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Bond Dissociation Energies of the Tungsten Fluorides and Their Singly Charged Ions: A Density Functional Survey

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The dissociation of WF_6 and the related singly charged cations and anions into the lower fluorides and fluorine atoms has been investigated theoretically using density functional theory (B3LYP) and relativistic effective core potentials, with estimates of spin−orbit effects included using a simple model. The inclusion of spin−orbit effects is essential for a correct description of the thermochemistry. The total atomization energy of the neutral and anionic WF_6 is reproduced to within 25 kcal/mol, but comparison of individual bond dissociation energies with available experimental data shows discrepancies of up to 10 kcal/mol. The results are nevertheless useful to help resolve discrepancies in experimental data and provide estimates of missing data.

I. Introduction

Tungsten hexafluoride is an important species in the manufacture of semiconductor devices. It is used for deposition of tungsten metal to form interconnects, because of its high conductivity and its compatibility with the silicon substrate. In the modeling of the deposition process,[1,2] knowledge of the bond dissociation energies of the various species in the gas phase is required, as well as that of surface species. The heat of formation of WF_6 is well-known,[3] and the heats of formation of several of the neutral tungsten fluorides were determined experimentally some time ago,[4] but some uncertainties in the data still remain. Moreover, WF_6 has a large electron affinity, so that in a plasma environment where there are many free electrons, there is the possibility of forming both positive and negative ions. Experimental data exist for some of the negative ion species as well,[5−9] but again there are large uncertainties in some of the data and large disagreements between some. Little is known about the positive ions apart from a few ionization potentials.[4−10]

On the theoretical front, there have been few accurate studies[11] of WF_6, and no studies of tungsten fluorides other than WF_6 until the recent study by Gutowski[12] of the performance of density functional theory (DFT) for WF_4. There is therefore considerable scope for a theoretical study both to interpret the experimental data and to fill in some of the missing data. The reactions which will be investigated in this paper are

$$WF_n \rightarrow WF_{n-1} + F \tag{1}$$

$$WF_n^+ \rightarrow WF_{n-1}^+ + F \tag{2}$$

$$WF_n^- \rightarrow WF_{n-1}^- + F \tag{3}$$

$$WF_n^- \rightarrow WF_n + e^- \tag{4}$$

$$WF_n \rightarrow WF_n^+ + e^- \tag{5}$$

For the lower n values in which there are several electrons in the 5d shell of the metal, there are a number of possible states and spin multiplicities to be considered. If any of these are very low-lying, there is a chance that they may be thermally populated, and at the elevated temperatures common in plasma processing, higher excited states may be populated as well.

The purpose of this study is to survey the thermochemistry of tungsten hexafluoride and its singly charged cations and anions and in the process to obtain estimates of the bond dissociation energies at a modest level of accuracy. High accuracy results, of better than 1 kcal/mol, are at present unobtainable, for the reason that it is necessary to take into account both scalar and spin−orbit relativistic effects along with electron correlation and there are no computer programs currently available that will do all three simultaneously to the desired level of accuracy. The magnitude of the problem is in fact illustrated in this paper. Instead we content ourselves with a goal of 2−4 kcal/mol, which is generally achievable with density functional theory (DFT) combined with estimates of spin−orbit interaction.

II. Methods

Since tungsten is a heavy atom where relativistic effects are important, the calculations have been performed using the Hay/Wadt relativistic effective core potentials (RECPs).[13] The supplied double zeta basis sets (LANL2DZ) were used on the tungsten atom, and the augmented correlation-consistent double zeta basis sets of Dunning,[14] which are of 3s2p1d quality with a 1s1p1d diffuse set added, were used for fluorine. Given the level of accuracy of the calculations, it was not considered necessary to use larger basis sets. In any case, DFT is relatively insensitive to the quality of the basis set, provided a reasonable basis is used in the first place. A few exceptions were made for the anions. For W^- and WF^-, where there is a substantial charge on the W atoms, a diffuse s and a diffuse d function with exponents 0.017 and 0.035 were added to the W basis. Tests on the W neutral atom lowered the energy by only 0.6 kcal/mol, but for W^- the energy lowering was 4.5 kcal/mol. A lowering of 1.5 kcal/mol with little geometric change was observed for WF^-. The negative charge in the higher fluorides resides more on the F atoms, so the diffuse functions are not needed.

