF, $C_{\infty v}$	0.00188	−497.77629	−497.77292	−497.79811	−497.43546
SF^-, $C_{\infty v}$	0.00149	−497.86162	−497.85818	−497.88294	−497.51996
SF_2, C_{2v}	0.00457	−597.59999	−597.59571	−597.62498	−597.21504
SF_2^-, $D_{\infty h}$[b]	0.00230	−597.65777	−597.65276	−597.68344	−597.27143
SF_3, C_s	0.00734	−697.36933	−697.36407	−697.39744	−696.94087
SF_3^-, C_{2v}	0.00619	−697.48428	−697.47877	−697.51129	−697.05378
SF_4, C_{2v}	0.01184	−797.20226	−797.19654	−797.22999	−796.72972
SF_4^-, C_{4v}[c]	0.00841	−797.26253	−797.25577	−797.29147	−796.78855
SF_5, C_{4v}	0.01556	−896.94695	−896.94057	−896.97561	−896.43008
SF_5^-, C_{4v}	0.01316	−897.09811	−897.09110	−897.12666	−896.57958
SF_6, O_h	0.02097	−996.79743	−996.79081	−996.82419	−996.23564
SF_6^-, O_h[d]	0.01458	−996.84214	−996.83323	−996.87445	−996.27643

Zero point energies (in hartree), and enthalpy and free energy changes, which were used to express G3 and G3(MP2) results at 0 and 298 K, were calculated at the HF/6-31G(d) level of theory with vibrational frequencies scaled by 0.8929.

[a] 298.15 K and 1.0 atm standard state.

[b] The ZPE and thermal corrections are for the HF structure, bent (C_{2v}) SF_2^-. The high-level total energies are for linear ($D_{\infty h}$) SF_2^-. We estimate a 5 meV error at 0 K but have not attempted adjustments in the interest of remaining faithful to G2 and G3 formalism in the present work.

[c] For comparison, the C_{2v} isomer of SF_4^- has the following G3 energies, in the order of the figures in the table: 0.00855, −797.24549, −797.23871, −797.27521, and −796.77133.

[d] The ZPE and thermal corrections are for the HF structure, C_{4v} SF_6^-. The high-level total energies are for octahedral SF_6^-. We estimate error as large as 0.1 eV due to this issue alone.

differences in ZPEs are needed. The HF geometry, on which the ZPE and thermal corrections are based, can be rather different from that of the MP2(full) geometry on which the high-level calculations are based, as we saw with PCl_3^- some years ago [15]. In the present work, the optimized HF geometry for SF_6^- yields a C_{4v} structure with polar S–F bonds which are different from each other (1.59 and 2.03 Å) as well as being different from the equatorial S–F bond lengths (1.66 Å). But the optimized MP2(full) geometry for SF_6^- yields six equal S–F bonds (1.72 Å). Thus, the ZPE and thermal corrections derived from the HF geometry for SF_6^- are not strictly appropriate for the G2 and G3 calculations. The magnitude of the error is suggested by the DFT calculations detailed below, with a large basis set, where the SF_6^- ZPE for the correct O_h symmetry is found to be 96 meV lower than obtained from HF. (For SF_6 neutral the difference between DFT and HF, both with O_h symmetry, is 66 meV, so in the end the ZPEs will only contribute a 30-meV difference between DFT and G2 or G3 EAs.) We elected to adhere strictly to the G2 and G3 formalisms and use the HF results for the ZPE and thermal corrections to the G2 and G3 total energies, despite the error introduced in the vibrational symmetries, and in spite of the difference in rotational symmetry numbers (4 for C_{4v} vs. 24 for O_h), which causes a 40 meV error in the free energy for SF_6^-. The second case encountered in the present work is with SF_2^-. The HF geometry is bent (C_{2v}), while, as discussed below, the high-level portions of the G2 and G3 calculations were carried out for linear ($D_{\infty h}$) SF_2^-. The resulting error can again be indicated (∼5 meV) by the DFT ZPE. In all other cases, the HF geometry and the MP2(full) geometries had the same symmetry. A modification of the G3 method using DFT instead of HF has been proposed

Table 2
G2 and G2(MP2) total energies for F and SF_n neutrals and anions, in hartree units

