J. Phys. Chem. A **2008,** *112,* 3145−3156

Bond Dissociation Energies in Second-Row Compounds

Daniel J. Grant, Myrna H. Matus, Jackson R. Switzer, and David A. Dixon*

Chemistry Department, The University of Alabama, Shelby Hall, Box 870336, Tuscaloosa, Alabama 35487-0336

Joseph S. Francisco

Department of Chemistry, H. C. Brown Laboratory, Purdue University, West Lafayette, Indiana 47907-1393

Karl O. Christe

Loker Research Institute and Department of Chemistry, University of Southern California, California 90089-1661

Received: October 26, 2007; In Final Form: December 19, 2007

Heats of formation at 0 and 298 K are predicted for PF_3, PF_5, PF_3O, SF_2, SF_4, SF_6, SF_2O, SF_2O_2, and SF_4O as well as a number of radicals derived from these stable compounds on the basis of coupled cluster theory [CCSD(T)] calculations extrapolated to the complete basis set limit. In order to achieve near chemical accuracy (±1 kcal/mol), additional corrections were added to the complete basis set binding energies based on frozen core coupled cluster theory energies: a correction for core−valence effects, a correction for scalar relativistic effects, a correction for first-order atomic spin−orbit effects, and vibrational zero-point energies. The calculated values substantially reduce the error limits for these species. A detailed comparison of adiabatic and diabatic bond dissociation energies (BDEs) is made and used to explain trends in the BDEs. Because the adiabatic BDEs of polyatomic molecules represent not only the energy required for breaking a specific bond but also contain any reorganization energies of the bonds in the resulting products, these BDEs can be quite different for each step in the stepwise loss of ligands in binary compounds. For example, the adiabatic BDE for the removal of one fluorine ligand from the very stable closed-shell SF_6 molecule to give the unstable SF_5 radical is 2.8 times the BDE needed for the removal of one fluorine ligand from the unstable SF_5 radical to give the stable closed-shell SF_4 molecule. Similarly, the BDE for the removal of one fluorine ligand from the stable closed-shell PF_3O molecule to give the unstable PF_2O radical is higher than the BDE needed to remove the oxygen atom to give the stable closed-shell PF_3 molecule. The same principles govern the BDEs of the phosphorus fluorides and the sulfur oxofluorides. In polyatomic molecules, care must be exercised not to equate BDEs with the bond strengths of given bonds. The measurement of the bond strength or stiffness of a given bond represented by its force constant involves only a small displacement of the atoms near equilibrium and, therefore, does not involve any reorganization energies, i.e., it may be more appropriate to correlate with the diabatic product states.

Introduction

There is substantial interest in the bond dissociation energies in compounds containing second- and higher-row main group elements with coordination numbers beyond the standard values. These types of compounds have many practical applications and are of substantial interest as model systems.[1] In addition, they are broadly used as examples in basic chemistry courses. In a diatomic molecule, there is only one bond, and the dissociation products are the two atoms. In polyatomic molecules, the situation is more complicated, as each bond dissociation energy (BDE) can be quite different as one product is an atom and the other is a molecule that may have a substantially different electronic structure than the reactant molecule. The BDEs for individual steps in the stepwise dissociation of a polyatomic binary compound can be very different, as they depend on the relative stabilities of the starting compound and the products and can differ significantly from the average bond energy (total atomization energy divided by the number of broken bonds) in the molecule. In addition, there are different ways to define the BDE. The diabatic BDE is dissociation to the configurations most closely representing the bonding configuration in the reactant, and the adiabatic BDE is dissociation to the ground state of the separated species. The adiabatic BDE will always be equal to or less than the diabatic BDE. The adiabatic BDE may not be representative of the bonding near the minimum, so when comparing different BDEs, it may be more appropriate to compare diabatic BDEs, especially when addressing bond distances, stretching frequencies, and bond force constants that are representative of the minimum, and not to the lowest energy dissociation channel. Note that for the diabatic BDE, we require that the spin be conserved, whereas in the adiabatic BDE, the process may not occur on the same spin surface. We also constrain the diabatic BDE to correlate with no more than one excited state of the product atoms and molecules. The difference in the adiabatic and diabatic BDEs represents a reorganization or relaxation energy of the product atom or molecule. The difference in diabatic and adiabatic BDEs has been discussed

---

* Corresponding author. E-mail: dadixon@bama.ua.edu.

10.1021/jp710373e CCC: $40.75

relative to the strength of π-bonds in olefins and main group compounds.[2−4]

Because the separate experimental measurement of each individual step often is either very difficult (often due to the formation of atomic and polyatomic radicals) or cannot be measured under comparable conditions, high-level theoretical calculations of these processes offer a unique opportunity to obtain accurate self-consistent values for these processes.[5] Modern computational chemistry methods implemented on high-performance computer architectures can now provide reliable predictions of chemical bond energies to within about 1 kcal/mol for most compounds that are not dominated by multireference character. We can use the approach that we have been developing with collaborators at Pacific Northwest Laboratory and Washington State University for the prediction of accurate molecular thermochemistry[6] to determine BDEs in compounds containing a second-row element as the central atom. Our approach is based on calculating the total atomization energy of a molecule and using this value with known heats of formation of the atoms to calculate the molecular heat of formation at 0 K. The approach starts with coupled cluster theory with single and double excitations and including a perturbative triples correction [CCSD(T)],[7−9] combined with the correlation-consistent basis sets[10,11] extrapolated to the complete basis set limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive corrections including core−valence interactions and relativistic effects, both scalar and spin−orbit. The zero-point energy can be obtained from experiment, theory, or a combination of the two. Corrections to 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions in the rigid rotor−harmonic oscillator approximation[12] and appropriate corrections for the heat of formation of the atoms.[13]

Due to their large range of possible oxidation states, sulfur and phosphorus fluorides and oxofluorides are ideally suited for such an investigation. There have been numerous theoretical and experimental studies of the thermochemistry and BDEs of PF_xO_y and SF_xO_y compounds, but many of them have not been as accurate as one would hope for, and there are not as many reliable main group dissociation energies known as one would like. Many of the results are derived from the heats of formation in *NIST-JANAF Thermochemical Tables* or the updated values from the NIST Web site[14] and have recently been compiled by Luo.[15] The experimental P−F and S−F bond energies for a number of compounds are summarized in Table 1. Ahlrichs et al.[16] reported mass spectrometric and matrix isolation infrared investigations of PFO and obtained a value of −96.7 kcal/mol for the heat of formation at 298 K. They also reported ab initio calculations at the SCF (self-consistent field), CISD (single and double configuration interaction), and CPF (coupled pair functional) levels. Beckers et al.[17] further studied PFO by millimeter-wave spectroscopy, high-resolution infrared spectroscopy, and high-level ab initio calculations at the MP2 (second-order Møller−Plesset) and CCSD(T) levels with a series of correlation-consistent basis sets including additional diffuse functions and *d*-functions. Gustev[18] has studied the structure and stability of the phosphorus fluorides PF_n and their singly charged anions PF_n^- ($n = 1−6$) using density functional theory (DFT). Tschumper et al.[19] studied these systems with a range of density functional methods (four exchange-correlation functionals using DZP and DZP++ basis sets). Gu and Leszczynski[20] also studied the PF_n/PF_n^- series for ($n = 1 - 6$) with G2 theory and several of its modified versions and predicted bond dissociation energies as well as the atomization energies, enthalpies of formation, and adiabatic electron affinities.

TABLE 1: Experimental and Calculated Bond Dissociation Energies in kcal/mol at 0 K[a]

		calculated	
bond energy reaction	experiment	DTQ	Q5
$PF_5 \rightarrow PF_4 + F$		132.8	
$PF_4 \rightarrow PF_3 + F$		54.5	
$PF_3 \rightarrow PF_2 + F$	130.2 ± 5.9[b]	132.0	131.8
$PF_2 \rightarrow PF + F$	(123.2)[c]	119.2	119.1
$PF \rightarrow P + F$	106 ± 5[b]	107.2 [107.1]	107.1 [107.0]
$PF_3O \rightarrow PF_3 + O$	129.0 ± 2.8[b]	131.6 [131.4]	132.4 [132.2]
$PF_3O \rightarrow PF_2O + F$		143.8	143.9
$PF_2O \rightarrow PF_2 + O$		119.7	120.3
$PF_2O \rightarrow PFO + F$		74.3	74.2
$PFO \rightarrow PF + O$		164.6 [164.5]	165.2 [165.2]
$PFO \rightarrow PO + F$		130.9 [130.8]	130.8 [130.7]
$PO \rightarrow P + O$	141.8 ± 1[b]	140.9 [140.8]	141.6 [141.4]
$SF_6 \rightarrow SF_5 + F$	92.2 ± 3.8[b] (100.4 ± 2.4)[d] 75.92[e] 78[f] 92.0[g] (91.1 ± 3.2)[h] 88.1 ± 3.2[i] (94.5 ± 3.0)[j]	104.8	
$SF_5 \rightarrow SF_4 + F$	72[f] (53.1 ± 6.0)[h] 57.9 ± 3.0[i]	37.7	
$SF_4 \rightarrow SF_3 + F$	80 ± 13[b] ≤83.9 ± 1.2[k] 83[f] (84.1 ± 3.0)[h] 89.2 ± 2.3[i] 86.2 ± 7.8[l]	95.5	95.7
$SF_3 \rightarrow SF_2 + F$	63[f] (63.7 ± 7.1)[h] 60.9 ± 2.8[i]	54.8	54.6
$SF_2 \rightarrow SF + F$	91.8 ± 5.5[b] 94[f] (91.7 ± 4.3)[h] 94.3 ± 4.6[i]	89.1 [89.2]	89.3 [89.3]
$SF \rightarrow S + F$	81.0 ± 1.6[b] 82[f] (81.2 ± 1.6)[h] 77.5 ± 4.2[i]	83.2 [83.1]	83.2 [83.1]
$SF_5O \rightarrow SF_5 + O$		71.6	
$SF_5O \rightarrow SF_4O + F$		21.1	
$SF_4O \rightarrow SF_4 + O$	(102 ± 6)[m]	88.2 [88.0]	88.9 [88.7]
$SF_4O \rightarrow SF_3O + F$		89.7	89.8
$SF_3O \rightarrow SF_2O + F$		20.0	20.0
$SF_3O \rightarrow SF_3 + O$		94.0	94.8
$SF_2O \rightarrow SFO + F$		93.6	93.7
$SF_2O \rightarrow SF_2 + O$	118 ± 29.0[b]	128.8 [128.7]	129.4 [129.5]
$SFO \rightarrow SO + F$		85.4	86.2
$SFO \rightarrow SF + O$		124.3	125.0
$SF_2O_2 \rightarrow SF_2O + O$	(109 ± 27)[b] (110 ± 5)[m]	98.7 [98.5]	99.7 [99.3]
$SF_2O_2 \rightarrow SFO_2 + F$		106.9	107.2
$SFO_2 \rightarrow SO_2 + F$		40.4[n]	
$SFO_2 \rightarrow SFO + O$		85.4	86.2
$SO \rightarrow S + O$	123.58[o]	123.1 [123.0]	123.7 [123.6]

[a] Values in parentheses are at 298 K. Calculated values have scalar relativistic MVD correction. Calculated values in brackets have scalar relativistic DKH correction. [b] Reference 14. [c] Reference 15. [d] Reference 29. [e] Reference 21. [f] Reference 23. [g] Reference 24. [h] References 26 and 27. [i] Reference 30. [j] Reference 28. [k] Reference 22. [l] Reference 31. [m] Reference 25. [n] Calculated using the experimental heat of formation of SO_2 from ref 14. [o] Reference 55.

There have been a number of experiments measuring the thermochemistry of the sulfur fluorides. Bott and Jacobs[21] performed shock-tube experiments and used RRK reaction rate theory to determine the first S−F bond dissociation energy in SF_6 to be 75.9 kcal/mol. Thynne and Harland[22] studied negative ion formation of sulfur tetrafluoride and estimated the SF_3−F BDE to be ≤83.9 kcal/mol. Hildebrand[23] reported mass spectrometric studies of gaseous sulfur fluorides measuring the heats of formation of SF, SF_2, and SF_4. Coupled with other data, this gives the stepwise BDE of SF_6. Lyman[24] reanalyzed their data for the thermal dissociation of SF_6 using RRKM unimolecular reaction rate theory and found a value of 92 kcal/mol for the S−F BDE. Benson[25] reviewed the thermochemistry of sulfur-containing molecules and provided estimates for the heats of formation of SF_5, SF_4O, and SF_5O as well as the $SF_4{=}O$ BDE. Kiang et al.[26,27] studied the chemiluminescent reactions of SF_6 and SF_4 with metastable calcium and strontium atoms under single-collision conditions. Their experiments allowed them to determine the $F_5S{-}F$ (91.1 ± 3.2 kcal/mol) and $F_3S{-}F$ (84.1 ± 3.0 kcal/mol) BDEs, and when combined with known heats of formation, they obtained the stepwise BDEs for SF_6. Babcock et al.[28] measured the first BDE of SF_6 from ion−molecule reactions and found a value of 94.5 ± 3.0 kcal/mol at 298 K. Tsang and Herron[29] reevaluated most of the data for the $F_5S{-}F$ BDE and derived a new value for the BDE of 100.4 ± 2.4 kcal/mol at 298 K. Fisher et al.[30] used collision-induced dissociation and charge-transfer experiments to measure ionization energies of the sulfur fluoride ions, and when combined with BDEs, they were able to derive heats of formation for both ionic and neutral species. Later, Stevens-Miller et al.[31] used negative ion−molecule reactions in a selected ion flow tube and determined a $SF_3{-}F$ BDE of 86.2 ± 7.8 kcal/mol. Endo et al.[32] studied the FSO radical by microwave spectroscopy and obtained geometrical parameters and vibrational frequencies. Kronberg et al.[33] reported the spectroscopic characterization of the SF_5, SF_5O, and SF_5OO radicals as well as quantum chemical calculations at the DFT [B3LYP/6-311++G(3df,3pd] level. Their experiments examined the species resulting from the atmospheric oxidation of SF_6, a long-lived atmospheric species, initiated by photodissociation that breaks an S−F bond.

Ziegler and Gustev[34] studied the molecular and electronic structure of the sulfur fluorides using DFT. Irikura[35] used G2 theory to predict the molecular structure and thermochemistry of the sulfur fluorides SF_n ($n = 1-5$). Cheung et al.[36] have also reported G2 and G2(MP2) results for the heats of formation of the neutral, cationic, and anionic sulfur fluorides and their corresponding BDEs. King et al.[37] reported the BDEs of SF_n ($n = 1-6$) at the DFT level with a DZP++ basis set. Bauschlicher and Ricca[38] predicted the heats of formation of the SF_n ($n = 1-6$), series together with the corresponding ions SF_n^+ and SF_n^- at the CCSD(T) level of theory with extrapolation to the complete basis set limit. Miller et al.[39] also investigated the thermochemistry, specifically bond enthalpies and electron affinities, of the sulfur fluoride neutrals SF_n and anions SF_n^- ($n = 1-6$) at the G3 and G2 level of theory as well as at the G3(MP2) and G2(MP2) levels.

Computational Approach

For the current study, we started with the augmented correlation consistent basis sets aug-cc-pV*n*Z for O, F, P, and S (n = D, T, Q, 5).[10,11] For the sake of brevity, we abbreviate the names to aV*n*Z. Only the spherical components (5-*d*, 7-*f*, 9-*g*, 11-*h*) of the Cartesian basis functions were used. It has recently been found that tight *d* functions are necessary for calculating accurate atomization energies for second-row elements,[40] so additional tight *d* functions on P and S were included in our calculations. Basis sets containing extra tight *d* functions are denoted aug-cc-pV(n+d)Z, in analogy with the original augmented correlation consistent basis sets. We use aug-cc-pV(n+d)Z to represent the combination of aug-cc-pV(n+d)Z (on the second-row atoms P and S) and aug-cc-pV*n*Z (on O and F) basis sets and abbreviate this as aV(n+d)Z.

All of the current work was performed with the MOLPRO suite of programs.[41] The open-shell CCSD(T) calculations for the atoms were carried out at the R/UCCSD(T) level. In this approach, a restricted open-shell Hartree−Fock (ROHF) calculation was initially performed, and the spin constraint was relaxed in the coupled cluster calculation.[42−44] All of the calculations were done on a massively parallel HP Linux cluster with 1970 Itanium-2 processors in the Molecular Sciences Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory or on the 144 processor Cray XD-1 computer system at the Alabama Supercomputer Center.

The geometries were optimized numerically at the frozen core CCSD(T) level with the aVDZ and aVTZ as well as the aV(D+*d*)Z and aV(T+*d*)Z correlation-consistent basis sets. The geometries of the diatomics were also optimized at the aV(Q+*d*)Z level. The CCSD(T)/aug-cc-pV(Q+*d*)Z geometries were then used in single-point CCSD(T)/aV(5+*d*)Z calculations. For the polyatomic molecules, the CCSD(T)/aV(T+*d*)Z geometries were then used in single-point CCSD(T)/aV(Q+*d*)Z and CCSD(T)/aV(5+*d*)Z calculations. For the large open-shell molecules, due to the computational expense of open-shell CCSD(T) calculations, the largest basis set used for the CBS extrapolations for PF_4, SF_5, and SF_5O was the aV(Q+*d*) basis set.

Frequencies for the polyatomic molecules were calculated at the MP2/aug-cc-pV(T+*d*)Z level using the Gaussian program system[45] in order to obtain zero-point energies and thermal corrections at 298 K. Zero-point energies were obtained either directly from the experimental values or from the calculated frequencies if experimental values were not available. Bond distances, harmonic frequencies, and anharmonic constants for the diatomics were obtained from a fifth-order fit[46] of the potential energy curve at the CCSD(T)/aug-cc-pV(Q+*d*)Z level.

The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form

$$E(n) = \mathrm{E}_{\mathrm{CBS}} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \qquad (1)$$

with n = 2 (DZ), 3 (TZ), and 4 (QZ), as first proposed by Peterson et al.[47] This extrapolation method has been shown when combined with the other corrections given below to yield atomization energies in the closest agreement with experiment (by a small amount) as compared to other extrapolation approaches up through $n = 4$.[6] The total atomization energies for the molecules were also obtained by extrapolating the aug-cc-pV(Q+*d*)Z and aug-cc-pV(5+*d*)Z values using the formula

$$E(l_{\mathrm{max}}) = E_{\mathrm{CBS}} + B/l_{\mathrm{max}}{}^3 \qquad (2)$$

We abbreviate the extrapolation with eq 1 as the DTQ extrapolation and that with eq 2 as the Q5 extrapolation. The T_1 diagnostics[48] (Supporting Information) are small, with the largest values being 0.025 for the diatomics PO and SO, suggesting that our CCSD(T) approach based on a single reference should provide good results.

Core-valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[49] Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CISD level of theory using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass-velocity and one-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[50] ΔE_{SR} were also calculated at the MP2 level with the cc-pVTZ DK basis set and the spin-free, one-electron

TABLE 2: Optimized Bond Lengths (Å) and Angles (deg) for PF_xO_y Equilibrium Geometries[a]

molecule	basis set	R_{PF}	R_{PO}	∠FPF	∠FPO
PO ($^2\Pi$, $C_{\infty v}$)	aV(T+*d*)Z		1.4889		
	aV(Q+*d*)Z		1.4828		
	exp[b]		1.4759		
PF ($^3\Sigma^-$, $C_{\infty v}$)	aV(T+*d*)Z	1.6028			
	aV(Q+*d*)Z	1.5960			
	exp[b]	1.589_7			
PFO ($^1A'$, C_s)	aV(T+*d*)Z	1.5855	1.4646		110.13
	exp[c]	1.5727 ± 0.0002	1.4528 ± 0.0001		110.16 ± 0.02
PF_2 ($^2B_1$, C_{2v})	aV(T+*d*)Z	1.5883		98.16	
PF_3 ($^1A_1$, C_{3v})	aV(T+*d*)Z	1.5723		97.45	
	exp[d]	1.561(1)		97.7(2)	
PF_2O ($^2A'C_s$)	aV(T+*d*)Z	1.5581	1.4654	98.93	115.94
PF_3O ($^1A_1$, C_{3v})	aV(T+*d*)Z	1.5314	1.4429	100.84	117.13
	exp[e]	1.522	1.437	101.14	
	exp[f]	$1.524_0 \pm 0.003$	$1.435_6 \pm 0.006$	101.3 ± 0.2	116.76
PF_4 ($^2A_1$, C_{2v})	aV(T+*d*)Z	1.5470 eq 1.6023 ax		94.63 eq 104.46 ax	
PF_5 ($^1A_1$, D_{3h})	aV(T+*d*)Z	1.5415 eq 1.5813 ax		120.0 eq 90.0 ax	
	exp[g]	1.5340 eq 1.5770 ax			

[a] CCSD(T) optimizations on the PF_xO_y compounds up to aug-cc-pV(T+*d*)Z and up to aug-cc-pV(Q+*d*)Z for diatomics; ax = axial and eq = equatorial. [b] PF and PO electronic spectroscopy; ref 55. [c] Millimeter-wave and high resolution infrared spectrocopies; ref 17. [d] Microwave R_e; ref 58. [e] Microwave; ref 60. [f] Electron diffraction; ref 59. [g] Electron diffraction; ref 61.