Species, point group	Zero-point energy	G2			G2(MP2)
		Total energy (0 K)	Enthalpy (298 K)[a]	Free energy (298 K)[a]	Total energy (0 K)
S	0	−397.65494	−397.65258	−397.67087	−397.64699
S^-	0	−397.72855	−397.72619	−397.74411	−397.71964
F	0	−99.63281	−99.63045	−99.64763	−99.62894
F^-	0	−99.76060	−99.75824	−99.77476	−99.75569
SF, $C_{\infty v}$	0.00188	−497.41820	−497.41482	−497.44002	−497.40721
SF^-, $C_{\infty v}$	0.00149	−497.50370	−497.50027	−497.52502	−497.49127
SF_2, C_{2v}	0.00457	−597.19214	−597.18786	−597.21713	−597.17870
SF_2^-, $D_{\infty h}$[b]	0.00230	−597.24981	−597.24480	−597.27548	−597.23388
SF_3, C_s	0.00734	−696.91005	−696.90480	−696.93816	−696.89428
SF_3^-, C_{2v}	0.00619	−697.02652	−697.02102	−697.05354	−697.00810
SF_4, C_{2v}	0.01184	−796.69278	−796.68705	−796.72051	−796.67506
SF_4^-, C_{4v}[c]	0.00841	−796.75251	−796.74575	−796.78145	−796.73136
SF_5, C_{4v}	0.01556	−896.38539	−896.37901	−896.41405	−896.36462
SF_5^-, C_{4v}	0.01316	−896.53729	−896.53028	−896.56583	−896.51422
SF_6, O_h	0.02097	−996.18664	−996.18002	−996.21340	−996.16335
SF_6^-, O_h[d]	0.01458	−996.22746	−996.21855	−996.25976	−996.20185

Zero point energies (in hartree), and enthalpy and free energy changes, which were used to express G2 and G2(MP2) results at 0 and 298 K, were calculated at the HF/6-31G(d) level of theory with vibrational frequencies scaled by 0.8929.

[a] 298.15 K and 1.0 atm standard state.

[b] See footnote (b) to Table 1.

[c] For comparison, the C_{2v} isomer of SF_4^- has the following G2 energies, in the order of the figures in the table: 0.00855, −796.73456, −796.72777, −796.76427, and −796.71366.

[d] See footnote (d) to Table 1.

[16], but the unpredictable nature of DFT has made us reluctant to use this modification. We recently found a spectacular disagreement between DFT and G2(MP2) for the weak bond in SF_5CF_3, and noted that the measured heat of formation and other properties agreed much better with the G2(MP2) result [17].

In the G2(MP2) [18] and G3(MP2) [19] methods, computational time is saved by calculating basis set corrections at the MP2 level instead of the MP4 level. Also, in G3(MP2), computational time is saved relative to that for G3 in carrying out all calculations as frozen-core, aside from the MP2(full)/6-31G(d) geometry optimization. Otherwise, the G2(MP2) method uses the same ZPE, thermal, and empirical corrections as in G2. The G3(MP2) method uses the same ZPE, thermal, and spin–orbit corrections as in G3, but uses an empirical correction that was optimized for G3(MP2) energies and which is different for atoms and molecules. G2(MP2) and G3(MP2) total energies at 0 K are given in Tables 1 and 2, respectively. Adjustments to the 0 K energies to obtain G2(MP2) and G3(MP2) enthalpies and free energies at 298 K may be readily calculated from differences in the G3 or G2 energies given in the table, since all four methods utilize the same enthalpy and free energy adjustments. To give one example, consider neutral SF: the G3 enthalpy at 298 K is 0.00337 hartree higher in energy than the 0 K value. The G3(MP2) enthalpy for SF is greater than the G3(MP2) energy at 0 K by the same amount, and is thus −497.43209 hartree. By a similar reasoning, the G3(MP2) free energy for SF is −497.45728 hartree. G2(MP2) results for ionization potentials and electron affinities have been calculated for the so-called “G2/97 test set” of molecules, and the method has been found to have an average absolute deviation (AAD) from experiment of 82 meV, which may be compared with that for the full G2 method, 68 meV [18]. The AAD for G3(MP2) is 56 meV, which may be compared with that for the full G3 method, 41 meV [19].