Douglas–Kroll–Hess (DKH) Hamiltonian for some molecules.[51–53] As shown below, the two approaches for ΔE_{SR} are in agreement within better than 0.5 kcal/mol in the worst case and usually within 0.3 kcal/mol.[6i,n] Most calculations using available electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state as the spin–orbit in the atom is usually not included. Instead, the energy is a weighted average of the available multiplets. For P in the ^4S state, no spin–orbit correction is needed, but corrections of 0.22, 0.38, and 0.56 kcal/mol for O, F, and S, respectively, are needed and are taken from the excitation energies of Moore.[54] The spin–orbit corrections for the diatomic molecules PO and SF were taken from Huber and Herzberg.[55]

By combining our computed $\sum D_0$ (total atomization energies) values with the known heats of formation[14] at 0 K for the elements $\Delta H_f^0(O) = 58.99$ kcal/mol, $\Delta H_f^0(F) = 18.47$ kcal/mol, $\Delta H_f^0(P) = 75.42$ kcal/mol, and $\Delta H_f^0(S) = 65.66$ kcal/mol, we can derive ΔH_f^0 values for the molecules under study in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[13]

Results and Discussion

Geometries. The optimized geometry parameters for the P derivatives are shown in Table 2 and for the S derivatives in Table 3. The point groups and ground-state symmetry labels are given in these tables for the molecules under study. For the P derivatives, the P–F and P–O bond distances are too long as compared to experiment by >0.013 Å at the CCSD(T)/aug-cc-pV(T+*d*)Z level, and by >0.006 Å at the CCSD(T)/aug-cc-pV(Q+*d*)Z level. In fact, we found that it was very important to include the tight *d* functions in the geometry optimizations of these species, as the bond lengths were much too long without their inclusion. For PFO, even larger calculations showed that inclusion of core–valence correlation as well as large basis sets up to aV5Z with a correction for the tight *d* functions was required to obtain the best agreement with experiment.[17] Similar results are found for the MP2 optimizations for the S derivatives.

For the diatomics PO ($^2\Pi$), PF ($^3\Sigma^-$), SF ($^2\Pi$), and SO ($^3\Sigma^-$), our calculated values are in agreement with the experimental data,[55] with the largest discrepancy in the S–F distance being 0.0073 Å longer than experiment. High level calculations on SO have been discussed in detail previously, and we note that it is important to include tight d functions in the description of the structures and energetics.[40,56,57] Our values, which are included for completeness, are in agreement with the previous calculations.

The P–F distance in PF_3 was found to be 0.01 Å longer than the experimental value of 1.561 Å,[58] whereas the ∠FPF was slightly smaller by 0.3° than the experimental value of 97.7°.[58] In PF_3O, the calculated P–F and P–O distances of 1.531 and 1.443 Å are in agreement with experiment, being only 0.007 and 0.008 Å longer, respectively, whereas the bond angles ∠FPF and ∠FPO are 0.5° smaller and 0.4° larger compared to experiment.[59,60] In PF_5, the $P-F_{eq}$ bond is slightly longer by 0.008 Å than the experimental value of 1.534 Å,[61] and the $P-F_{ax}$ bond is also slightly longer by 0.004 Å as compared to the experimental value of 1.577 Å.[61]

For SF_2, the geometrical parameters are in agreement with experiment, with the S–F bond distance being only 0.009 Å longer than the experimental value of 1.58745(12) Å[62] and the ∠FSF being only 0.3° larger. The S–F and S–O distances in SF_2O are both slightly longer by 0.01 Å compared to experiment, while the ∠FSF and ∠FSO angles are within 0.2° of experiment.[63] For SF_4, the calculated $S-F_{eq}$ bond of 1.553 Å is slightly longer by 0.008 Å as compared to experiment, whereas the $S-F_{ax}$ bond of 1.654 Å is only 0.008 Å longer than the experimental value. The $\angle FSF_{eq}$ bond angle is practically the same as the experimental value of 101.5° (with only a 0.01° difference), whereas the $\angle FSF_{ax}$ angle is 0.7° larger than experiment.[64,65] In SF_2O_2, the S–F and S–O bond distances are slightly longer than experiment by 0.015 and 0.007 Å, respectively.[66] The ∠FSF bond angle is slightly smaller than the experimental value of 96.1° by 0.8°, whereas the ∠OSO angle is 1.2° larger than experiment. There have been several experimental studies[65,67,68] of the molecular geometry of SF_4O. The S–F bond of 1.567 Å in SF_6 is in agreement with the experimental bond distance of 1.561 Å.[58]

Vibrational Frequencies. The calculated MP2 frequencies for the P derivatives are in excellent agreement with the experimental values[17,55,69–72] considering the level of the

TABLE 3: Optimized Bond Lengths (Å) and Angles (deg) for SF_xO_y Equilibrium Geometries[a]

molecule	basis set	R_{SF}	R_{SO}	∠FSF	∠FSO	∠OSO	$\angle F_{eq}SF_{eq}F_{ax}$/ $\angle F_{ax}SF_{ax}F_{eq}$	∠FSFO/ ∠OSOF
SF($^2\Pi$, $C_{\infty v}$)	aV(T+*d*)Z	1.6057						
	aV(Q+*d*)Z	1.6013						
	exp[b]	1.600574						
SO ($^3\Sigma^-$, $C_{\infty v}$)	aV(T+*d*)Z		1.4932					
	aV(Q+*d*)Z		1.4866					
	exp[b]		1.481087					
SF_2 ($^1A_1$, C_{2v})	aV(T+*d*)Z	1.5969		98.36				
	exp[c]	1.58745(12)		98.048(13)				
SFO ($^2A''$, C_s)	aV(T+*d*)Z	1.6139	1.4474		109.19			
SF_3 ($^2A'$, C_s)	aV(T+*d*)Z	1.5695 eq		87.96 eq			−76.98	
		1.6632 ax		162.02 ax				
SF_2O ($^1A'$, C_s)	aV(T+*d*)Z	1.5958	1.4268	92.64	106.72			108.34
	exp[d]	1.5854 ± 0.0002	1.4127 ± 0.0003	92.83 ± 0.02	106.82 ± 0.03			
SFO_2 ($^2A'$, C_s)	aV(T+*d*)Z	1.5885	1.4356		106.88	124.63		−125.34
SF_4 ($^1A_1$, C_{2v})	aV(T+*d*)Z	1.5531 eq		101.51 eq			50.82	
		1.6536 ax		187.56 ax			−50.82	
	exp[e]	1.545 ± 0.003 eq		101.5 ± 0.5 eq				
		1.646 ± 0.003 ax		186.9 ± 0.5 ax				
	exp[f]	1.542 ± 0.005 eq		103.8 ± 0.6 eq				
		1.643 ± 0.005ax		176.8 ± 2.5 ax				
SF_3O ($^2A'$, C_s)	aV(T+*d*)Z	1.5526 eq	1.4188	90.26 eq	111.17 eq		−90.90	157.07
		1.6362 ax		147.54 ax	105.01 ax			
SF_2O_2 ($^1A_1$, C_{2v})	aV(T+*d*)Z	1.5447	1.4117	95.31	108.07	125.15		110.98 128.97
	exp[g]	1.530	1.405	96.1		124.0		
SF_5 ($^2A_1$, C_{4v})	aV(T+*d*)Z	1.5983 eq		89.95 eq			91.62	
		1.5467 ax		91.62 ax				
SF_4O ($^1A_1$, C_{2v})	aV(T+*d*)Z	1.5475 eq	1.4155	112.50 eq	123.75 eq		83.49	180.0
		1.6046 ax		164.37 ax	97.81 ax		−83.49	
				85.67 eq−ax				
	exp[h]	1.535(4) eq	1.406(3)	114.9(3.4) eq	122.5 eq			
		1.593(4) ax		164.4(6) ax	97.8 ax			
				85.8 eq−ax				
	exp[i]	1.552(4) eq	1.403(3)	110.1(1.8) eq	124.9(9) eq			
		1.575(3) ax		89.6(2) eq−ax	90.6(4) ax			
	exp[j]	1.550 ± 0.003 eq	1.413 ± 0.001	110.01 ± 0.74 eq				
		1.583 ± 0.003 ax		178.35 ± 0.48 ax				
	exp[f]	1.539 ± 0.005 eq	1.422 ± 0.008	122.8 ± 1.8 eq				
		1.602 ± 0.005 ax		182.8 ± 0.7 ax				
SF_5O ($^2B_1$, C_{2v})	aV(T+*d*)Z	1.5785 eq	1.6175	90.1 eq	92.12 eq		87.9	
		1.5699 eq		87.9 eq	88.0 eq		92.0	
		1.5673 ax		92.0 eq	180.0 ax			
SF_6 ($^1A_{1g}$, O_h)	aV(T+*d*)Z	1.5666		90.0 eq				
				180.0 ax				
	exp[k]	1.560722(7)		90.0 eq				
				180.0 ax				