The G2 and G2(MP2) total energies (0 K) presented in Table 2 for neutral SF_n agree with those given by Irikura [4] for the cases he considered. Irikura has discussed the SF_n geometries, vibrational frequencies, bond energies and heats of formation. The G2 total energies in Table 1 are quite close to the ones given by Cheung et al. [5] for $n = 1, 2$ despite the departure of Cheung et al. from the strict G2 formalism; the largest discrepancy is 6 meV (for SF_2), not counting the 55-meV discrepancy for SF_2^-, where a different molecular symmetry is used in the present work, as detailed below. Similarly, the G2(MP2) total energies are close to those given by Cheung et al. for $n = 1$–6, with the largest discrepancy 33 meV for SF_6. Because the differences affect neutral and anion similarly, $EA(SF_n)$ are largely unaffected by the improved ZPE analysis of Cheung et al., who also discussed SF_n neutral and anion geometries, bond strengths, and heats of formation. They noted a C_{2v} isomer of SF_4^-; we verified the existence of this isomer, and find at the G3 level of theory that it lies 0.46 eV above the energy of C_{4v} SF_4^-. We also agree with Irikura's [4] recommendation toward a nonplanar C_s geometry for SF_3. As Irikura pointed out, this matter is significant because of the different rotational symmetry numbers for C_s vs. C_{2v} symmetry, which affects the entropy and hence the free energy. In conflict with earlier work, King et al. [10] and Bauschlicher and Ricca [11] concluded that SF_2^- is linear because geometry optimizations with larger basis sets led to the planar geometry. It takes a surprisingly high level of theory to attain the linear geometry: we found that with MP2(Full)/6-311+G(3df), the bond angle is 169.7°. At the MP4(Full)/6-311+G(3df) level, the bond angle is 180.0°. The total energy for linear SF_2^- is only ∼25 meV lower than that of bent SF_2^-, an amount smaller than the precision of G3 and G2 theory. The rotational symmetry number for linear ($D_{\infty h}$) SF_2^- is the same as for bent (C_{2v}), but the state specification is obviously different. At the HF level of theory used in G3 and G2 calculations to determine the ZPE and 298 K corrections, linear SF_2^- has one negative force constant for a bending motion. In density functional theory, specifically B3LYP/6-311+G(3df)//B3LYP/6-311+G(d) as detailed below, both bent and linear SF_2^- possess all positive force constants, and the linear form lies 9 meV lower in energy than the bent structure at 0 K. (This energy difference is, however, far below the precision of DFT.)

In Table 3, we present quantities derived from the total energies of Tables 1 and 2, including $EA(SF_n)$, and $D^\circ_{298}(SF_{n-1}–F)$, $D^\circ_{298}(SF_{n-1}–F^-)$, and $D^\circ_{298}(F–SF_{n-1}^-)$ bond enthalpies. (EAs are 0 K values, by definition; bond strengths at 0 K are not shown but may be readily obtained from differences in the 0 K total energies in Tables 1 and 2.) Experimental values are included in Table 3 for comparison. In our 1995 work [20] we reviewed the available experimental values and limits on $EA(SF_n)$, which also necessitated examination of literature S–F bond strengths (relying heavily on the analysis performed in great depth by Tsang and Herron [21]) since some EA values were arrived at through thermochemical relations. For SF_2, SF_3, and SF_5, the experimental EAs were quite uncertain. For SF_2, there were no measurements except for broad limits placed on $EA(SF_2)$ by observation of SF_2^- product from ion–molecule reactions. For SF_3, two experimental results were in conflict, so the recommended value quoted in Table 3 for $EA(SF_3)$ was given with some trepidation. For SF_5, there were a number of ionization measurements from which one could obtain $EA(SF_5)$, but the interpretation required knowledge of $D^\circ_0(SF_4–F)$. The literature value of $D^\circ_{298}(SF_4–F)$ at that time put the resulting $EA(SF_5)$ in severe conflict with the measured fluoride affinity of SF_4 [22] through the thermochemical cycle,

$$EA(SF_5) = EA(F) - D^\circ_0(SF_4–F) + D^\circ_0(SF_4–F^-) \qquad (1)$$

where the fluoride affinity $FA(SF_4)$ is $D^\circ_{298}(SF_4–F^-)$, which differs from $D^\circ_0(SF_4–F^-)$ by only tens of meV. Given all these uncertainties, the agreement between experiment and theory shown in Table 3 is quite remarkable. Further, we note that the calculated value of $D^\circ_{298}(SF_4–F) = 1.69$ eV is indeed much lower than thought in 1995 (2.30 ± 0.26 eV [23,24]). This point