[a] CCSD(T) optimizations on SF and SO, and MP2 optimizations on the SF_xO_y compounds; ax = axial and eq = equatorial. [b] SF and SO, microwave; ref 55. [c] Microwave R_e; ref 62. [d] Microwave, R^0; ref 63. [e] Microwave; ref 64. [f] Electron diffraction; ref 65. [g] Microwave; ref 66. [h] Electron diffraction, structure D; ref 67. Used by Oberhammer and Boggs (Oberhammer, H.; Boggs, J.E. *J. Mol. Spectrosc.* **1979**, *56*, 107) in their computational study. [i] Electron diffraction, structure B; ref 67. [j] Electron diffraction; ref 68. [k] R_0, computed in ref 58 from rotational constant from Patterson et al. (Patterson, C. W.; Herlemont, F.; Azzizi, M.; LeMaire, K. *J. Mol. Spectrosc.* **1984**, *108*, 31). Doppler-free two-photon spectroscopy of the $2\nu_3$ band.

calculations presented in Supporting Information (Table S-3). Most of the stretching frequencies are too low by a few wave numbers due to the fact that the calculated bond distances are slightly too long. The largest discrepancy is found for PFO, with about 30 cm^{-1} difference in the P−O stretch. CCSD(T) calculations with an augmented aVQZ basis set yield values within a few cm^{-1} of experiment.[17] For the S derivatives shown in the Supporting Information (Table S-4), there is overall excellent agreement with experiment for most of the modes.[55,73−81] The largest discrepancy is for the S−O stretch in FSO, but we note that this mode has never been measured and that the "experimental" frequency uses an estimated force constant to fit centrifugal distortion constants.[74] We suggest that our value is substantially more accurate. Overall, the excellent agreement between theory and experiment for the frequencies suggests that our calculated frequencies for the compounds whose frequencies have not been measured should be good to better than 30−40 cm^{-1}. In addition, the anharmonic contributions for the diatomics and for PFO are not large, so we can estimate that our zero-point energies should have an accuracy of ±0.2 kcal/mol.

Calculated Heats of Formation. The contributions to the total dissociation energy are given in Table 4. We first describe some trends in various contributions. For the P derivatives, the agreement between the DTQ and Q5 extrapolations with only F as a substituent is essentially the same within ~0.2 kcal/mol. When one of the substituents is O, the difference grows to as large as ~0.7 kcal/mol for PO, with the Q5 value being larger. This is similar to what was observed in the acid oxides of S. Use of a larger basis set (aug-cc-pV5Z) in the CBS extrapolation improves the agreement with experiment for both H_2SO_4 and

TABLE 4: Components for Calculating the Atomization Energies in kcal/mol[a]

	CBS							D_0(0K)[h]	
molecule	DTQ[b]	Q5[c]	ΔE_{ZPE}	ΔE_{CV}[d]	$\Delta E_{\mathrm{SR-DKH}}$[e]	ΔE_{SR}[f]	ΔE_{SO}[g]	DTQ	Q5
PO	142.36	143.03	1.75[k]	0.51	−0.44	−0.29	0.10[i]	140.93 [140.77]	141.59 [141.44]
PF	108.91	108.81	1.20[k]	0.25	−0.45	−0.34	−0.38	107.23 [107.12]	107.13 [107.02]
PFO	276.10	276.68	3.62[l]	0.67	−0.96	−0.75	−0.60	271.80 [271.60]	272.38 [272.18]
PF_2	230.49	230.28	2.94[l]	0.41		−0.80	−0.76	226.40	226.19
PF_3	365.86	365.51	5.41[l]	0.44	−1.56	−1.37	−1.14	358.38 [358.19]	358.03 [357.84]
PF_2O	354.65	355.06	6.18[l]	0.43		−1.79	−0.98	346.12	346.54
PF_3O	502.06	502.54	9.11[l]	0.55	−3.03	−2.61	−0.92	489.96 [489.55]	490.44 [490.02]
PF_4	424.32		7.56[l]	0.11		−2.45	−1.52	412.90	
PF_5	561.72	561.62	10.70[l]	0.04	−3.79	−3.42	−1.90	545.75 [545.37]	545.64 [545.27]
SF	84.87	84.93	1.20[k]	0.20	−0.40	−0.31	−0.37[j]	83.19 [83.11]	83.24 [83.16]
SO	125.36	126.04	1.64[k]	0.44	−0.47	−0.37	−0.94	123.00 [122.90]	123.68 [123.58]
SF_2	176.99	177.11	2.85[l]	0.30	−0.84	−0.76	−1.32	172.35 [172.27]	172.47 [172.39]
SFO	212.54	213.31	3.66[m]	0.60		−0.83	−1.16	207.48	208.25
SF_3	233.98	234.02	4.56[m]	0.39		−1.05	−1.70	227.06	227.11
SF_2O	309.46	310.33	5.99[l]	0.58	−1.49	−1.46	−1.54	301.05 [301.01]	302.92 [302.89]
SFO_2	302.40	303.93	6.86[m]	0.74		−1.97	−1.39	292.92	294.45
SF_4	333.49	333.71	7.40	0.32	−1.78	−1.81	−2.08	322.52 [322.55]	322.75 [322.77]
SF_3O	332.92	333.68	8.05[m]	0.48		−2.37	−1.92	321.06	321.82
SF_2O_2	413.61	415.38	9.89[l]	0.80	−3.30	−2.99	−1.77	399.76 [399.45]	401.53 [401.23]
SF_5	375.76		9.98[l]	0.10		−3.19	−2.46	360.24	
SF_4O	426.73	427.66	11.24[m]	0.33	−3.83	−3.63	−2.30	409.72 [410.53]	411.65 [411.46]
SF_5O	461.65		13.07	0.13	−4.19		−2.68	431.84	
SF_6	485.57	485.98	13.40[l]	0.03	−4.63	−4.40	−2.84	464.96 [464.74]	465.37 [465.15]

[a] $\Sigma D_0 = \Delta E_{\mathrm{elec}}(\mathrm{CBS}) - \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{SO}}$. [b] Valence electron dissociation energy extrapolated to the CBS limit by using eq 1 with n = D,T,Q. [c] Valence electron dissociation energy extrapolated to the CBS limit by using eq 2 with n = Q, 5. [d] Core/valence corrections were obtained with the cc-pwCVTZ basis sets at the optimized geometries. [e] The scalar relativistic correction is based on the DKH method. [f] The scalar relativistic correction is based on a CISD(FC)/cc-pVTZ MVD calculation. [g] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on Moore's tables (ref 54). [h] The theoretical value of the dissociation energy to atoms ΣD_0(0K). Values in square brackets are determined using the DKH relativistic correction. [i] Includes the spin orbit correction for the diatomic = 0.32 kcal/mol (112 cm^{-1}). [j] Includes the SO stabilization of the molecule (199 cm^{-1}). [k] Zero-point energy obtained from the fifth-order fitting of the PES at the CCSD(T)/aV(Q+*d*)Z geometry. [l] Zero-point energy obtained from the experimental values. [m] Zero point energy obtained from the calculated MP2/aV(T+*d*)Z value.

FSO_3H.[82] Compounds with a second-row atom where there is a large change in oxidation state from the atom in the molecules to the bare atom may require use of very large basis sets to recover the valence correlation energy for the total dissociation energy. The compounds with the largest basis set effect have the largest effective charges on the P, as seen in Table S-6 (Supporting Information), containing both the Mulliken atomic charges and NBO charges from a Natural Bond Orbital (NBO) analysis[83] for the closed-shell PF_xO_y and SF_xO_y molecules calculated at the density functional theory B3LYP/DGDZVP2 level.[84,85] The NBO charges predict the molecules to be more ionic than do the Mulliken charges, consistent with previous observations.[83f] The molecules are all predicted to have significant ionic character with larger negative charges on the O than on the F balanced by a positive charge on P or S. A summary of the NBO results is given in the Supporting Information. There is, of course, some dependence of the NBO charges on the basis set and computational method,[83] but we are simply using these values as qualitative guidelines. The dipole moments calculated at the MP2/aV(T+*d*) level are given as Supporting Information.

For the S derivatives, the same trends in the energy components are observed. When only F is present as a substituent, the difference between the DTQ and Q5 extrapolations is a maximum for SF_6 with a difference of 0.4 kcal/mol. However, for the compounds with O as a substituent, the difference is as large as 1.8 kcal/mol for SF_2O_2, just as found for SO_4H_2. Again, the largest effective charges are on the S with these substituents. For these compounds, the second-row sulfur atom is in a high oxidation state of +6. In terms of the atomization energy, the S atom is in oxidation state 0, and the difference between the two oxidation states requires the use of a very large basis set to recover the valence correlation energy for the total dissociation energy.

The core valence corrections are small, with the largest value being 0.8 kcal/mol for SF_2O_2. The scalar relativistic corrections are substantially larger than the core−valence corrections. The scalar relativistic effects increase with the number of substituents. For the P derivatives, the DKH correction is larger than the MVD correction by up to 0.37 kcal/mol for PF_5. For the S derivatives, the DKH and MVD values are within 0.3 kcal/mol of each other, with the largest difference found for SF_2O_2. The

TABLE 5: Heats of Formation (kcal/mol) at 0 and 298 K[a]

	$\Delta H_f(0K)_{theory}$			$\Delta H_f(298K)_{theory}$		
molecule	DTQ	Q5	$\Delta H_f(0K)_{exp}$	DTQ	Q5	$\Delta H_f(298K)_{exp}$
PO	−6.5 [−6.4]	−7.2 [−7.0]	−5.6 ± 4	−6.8 [−6.6]	−7.4 [−7.3]	−5.6 ± 1
PF	−13.3 [−13.2]	−13.2 [−13.1]	−12.3 ± 5	−13.6 [−13.4]	−13.5 [−13.3]	−12.5 ± 5
PFO	−118.9 [−118.7]	−119.5 [−119.3]		−119.7 [−119.5]	−120.2 [−120.0]	
PF_2	−114.0	−113.8	−116.0 ± 5.0	−114.8	−114.5	−116.6 ± 5.0
PF_3	−227.6 [−227.4]	−227.2 [−227.0]	−227.7 ± 0.9	−228.9 [−228.7]	−228.5 [−228.3]	−229.0 ± 0.9
PF_2O	−174.8	−175.2		−176.2	−176.6	
PF_3O	−300.1 [−299.7]	−300.6 [−300.2]	−297.7 ± 1.9	−302.2 [−301.8]	−302.7 [−302.3]	−299.6 ± 1.9
PF_4	−263.6			−265.4		
PF_5	−378.0 [−377.6]	−377.9 [−377.5]	−378.5 ± 0.7	−380.5 [−380.2]	−380.4 [−380.1]	−380.9 ± 0.7
SF	0.9 [1.0]	0.9 [1.0]	2.9 ± 1.5	1.0 [1.0]	0.9 [1.0]	3.1 ± 1.5
SO	1.6 [1.7]	1.0 [1.1]	1.2 ± 0.3	1.6 [1.7]	1.0 [1.1]	1.2 ± 0.3
SF_2	−69.7 [−69.7]	−69.9 [−69.8]	−70.4 ± 4.0	−70.2 [−70.1]	−70.3 [−70.3]	−70.9 ± 4.0
SFO	−64.4	−65.1		−64.9	−65.6	
SF_3	−106.0	−106.0	−119.3 ± 8.0	−106.9	−106.9	−120.2 ± 8.0
SF_2O	−139.5 [−139.4]	−140.3 [−140.3]	−129 ± 25	−140.6 [−140.6]	−141.5 [−141.5]	−130 ± 25
SFO_2	−90.8	−92.3		−92.1	−93.6	
SF_4	−183.0 [−183.0]	−183.2 [−183.2]	−180.9 ± 5.0	−184.7 [−184.7]	−184.9 [−184.9]	−182.3 ± 5.0
SF_3O	−141.0	−141.8		−142.7	−143.4	
SF_2O_2	−179.2 [−178.9]	−181.0 [180.6]	−179.3 ± 2.0	−181.2 [−180.9]	−182.9 [−182.6]	−181.2 ± 2.0
SF_5	−202.2		−214.7 ± 3.6 −207.9 ± 2.7[b]	−204.6		−217.0 ± 3.6 −210.2 ± 2.7[b]
SF_4O	−212.2 [−212.0]	−213.1 [−212.9]		−214.7 [−214.5]	−215.6 [−215.4]	
SF_5O	−214.8			−218.0		
SF_6	−288.5 [−288.3]	−288.9 [−288.7]	−288.4 ± 0.2	−291.8 [−291.6]	−292.2 [−292.0]	−291.6 ± 0.2

[a] Values in square brackets use the DKH method for the scalar relativistic correction. Experimental data from ref 14. [b] Reference 29.

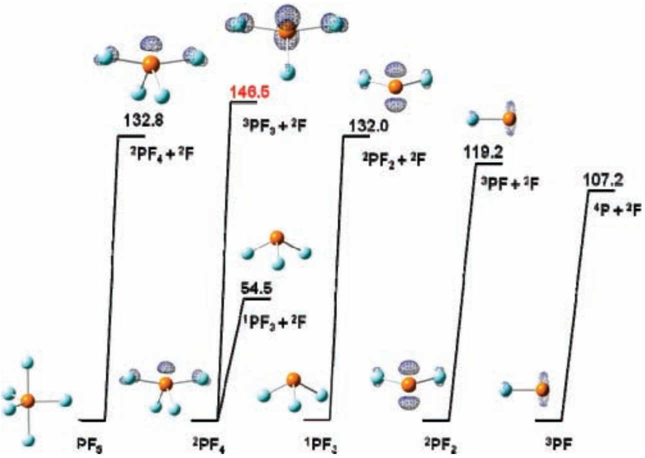

Figure 1. Adiabatic and diabatic BDEs for PF_x in kcal/mol. Unique diabatic BDEs are in red. Spin density contour level = 0.05 au in radicals, except for PF_2, with a contour level of 0.035 au. Orange = P, blue-green = F, red = O, and yellow = S. Contour levels obtained with density functional theory at the B3LYP/DZVP2 level.

fact that the DKH corrections are in general more negative than the CI−SD MVD corrections is consistent with previously observed differences.[82,86] The large values for ΔE_{SR} are consistent with the large change in the character of the P or S atom going from the free atom to the nominal +5/+6 charge on that atom in PF_3O or SF_2O_2.

The heats of formation (Table 5) of the diatomics are in good agreement with the experimental values,[14] and our values are expected to provide lower error limits. The heats of formation of PF_3 and PF_5 are in good agreement with the experimental values.[14] The value for PF_3 is more positive than the experimental value, as expected, and within the error bars. For PF_5, the calculated value is 1 kcal/mol higher than the experimental value and just outside the experimental error limits. The calculated heat of formation of PF_2 is within the experimental error limits,[14] and our value is more precise with an estimated error limit of ±1 kcal/mol. For PF_3O, our calculated value is more negative than the experimental value[14] and just outside the experimental error limits. For H_2SO_4, the calculated value[82] was above the experimental value, suggesting that our analysis of the experimental value for PF_3O is correct. This suggests that the value for PF_3O needs to be revised downward. The good agreement that we find for our calculated values with experiment for the P derivatives and our own assessment of the errors in the calculations lead us to estimate error bars of ±1 kcal/mol for the calculated heats of formation. The G2 method underestimates the heats of formation of PF_3 and PF_5 by 5−6 kcal/mol, whereas G2MP2 and G2M(CC5) methods show best agreement compared to experiment for the entire series.[20]

The heat of formation of SO is in excellent agreement with the experimental[55] and other high-level theoretical values.[40,56] The result for $\Delta H_f(SF_6)$ is in excellent agreement with the highly accurate experimental value.[14] The calculated values for the heats of formation of SF_2 and SF_4 are within the quite large experimental error limits,[14] and our values should be more reliable. For the SF_3 and SF_5 radicals, our calculated values differ from the best experimental values[14] by more than the error bars. However, the experimental values are not very reliable and our calculated values should be more reliable. The best experimental value for the heat of formation of SF_5 comes from an analysis of a number of experiments for the bond dissociation energy for SF_6 and is −210.2 ± 2.7 kcal/mol at 298 K[29] in comparison to our value of −204.6 kcal/mol, which should be good to ±1 kcal/mol. The heat of formation of SF_3 is predicted to be −107.0, which is above the experimental value[14] of −120 ± 8 kcal/mol. The heat of formation of SF_2O is within the very large experimental error limits,[14] and our value should be much better.

Bond Dissociation Energies. The BDEs are given in Table 1, where they are compared to experiment. The BDEs for a given central atom are compared to each other in Figures 1 and 3 for the perfluorocompounds and in Figures 2, 4, and 5 for the oxofluorides. For consistency, the BDEs in the figures are from the CCS(DTQ) values with eq 1.

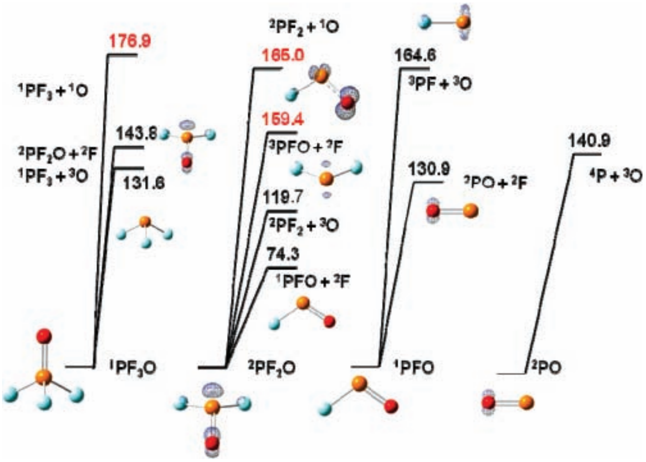

Figure 2. Adiabatic and diabatic BDEs for PF_xO in kcal/mol. See Figure 1 caption.

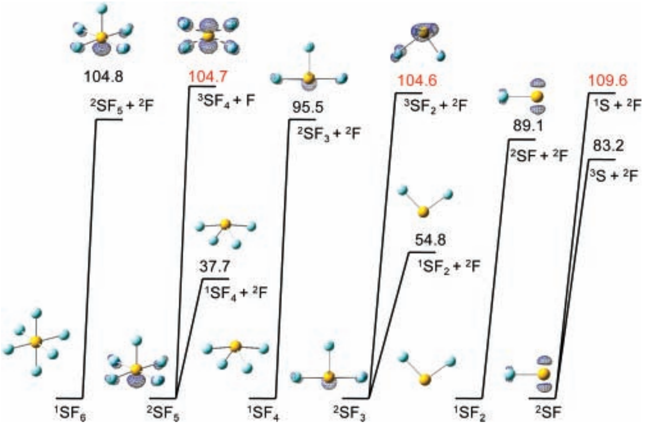

Figure 3. Adiabatic and diabatic BDEs for SF_x in kcal/mol. See Figure 1 caption.

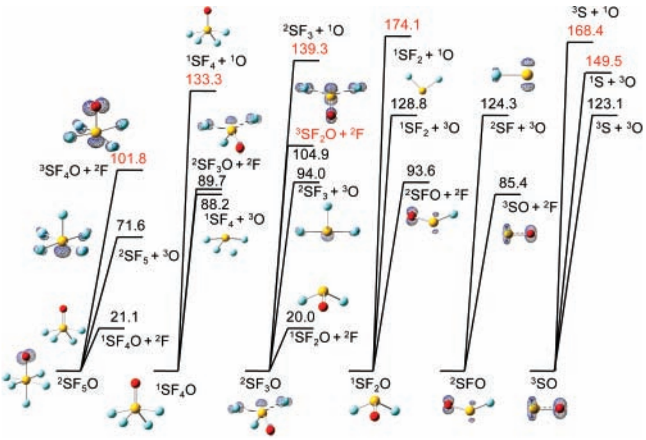

Figure 4. Adiabatic and diabatic BDEs for SF_xO in kcal/mol. See Figure 1 caption.

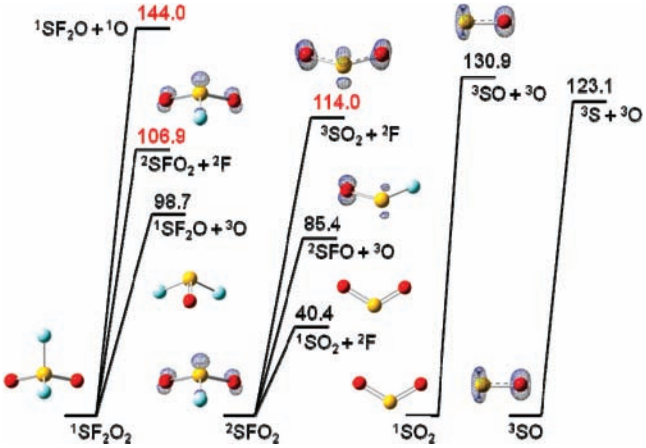

Figure 5. Adiabatic and diabatic BDEs for SF_xO_2 in kcal/mol. See Figure 1 caption.