Table 3
Quantities (in eV) derived from the G3, G2, and DFT total energies calculated in the present work, plus experimental values (Exp't) and earlier calculated values

Quantity/SF_n	SF	SF_2	SF_3	SF_4	SF_5	SF_6
$EA(SF_n)$						
G3	2.32	1.57	3.13	1.64	4.11	1.21
G2	2.33	1.57	3.17	1.63	4.13	1.11
Exp't	2.285(6)[d]	1.2(5)[e]	2.9(2)[f]	1.5(2)[e]	4.23(12)[g]	1.05(10)[h]
CCSD(T)[a]	2.32	1.41	3.10	1.44	4.08	0.90
DFT (0 K)[b]	2.31	1.82	3.05	2.07	4.28	2.06
DFT (0 K)[c]	2.27	1.73	3.29	2.08	4.34	1.78
$D^\circ_{298}(SF_{n-1}\text{–}F)$						
G3	3.60	3.84	2.35	4.10	1.69	4.58
G2	3.59	3.88	2.35	4.13	1.67	4.64
Exp't	3.52(9)[i]	3.98(19)[j]	2.74(31)[j]	3.74(34)[e]	2.30(26)[j]	4.35(10)[k]
CCSD(T)[a]	3.63	3.91	2.34	4.21	1.63	4.70
DFT (298 K)[b]	3.66	3.69	2.50	3.72	1.58	4.01
DFT (0 K)[c]	2.90	3.04	1.63	3.14	1.01	3.54
$D^\circ_{298}(SF_{n-1}\text{–}F^-)$						
G3	2.52	1.99	2.07	2.31	2.39	2.35
G2	2.43	1.95	2.04	2.25	2.31	2.21
Exp't	2.40(9)[d]	1.8(7)[l]	2.2(5)[l]	1.84(16)[e]	2.38(10)[m]	2.0(2)[l]
CCSD(T)[a]	2.52	1.86	1.99	2.18	2.26	2.16
DFT (298 K)[b]	2.52	2.03	2.09	2.30	2.38	2.53
DFT (0 K)[c]	2.20	1.83	1.99	2.27	2.41	2.37
$D^\circ_{298}(F\text{–}SF_{n-1}{}^-)$						
G3	3.86	3.07	3.92	2.59	4.18	1.65
G2	3.91	3.10	3.97	2.57	4.19	1.57
Exp't	3.73(10)[l]	2.9(7)[l]	4.4(10)[l]	2.3(7)[l]	5.0(6)[l]	≤1.85(12)[m]
CCSD(T)[a]	3.77	2.97	4.05	2.53	4.29	1.53
DFT (298 K)[b]	3.78	3.25	3.80	2.78	3.86	1.80
DFT (0 K)[c]	3.17	2.50	3.19	1.92	3.27	0.96

The experimental uncertainty in the final digit or digits is given in parentheses.

[a] CBS CCSD(T) with input from well-established heats of formation and spin–orbit splittings. The $D^\circ_{298}(SF_{n-1}\text{–}F^-)$ values above were obtained from the recommended heats of formation [11].

[b] Present work: B3LYP/6-311+G(d) geometries and frequencies (scaled by 0.9613), and total energies using B3LYP/6-311+G(3df)+ZPE, plus enthalpy correction for bond strengths at 298 K.

[c] Results at 0 K using BHLYP/DZP++ corrected for ZPE [10].

[d] Polak et al. [31].

[e] Miller et al. [20].

[f] Thynne [32].

[g] Španel et al. [33].

[h] Grimsrud et al. [34].

[i] JANAF tables [35].

[j] Kiang and Zare [23].

[k] Tsang and Herron [21].

[l] Values obtained from the other experimental results in the table using thermochemical cycles analogous to Eq. (1).

[m] Lobring et al. [25].

has been made earlier by King et al. [10] and by Bauschlicher and Ricca [11]. Some new experimental results are reported in this issue of the journal [25] for $D^\circ_{298}(SF_4\text{–}F^-)$, and $D^\circ_{298}(F\text{–}SF_5{}^-)$ and are included in the table. In Table 3 we have not shown quantities derived from the G2(MP2) and G3(MP2) total energies, but they are easily deduced from the information in Tables 1 and 2.