The value for $D_0{}^0$(PO) from the JANAF tables[14] is 140.7 ± 1 kcal/mol and from Huber and Herzberg[55] is 141.1 8 kcal/mol. Our value of 141.4 kcal/mol is in excellent agreement with both. The reaction for the adiabatic BDE of PO, PO($^2\Pi$) → P(^{4}S) + O(^{3}P), is the same as the diabatic BDE; i.e., two of the unpaired electrons on the P can bond with the two unpaired electrons on the O, leaving an extra unpaired electron on P. The ^{2}PO molecule cannot correlate on the same spin surface with the singlet excited-state of O and ^{4}P. The bond dissociation energy for PF has been estimated to be 4.60 ± 0.2 eV (106 ± 5 kcal/mol).[14] Our best calculated value of 107.0 kcal/mol is in excellent agreement with this value. The reaction for the adiabatic BDE of PF, PF($^3\Sigma^-$) → P(^{4}S) + F(^{2}P), is the same as the diabatic BDE.

For SF, the heat of formation was measured from Knudsen cell mass spectrometry experiments,[14] and a bond energy of 81.2 ± 2.0 kcal/mol can be derived, in excellent agreement with our best value of 83.0 kcal/mol. Our best calculated value for the total dissociation energy of SO is 123.7 kcal/mol, in excellent agreement with the experimental value of 123.58 kcal/mol.[55] Our extrapolated CBS(Q5) value for the valence correlation energy is in excellent agreement with Martin's best estimated value[56] of 126.03 kcal/mol obtained with a somewhat different basis sets for the tight *d* functions and differs by 0.4 kcal/mol from the extrapolated value of 125.62 kcal/mol obtained by Dunning et al.[40] at the RCCSD(T) level using the aug-cc-pV-(n+*d*)Z basis sets up through $n = 6$. If ^{2}SF correlates with S(^{1}D), then the S−F diabatic BDE would be 109.6 kcal/mol using a singlet−triplet splitting in S of 26.4 kcal/mol.[54] If ^{3}SO correlates with the excited singlet state of O and ground state ^{3}S, the diabatic BDE would be 168.4 kcal/mol using the singlet−triplet splitting in O (45.3 kcal/mol).[54] If ^{3}SO correlates with ^{1}S and ^{3}O, then the diabetic BDE would be 149.5 kcal/mol.

The best experimental value for the first bond dissociation energy for SF_6 from the analysis of a number of experiments is a value of 100.4 ± 2.4 kcal/mol at 298 K.[29] Our calculated value is 106.8 kcal/mol, somewhat larger than this value, and our value should be good to ±1 kcal/mol. Our value confirms the conclusions of Tsang and Herron[29] that the value of the SF_5−F BDE is higher than that determined by Zare and co-workers[26,27] and that the reaction of Sr + SF_5 → SrF + SF_4 may play a role. Our predicted value for the exothermicity of this reaction is −89.9 ± 4 kcal/mol at 298 K (using experimental values[14] for the heats of formation of Sr and SrF), consistent with the maximum observed in the chemiluminescence corresponding to 87.2 kcal/mol.

Our calculated heats of formation enable us to calculate a wide range of BDEs. All possible P−F and P−O BDEs are given in Table 1 and are compared graphically in Figures 1 and 2. The first P−F adiabatic BDEs of all the binary phosphorus fluorides are all quite strong, except for that of PF_4, which is much lower due to the relative instability of the PF_4 radical and the stability of the product PF_3. For PF_5, PF_3, PF_2, and PF, the adiabatic and diabatic BDEs are the same. The adiabatic P−F BDE for $^2PF_4$ produces $^1PF_3$ and F(^{2}P). In order to compare the BDEs, it may be more appropriate to consider the diabatic BDE with the formation of $^3PF_3$, where there are

TABLE 6: Electronic Contribution to the CCSD(T) Singlet−Triplet Splitting (kcal/mol) for SF_xO_y and PF_xO_y Compounds

molecule	aV(D+*d*)Z	aV(T+*d*)Z	aV(Q+*d*)Z	CBS	CBS + ZPE[a]
PFO	79.3	83.5	85.1	86.0	85.1
PF_3	88.4	90.4	91.7	92.5	92.0
SF_2	44.8	48.5	49.5	50.1	49.8
SF_2O	78.0	84.0	85.1	85.6	84.9
SF_4	61.0	65.9	66.9	67.4	67.0
SF_4O	67.6	78.4	81.0	82.3	80.7

[a] ZPE for singlets in Table 4. ZPE for triplets from MP2/aV(T+*d*)Z calculations.

two unpaired electrons, one from the unpaired electron on PF_4 and one from the P−F bond that was broken (see Figure 1). Addition of the singlet−triplet splitting in PF_3 obtained at the CCSD(T)/CBS//MP2/aVTZ level (Table 6) (an estimate of the reorganization energy) gives 146.5 kcal/mol, which is more in line with the other P−F BDEs. The reorganization energy in this case is the pairing of the two electrons to form the lone pair on PF_3 (see the spin density in Figure 1). The P−F bonds in PF_5 and PF_3 are comparable to the first C−F BDE in CF_4 (129.6 ± 1.0) and are slightly lower than the first Si−F BDE in SiF_4.[15]

The first PF adiabatic BDE in PF_3O is higher than the adiabatic BDE for the P−O bond, because the POF_2 radical is energetically less stable than the closed-shell PF_3 molecule. Note that the adiabatic P−O BDE is defined by the reaction $^1POF_3 \rightarrow {}^1PF_3 + O(^3P)$ (Figure 2). The situation is reversed when the diabatic BDE for O is considered on the singlet surface for the reaction $^1POF_3 \rightarrow {}^1PF_3 + O(^1D)$. Addition of the singlet−triplet splitting in O (45.3 kcal/mol)[54] to the P−O adiabatic BDE yields a diabatic BDE of 176.9 kcal/mol [CBS(DTQ)], consistent with the differences in the bond distances and force constants at the minimum in PF_3O. The adiabatic P−F BDE in PF_2O is about half that in PF_3O, whereas the P−O BDE is only 12 kcal/mol lower than that in PF_3O, again reflecting the different stabilities of the reactants and products. Use of the singlet−triplet splitting in FPO (Table 6) leads to a diabatic P−F bond energy of 159.4 kcal/mol. This is probably not the best model for the P−F diabatic BDE, because much of the spin is on the O. One can also correlate the P−O bond in PF_2O with the singlet excited state of O. This yields a diabatic P−O BDE of 165.0 kcal/mol, very similar to the adiabatic value in PFO and PF_3O. We note that the spin density in PF_2O is not fully localized on the P, as there is some on the O atom. The adiabatic P−O BDE in PFO is ∼24 kcal/mol higher than in PO and ∼33 kcal/mol higher than the adiabatic P−O BDE in PF_3O. The adiabatic P−O BDE in PFO correlates with the products PF ($^3\Sigma^-$) + F(^{2}P) as does the diabatic value. The PFO molecule cannot correlate on the same spin surface with the singlet excited state of O and ^{3}PF. Thus, it may be more appropriate to compare the diabatic P−O BDE in PF_3O with that in PFO, and the diabatic BDE in the latter is then lower than that in the former. The P−F BDE in PFO is comparable to the first BDE in PF_3 or PF_5, consistent with the result that the adiabatic and diabatic asymptotes are the same in these molecules.

On average, S−F bonds are weaker than P−F bonds, which results in lower BDEs. The adiabatic S−F BDE in SF_6 is the highest adiabatic BDE for the SF_x compounds, as expected from the exceptional stability of octahedral closed-shell SF_6 and the relative instability of the SF_5 radical. Similarly, the closed-shell SF_4 and SF_2 molecules exhibit much larger adiabatic BDEs than do the SF_5 and SF_3 radicals. In these cases, the adiabatic and diabatic BDEs for the closed-shell species are the same as they dissociate to a doublet SF_x radical and F(^{2}P). For the radical SF_x species, the first S−F adiabatic BDEs increase in the opposite order with SF_5 having the lowest adiabatic BDE (38 kcal/mol) and S−F the highest. The adiabatic BDEs of the doublet SF_x radicals correlate with a closed-shell singlet species and F(^{2}P). As for the BDE in $^2PF_4$, it is more appropriate to compare the diabatic BDEs where $^3SF_4$ and $^3SF_2$ are formed from $^2SF_5$ and $^2SF_3$ (Figure 3). Use of the singlet−triplet splittings in SF_4 and SF_2 (Table 6) yields respective diabatic S−F BDEs for SF_5 and SF_3 of 104.7 and 104.6 kcal/mol, consistent with the adiabatic S−F BDEs of the closed-shell molecules and essentially the same as that in SF_6. These results are consistent with the inherent instability of the sulfur radicals as compared to the closed-shell species and show the reorganization of electron density that occurs on spin pairing to form the lone pairs in SF_4 and SF_2.

By analogy with PF_3O, the S−F and S═O adiabatic BDEs in SF_4O are similar (Figure 4). This contrasts with the BDEs in the diatomics, where the S═O double bond is much stronger [123.1 kcal/mol, CBS(DTQ)] than the S−F single bond [83.2 kcal/mol, CBS(DTQ)]. The similarity of the S−F and S═O adiabatic BDEs in SF_4O is due to the fact that oxygen loss results in the energetically favored closed-shell SF_4 molecule, whereas fluorine loss produces an unstable SF_3O radical. If we perform the same correlation with O(^{1}D) as done for PF_3O, the diabatic S−O BDE on the singlet surface for SF_4O is 133.3 kcal/mol, substantially higher than the adiabatic value and more consistent with the diatomic BDE (Figure 4). This is representative of the BDE of an S═O double bond and is consistent with the geometry and the S−O stretching force constants. The S−O BDE in SF_2O is substantially larger than the S−F bond, even though the stable SF_2 molecule is being formed for the former as compared to the SFO radical for the latter. The diabatic value for the S−O BDE in SF_2O correlating to O(^{1}D) + $^1SF_2O$ is even higher, 174.1 kcal/mol, and comparable to the diabatic BDE for SO correlating with ^{1}O and ^{3}S. The adiabatic S−O BDE in SF_2O is comparable to that for diatomic SO.

The S−O adiabatic BDE in SF_5O is much lower (71.6 kcal/mol) than the S−O adiabatic BDE in SF_4O, consistent with an S−O single bond, as would be expected from the simplest description of the structure with the unpaired electron on the O (Figure 4). For SF_5O, the adiabatic and diabatic limits [$^2SF_5$ + O(^{3}P)] are the same on the basis of the spin density. The adiabatic S−O BDE in the radical SF_3O is 94 kcal/mol and is larger than the adiabatic S−O BDE in SF_5O. The adiabatic S−O BDE in SF_3O is similar to the adiabatic BDEs in SF_2O_2 (see below) and in SF_4O. The spin density in SF_3O shows little excess on O, so it may have some double-bond character. In this case, the diabatic S−O BDE arising from $^2SF_3$ + ^{1}O is 139.3 kcal/mol, very similar to the diabatic SO BDE in SF_4O of SF_2O_2.

As for PF_xO, the loss of a fluorine atom from a closed-shell SF_xO molecule to give a radical results in a large adiabatic BDE, whereas the loss of a fluorine atom from a radical to give a stable closed-shell molecule gives rise to a much smaller adiabatic BDE. The first adiabatic S−F BDE in the radical SF_5O is very low, 21 kcal/mol. If we consider the diabatic S−F BDE in SF_5O to form $^3SF_4O$ + F(^{2}P), we obtain a value of 101.8 kcal/mol using the singlet−triplet splitting (Table 6 and Figure 4). The S−F diabatic BDE is higher than the adiabatic S−O single BDE, as expected. The adiabatic S−F BDE in the radical SF_3O is also small, 20 kcal/mol. The diabatic S−F BDE in SF_3O correlates with $^3SF_2O$ + F(^{2}P) and is 104.9 kcal/mol with the singlet−triplet splitting from Table 6. Thus, the diabatic S−F

BDEs in SF_3O and SF_5O are comparable to the diabatic S−F BDEs for SF_3 and SF_5 and the adiabatic BDEs of the closed-shell SF_x and SF_xO compounds.

The adiabatic S−F BDE in SF_2O_2 is larger than the adiabatic S−O BDE by ~8 kcal/mol, again reflecting the stability of the radicals. If we consider the diabatic BDE for the S−O bond correlating with $O(^1D) + {}^1SF_2O$, we obtain a value of 144.0 kcal/mol (Figure 5), slightly higher than the diabatic value in SF_4O and again consistent with the geometry and force constants. The adiabatic S−O BDE in SFO_2 is 85.4 kcal/mol and is in the range of an S−O single bond, consistent with the spin distribution and the S−O single bond values given above. The adiabatic S−O BDE in SO_2 is consistent with the other S═O BDEs. Note that, in SO_2, the excited state of O or SO is not appropriate for use in the diabatic BDE calculation, as the reaction no longer occurs on a single spin state and we do not want to include two excited states in the calculation.

The adiabatic S−F BDE in SFO_2 is relatively low, 40 kcal/mol, but is higher than the adiabatic S−F bond in SF_3O. This BDE was evaluated using the experimental heat of formation of SO_2 at 0 K [$\Delta H_f(SO_2) = -70.34 \pm 0.05$ kcal/mol].[14] Extensive calculations on SO_2 show that it is possible to calculate the heat of formation reliably by using the above approaches as long as tight d functions are included.[56,57] The diabatic value for the S−F BDE in FSO_2 correlating with $SO_2(^3B_1) + F(^2P)$ is 114.0 kcal/mol using the experimental singlet−triplet splitting[87] of 73.6 kcal/mol in SO_2. The adiabatic S−O BDE in SFO_2 is much larger than the adiabatic S−F BDE and is comparable to the adiabatic S−O BDE in SF_4O.

The various bond energies provide insights into the stability of the various species. The nonradical species are very stable with large adiabatic BDEs, and the radicals tend to be less stable with smaller adiabatic BDEs. There is a difference in the effective stability between the radicals with P and S as the central atom. For the PF_n series, PF_4 has the lowest adiabatic P−F BDE, 54 kcal/mol. For PF_2O, the adiabatic P−F BDE is smaller than the P−O BDE, but the radical is still quite stable with respect to bond breaking with a P−F bond energy of 74 kcal/mol. In the SF_n series, the S−F adiabatic BDE is the lowest in SF_5, 38 kcal/mol. The adiabatic S−F BDEs in SF_5O and SF_3O are small, ~20 kcal/mol, showing that these radicals will be highly reactive with respect to loss of an F atom. The S−O BDEs are much larger in the S radicals, just as found for the P radicals. The fact the SF_xO radicals are less stable with respect to breaking an S−F bond as compared to breaking a P−F bond in the PF_xO radicals is consistent with the fact that overall the P−F BDEs are larger than the S−F BDEs.

Conclusions

The heats of formation at 0 and 298 K are predicted for PF_3, PF_5, PF_3O, SF_2, SF_4, SF_6, SF_2O, SF_2O_2, and SF_4O as well as a number of radicals derived from these stable compounds on the basis of coupled cluster theory [CCSD(T)] calculations extrapolated to the complete basis set limit. The calculated values should be good to ±1 kcal/mol. The calculated heats of formation are in excellent agreement with the available experimental data for the closed-shell molecules. The calculated values allow us to predict the adiabatic bond dissociation energies for all of the compounds to within ±1 kcal/mol, dramatically improving the estimates of these important quantities, particularly for the radicals.

The calculated BDEs provide important insight into the reactivity of these molecules. For example, the adiabatic BDEs in the closed-shell phosphorus fluorides are quite high, 130−140 kcal/mol. In PF_3O, the P═O bond is more easily broken than the P−F bond, a surprising result, but in the PF_2O radical and the closed-shell PFO molecule, the situation is reversed.

The first S−F adiabatic BDEs are predicted to be substantially smaller than those of the P−F bonds with the largest first S−F BDE being 105 kcal/mol in SF_6. The calculated value for the S−F bond dissociation energy in SF_6 is about 6 kcal/mol higher than the most recent value based on analyzing a range of experiments and substantially higher than earlier estimates by up to 30 kcal/mol. Thus, SF_5 is predicted to be a less stable radical than previously thought, and the calculated S−F BDE in SF_5 is substantially lower than the estimated experimental values. Similarly, the S−F bond dissociation energy in SF_4 is higher than the experimental estimates, and the SF_3 radical is less stable than previously thought. The calculated values for the bond dissociation energies in SF_2 and SF are in good agreement with the experimental estimates. The S−O BDE is stronger than the first S−F BDE in SF_2O, weaker than the first S−F BDE in SF_2O_2, and comparable to the first S−F BDE in SF_4O.

The results in combination with singlet−triplet splittings enable us to compare the adiabatic and diabatic BDEs. In diatomics, the BDE is a direct measure for the bond strength, and frequently, the same assumption is applied incorrectly to polyatomic species for which reorganization energies in the product are important. Therefore, for polyatomic species, adiabatic bond dissociation energies and bond strengths are not the same, and a clear distinction must be made between the two. The measurement of the strength or stiffness of a given bond involves only a small displacement of its atoms and no reorganization of the molecule. Appropriate criteria for judging the bond strength include the curvature of the bond energy plots, bond lengths, vibrational frequencies, force constants, bond orders, etc., and it is these that form the basis for writing representative valence bond structures for polyatomic molecules in their ground states. The differences between the adiabatic and diabatic BDEs, which are related to the reorganization energy in the products, can be estimated in the molecules under study from singlet−triplet splittings. The reorganization energies can account for the large fluctuations in adiabatic BDEs observed during the stepwise loss of fluorine atoms. In contrast, the diabatic BDEs of a given type are often very similar in size to each other and thus exhibit more regular trends.

Acknowledgment. This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE) under Grant No. DE-FG02-03ER15481 (catalysis center program) and the National Science Foundation under Grant No. CHE-0456343. D.A.D. also thanks the Robert Ramsay Chair Fund of The University of Alabama for support. Part of this work was performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, operated for the DOE by Battelle. K.O.C. also thanks the Air Force Office of Scientific Research and the Office of Naval Research for financial support.

Supporting Information Available: Total CCSD(T) energies, CBS energies (in hartrees) (Table S-1); CCSD(T)/aV(D+*d*)Z geometry parameters for the PF_xO_y compounds (Table S-2); calculated MP2/aug-cc-pV(T+*d*)Z frequencies (cm^{-1}) for the PF_xO_y compounds (Table S-3); calculated MP2/aug-cc-pV(T+*d*)Z frequencies (cm^{-1}) for the SF_xO_y compounds (Table

S-4); T_1 diagnostics for PF_xO_y and SF_xO_y compounds (Table S-5); and Mulliken and natural charges (Table S-6) and natural bond orbital analysis (Table S-7) for closed-shell PF_xO_y and SF_xO_y compounds. Summary of NBO analysis. Dipole moments at the MP2/aV(T+*d*)Z level (Table S-8). Total CCSD(T) energies, CBS energies (in hartrees) for triplets (Table S-9); MP2/aV(D+*d*)Z geometry parameters for the triplets (Table S-10); calculated MP2/aug-cc-pV(T+*d*)Z frequencies (cm^{-1}) for the triplets (Table S-11); and, T_1 diagnostics for the triplets (Table S-12). Spin densities for the triplets (Figure S-1); spin densities for the PF_xO doublets (Figure S-2); spin densities for the SF_xO_y doublets (Figure S-3). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984.

(2) (a) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 6750. (b) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282.

(3) (a) Carter, E. A.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1988**, *110*, 4077. (b) Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* **1986**, *90*, 998.

(4) Grant, D. J.; Dixon, D. A. *J. Phys. Chem.* **2006**, *110*, 12955.

(5) Dunning, T. H., Jr. *J. Phys. Chem*. **2000**, *104*, 9062.