Bauschlicher and Ricca [11] used complete basis set coupled cluster [CBS CCSD(T)] methods with well-established heats of formation and spin–orbit splittings to arrive at accurate heats of formation for the SF_n neutrals, anions, and cations. Some results of those calculations are listed in Table 3. There is generally good agreement with the G2- and G3-derived quantities, though EA(SF_6) differs by more than expected.

Table 3 also gives results from density functional theory, using a procedure we have found in the past to give electron affinities accurate within about 0.3 eV [15,26]. We carried out geometry optimizations and harmonic frequency analyses using Becke's hybrid functional [27] with the Lee–Yang–Parr correlation functional [28] and the 6-311+G(d) basis set. Frequencies were scaled by an empirical factor of 0.9613 [26,29]. The total energy was then calculated using a larger basis set denoted by 6-311+G(3df). The method usually yields EAs greater than the experimental value. The one major failing of this DFT procedure that we have noted involved the weak SF_5–CF_3 bond in SF_5CF_3 [17]. The DFT procedure performed remarkably well for isolated SF_5 and CF_3 radicals, but yielded an EA(SF_5CF_3) which was 0.9 eV above that obtained by the G2(MP2) method. For EA(SF_n), Table 3 indicates that the DFT method seems to work as well as expected except for EA(SF_6). It is worthwhile understanding the successes and failures of the DFT method because it is considerably more economical than the brute force Møller–Plesset methods. Although the DFT method used here is roughly 4–5 times less accurate than the G3 and G2 methods, the DFT calculation for SF_4 (to take one example) required only one-ninth the computational time, and used little computer disk space. A broad review of DFT calculations for neutrals and anions has been given recently by Rienstra-Kiracofe et al. [30]. King et al. [10] carried out a thorough DFT study of the SF_n neutrals and anions using a variety of functionals. Their results are in concert with the ones given here, using different basis sets. A small sampling of the results of King et al. is included in Table 3, namely the ones that seemed to best match available experimental data overall, obtained using the BHLYP functional with DZP++ basis set [10]. We have included ZPE corrections in quoting King et al. in order to be consistent with the other values in Table 3. Even so, the King et al. bond strengths were calculated for 0 K, and thus will lie from a few to tens of meV below (most likely) the other (298 K) bond strengths in the table. It is interesting that all DFT calculations for EA(SF_6) perform poorly. Some clue as to the problem comes from a thermochemical cycle analogous to Eq. (1): the DFT method applied in the present work yields EA(F) accurately, 55 meV higher than experiment. But it *overestimates* $D_0^\circ(SF_5–F^-)$ and *underestimates* $D_0^\circ(SF_5–F)$, so the result *via* Eq. (1) is a doubly-erroneous EA(SF_6).

In summary, we report true G3, G2, G3(MP2), and G2(MP2) total energies for neutral and anionic SF_n, $n = 1–6$. These energies agree with previous work where there is overlap of effort. Thermochemical quantities were calculated from the G2 and G3 energies and are estimated accurate within 0.1 eV, except for SF_6, where there is additional uncertainty regarding the ZPE and thermal corrections. The G2 and G3 thermochemical quantities agree quite well, with the largest discrepancy being 0.14 eV (for SF_6). G2 and G3 adiabatic EAs agree well with experimental values. G2 and G3 first dissociation energies for neutral SF_n likewise agree with experiment, within combined uncertainties, except for SF_5, where a discrepancy between literature $D_{298}^\circ(SF_4–F)$, FA(SF_4), and EA(SF_5), related through a thermochemical cycle (Eq. (1)) has been noted earlier [10,11,20]. Since none of the SF_n or $SF_n{}^-$ is likely to be a pathological molecule, computationally, we expect that the calculated quantities are more accurate (±0.1 eV) than many of the experimental results, and should act as a guide to where further experimental work is desirable. The present results are in general agreement with coupled cluster calculations [11]. We have also made a limited comparison with DFT results ([10] and present work) because of the great economy of DFT computation and the need to understand where DFT occasionally fails.

Acknowledgements

We are grateful for the support of the Air Force Office of Scientific Research for this work. We thank Prof. Lee Sunderlin for allowing us to include results from his laboratory (published in this issue of the journal [25]). T.M.M. is under contract (F19628-99-C-0069) with Visidyne, Inc.

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