(6) (a) Peterson, K. A.; Xantheas, S. S.; Dixon, D. A.; Dunning, T. H., Jr. *J. Phys. Chem. A* **1998**, *102*, 2449. (b) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1998**, *108*, 154. (c) Dixon, D. A.; Feller, D. *J. Phys. Chem. A* **1998**, *102*, 8209. (d) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1999**, *110*, 8384. (e) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 6413. (f) Feller, D. *J. Chem. Phys.* **1999**, *111*, 4373. (g) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2000**, *104*, 3048. (h) Feller, D.; Sordo, J. A. *J. Chem. Phys.* **2000**, *113*, 485. (i) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484. (j) Dixon, D. A.; Feller, D.; Sandrone, G. *J. Phys. Chem. A* **1999**, *103*, 4744. (k) Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727. (l) Feller, D.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem. A* **1998**, *102*, 7053. (m) Dixon, D. A.; Feller, D.; Peterson, K. A. *J. Chem. Phys*. **2001**, *115*, 2576. (n) Pollack, L.; Windus, T. L.; de Jong, W. A.; Dixon, D. A. *J. Phys. Chem. A* **2005**, *109*, 6934.

(7) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(8) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(9) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(10) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(11) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(12) McQuarrie, D. A. *Statistical Mechanics*, University Science Books: Sausalito, CA, 2001.

(13) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(14) Chase, M. W., *Jr. NIST-JANAF Thermochemical Tables*, 4th ed.; Journal of Physical Chemistry Reference Data Monograph 9; American Institute of Physics: Woodbury, NY, 1998; Suppl. 1. See also Linstrom, P. J.; Mallard, W. G., Eds. *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, June 2005, National Institute of Standards and Technology: Gaithersburg MD (http://webbook.nist.gov/chemistry/).

(15) Luo, T.-R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007.

(16) Ahlrichs, R.; Becherer, R.; Binnewies, M.; Borrmann, H.; Lakenbrink, M.; Schunck, S.; Schnöckel, H. *J. Am. Chem. Soc.* **1986**, *108*, 7905.

(17) Beckers, H.; Bürger, H.; Paplewski, P.; Bogey, M.; Demaison, J.; Dréan, P.; Walters, A.; Breidung, J.; Thiel, W. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4247.

(18) Gustev, G. L. *J. Chem. Phys.* **1993**, *98*, 444.

(19) Tschumper, G. S.; Fermann, J. T.; Schaefer, H. F., III. *J. Chem. Phys.* **104**, *10*, 3676.

(20) Gu, J.; Leszczynski, J. *J. Phys. Chem. A* **1999**, *103*, 7856.

(21) Bott, J. F.; Jacobs, T. A. *J. Chem. Phys.* **1969**, *50*, 3850.

(22) Harland, P. W.; Thynne, J. C. J. *J. Phys. Chem.* **1971**, *75*, 3517.

(23) Hildebrand, D. L. *J. Phys. Chem.* **1973**, *77*, 897.

(24) Lyman, J. L. *J. Chem. Phys.* **1977**, *67*, 1868.

(25) Benson, S. W. *J. Am. Chem. Soc*. **1978**, *78*, 23.

(26) Kiang, T.; Estler, R. C.; Zare, R. N. *J. Chem. Phys.* **1979**, *70*, 5925.

(27) Kiang, T.; Zare, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 4024.

(28) Babcock, L. M.; Streit, G. E. *J. Chem. Phys.* **1981**, *74*, 5700.

(29) Tsang, W.; Herron, J. T. *J. Chem. Phys.* **1992**, *96*, 4272.

(30) Fisher, E. R.; Kickel, B. L.; Armentrout, P. B. *J. Chem. Phys.* **1992**, *97*, 4859.

(31) Stevens-Miller, A. E.; Miller, T. M.; Viggiano, A. A.; Morris, R. A.; Van, Doren, J. M.; Arnold, S. T.; Paulson, J. F. *J. Chem. Phys.* **1995**, *102*, 8865.

(32) Endo, Y.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1981**, *74*, 1568.

(33) Kronberg, M.; von Ahsen, S.; Willner, H.; Francisco, J. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 253.

(34) Ziegler, T.; Gustev, G. L. *J. Chem. Phys.* **1992**, *96*, 7623.

(35) Irikura, K. K. *J. Chem. Phys.* **1995**, *102*, 5357.

(36) Cheung, Y.-S.; Chen, Y.-J.; Ng, C. Y.; Chiu, S.-W.; Li, W.-K. *J. Am. Chem. Soc.* **1995**, *117*, 9725.

(37) King, R. A.; Galbraith, J. M.; Schaefer, H. F., III. *J. Phys. Chem.* **1996**, *100*, 6061.

(38) Bauschlicher, C. W., Jr.; Ricca, A. *J. Phys. Chem.* **1998**, *102*, 4722.

(39) Miller, T. M.; Arnold, S. T.; Viggiano, A. A. *Inter. J. Mass. Spec.* **2003**, *227*, 413.

(40) Dunning, T. H., Jr.; Peterson, K. A., Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.

(41) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R. M.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. MOLPRO-2002, a package of initio programs; Universität Stüttgart, Stüttgart, Germany, University of Birmingham, Birmingham, United Kingdom, 2002.

(42) Rittby, M.; Bartlett, R. J. *J. Phys. Chem*. **1988**, *92*, 3033.

(43) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys*. **1994**, *99*, 5219.

(44) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett*. **1994**, *227*, 321.

(45) 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.; Bakken, V.; 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 C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(46) Dunham, J. L. *Phys. Rev.* **1932**, *41*, 721.

(47) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.

(48) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F., III. *Theor. Chim. Acta* **1989**, *75*, 81.

(49) (a) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(50) Davidson, E. R.; Ishikawa, Y.; Malli, G. L. *Chem. Phys. Lett*. **1981**, *84*, 226.

(51) (a) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89−155. (b) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756−763. (c) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742−3748.

(52) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48.

(53) EMSL basis set library. http://www.emsl.pnl.gov/forms/basisform-.html.

(54) Moore, C. E. *Atomic Energy Levels*; U.S. National Bureau of Standards Circular: Washington, DC, 1949; p 467.

(55) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold Co.: New York, 1979.

(56) (a) Martin, J. M. L.; Uzan, O. *Chem. Phys. Lett.* **1998**, *282*, 16. (b) Martin, J. M. L. *J. Chem. Phys.* **1998**, *108*, 2791.

(57) (a) Bauschlicher, C. W., Jr.; Partridge, H. *Chem. Phys. Lett.* **1995**, *240*, 533. (b) Bauschlicher, C. W., Jr.; Ricca, A. *J. Phys. Chem.* **1998**, *102*, 8044.

(58) Kuchitsu, K. Ed. *Structure of Free Polyatomic Molecules*—Basic Data; Springer: Berlin, 1998.

(59) Hellwege, K. H.; Hellwege, A. M.; Eds. *Landolt-Bornstein: Group II: Atomic and Molecular Physics Volume 7: Structure Data of Free Polyatomic Molecules*; Springer-Verlag: Berlin, 1976. Moritani, T.; Kuchitsu, K.; Morino, Y. *Inorg. Chem*. **1971**, *10*, 344.

(60) (a) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsey, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J.*

Phys. Chem. Ref. Data **1979**, *8*, 619. (b) Kagann, R. H.; Ozier, I.; Gerry, M. C. L. *Chem. Phys. Lett.* **1977**, *47*, 572. (c) Smith, J. G. *Mol. Phys.* **1976**, *32*, 621.

(61) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B., *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere Pub. Co.: New York, 1989.

(62) Endo, Y.; Saito, S.; Hirota, E.; Chikaraishi, T. *J. Mol. Spectrosc.* **1979**, *77*, 222.

(63) (a) Ferguson, R. C. *J. Am. Chem. Soc.* **1954**, *76*, 850. (b) Lucas, N. J. D.; Smith, J. G. *J. Mol. Spectrosc.* **1972**, *43*, 327.

(64) Tolles, W. M.; Gwinn, W. D. *J. Chem. Phys.* **1962**, *36*, 1119.

(65) Kimura, K.; Bauer, S. H. *J. Chem. Phys.* **1963**, *39*, 3172.

(66) Lide, D. R.; Mann, D. E.; Fristom, R. M. *J. Chem. Phys.* **1957**, *26*, 734.

(67) Gundersen, G.; Hedberg, K. *J. Chem. Phys*. **1969**, *51*, 2500.

(68) Hencher, J. L.; Cruickshank, D. W. J.; Bauer, S. H. *J. Chem. Phys*. **1968**, *48*, 518.

(69) Zhao, Y.; Setser, D. W. *Chem. Phys. Lett*. **1993**, *210*, 362.

(70) Saito, S.; Endo, Y.; Hirota, E. *J. Chem. Phys*. **1986**, *85*, 1778.

(71) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated Volume I*, NSRDS-NBS 39; National Bureau of Standards: Washington, DC, 1972.

(72) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1977**, *6*, 993.

(73) Haas, A.; Willner, H. *Spectrochim. Acta* **1978**, *34A*, 541.

(74) Endo, Y.; Saito, S.; Hirota, E. *J. Chem. Phys.* **1981**, *74*, 1568.

(75) Hassanzadeh, P.; Andrews, L. *J. Phys. Chem.* **1992**, *96*, 79.

(76) Christe, K. O.; Willner, H.; Sawodny, W. *Spectrochim. Acta, Part A* **1979**, *35A*, 1347.

(77) Sawodny, W.; Birk, K.; Fogarasi, G.; Christe, K. O. *Z. Naturforsch., B* **1980**, *358*, 1137.

(78) Kronberg, M.; von Ahsen, S.; Willner, H.; Francisco, J. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 253.

(79) Christe, K. O.; Schack, C. J.; Curtis, E. C. *Spectrochim. Acta, Part A* **1977**, *33A*, 323.

(80) Christe, K. O.; Dixon, D. A.; Goldberg, I. B.; Schack, C. J.; Walther, B. W.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1993**, *115*, 1129.

(81) McDowell, R. S.; Aldridge, J. P.; Holland, R. F. *J. Phys. Chem.* **1976**, *80*, 1203.

(82) Gutowski, K. E.; Dixon, D. A. *J. Phys. Chem. A* **2006**, *110*, 12044.

(83) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (d) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (e) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736.(f) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: New York, 2003.

(84) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(85) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

(86) Bauschlicher, C. W., Jr. *J. Phys. Chem. A* **2000**, *104*, 2281.

(87) Herzberg, G., *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrand Reinhold Co.: New York, 1966.