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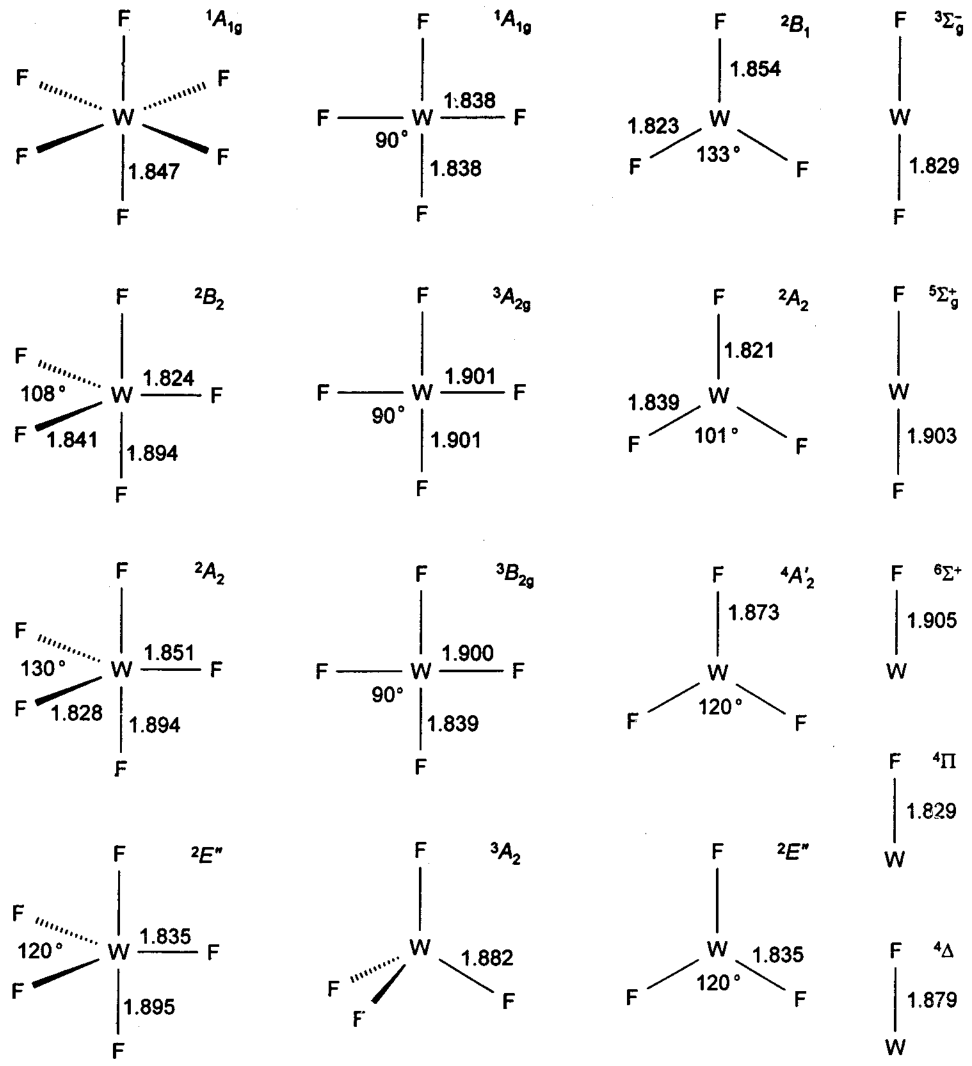

Figure 1. Geometries of neutral tungsten fluorides, with bond lengths in angstroms and angles in degrees.

All of the calculations were performed with the B3LYP hybrid density functional.[15,16] Gaussian 94[17] was used for all calculations with the fine grid option. For some species such as WF_2, calculations were performed with a (100,434) Lebedev grid, to confirm the linearity of the ground state. Optimization of geometries was performed for species in several spin states and symmetries to obtain information on the excited states, within the constraints of what is feasible with DFT. The zero-point and thermal corrections were computed only for the neutral systems. Since these cancel to within 1−2 kcal/mol, which is well within the desired accuracy, it was not felt to be necessary to compute them for the ionic systems.

Spin−orbit effects were estimated using a simple model of the spin−orbit operator. It is assumed that the only orbitals which contribute are the 5d orbitals, and among these, only those into which the fluoride ions do not donate. The problem therefore reduces to an atomic problem in a restricted space of atomic orbitals. An estimate of the radial spin−orbit integral, $R = \int_0^\infty dr\, R_{5d}^2 Z/r^3$, was obtained by deperturbing Dirac−Hartree−Fock calculations on W^{5+} d^1 and W^{4+} d^2 states. Although the spin−orbit parameter is somewhat dependent on the charge state, the W atom in the complexes is likely to carry a substantial charge, so the error in the selection of the parameter should be well within the desired accuracy of the results. The value selected was 8 kcal/mol. The coefficients of the radial integrals are obtained from elementary angular momentum theory with the angular part of the one-particle spin−orbit operator, $\mathbf{s}\cdot\mathbf{l}$. Spin−orbit effects were obtained by diagonalizing a small matrix of determinants in the space of 5d orbitals discussed above. Any determinants which were considered too high in energy were deleted, though in most cases an estimate from second-order perturbation theory of the effect of higher lying determinants was made.

III. Geometries and Energies

The geometries of the neutral molecules are shown in Figure 1, and the corresponding energetic data are reported in Table 1. For the most part, the structures are those expected from simple crystal field theory. WF_6 is octahedral. WF_5 Jahn−Teller distorts from the trigonal bipyramidal (D_{3h}) geometry because the unpaired electron is in an e″ orbital. The lowest two states therefore have $^2B_2$ and $^2A_2$ C_{2v} symmetry. This means that both of them will be populated thermally, and the ground state should essentially be considered to have a degeneracy of 4. The ground state of WF_4 is the square planar D_{4h} $^1A_{1g}$ state, though the calculations give a small out-of-plane D_{2d} distortion. This is likely to be a feature of the use of DFT. There are two triplet states, both of which are approximately 11 kcal/mol higher in energy. One is tetrahedral, with the two unpaired electrons occupying the e orbital and coupling to give a $^3A_2$ state. The other arises from the square planar $(a_{1g})^1(e_g)^1$ state which

TABLE 1: Symmetries and Energies of Neutral Species (Total Energies in Hartrees, Relative Energies in kcal/mol)

species	mol sym	state sym	total energy	rel energy
WF_6	O_h	$^1A_{1g}$	−667.223 41	
WF_5	C_{2v}	$^2B_2$	−567.302 58	
		$^2A_2$	−567.302 41	0.1
	D_{3h}	$^2E''$	−567.300 05	1.5
WF_4	D_{4h}	$^1A_{1g}$	−467.397 10	
	D_{2d}	$^1A_1$	−467.398 75	−1.0
	T_d	$^3A_2$	−467.381 28	9.9
	D_{4h}	$^3A_{2g}$	−467.316 67	50.5
	D_{2h}	$^3B_{2g}$	−467.377 25	12.5
WF_3	D_{3h}	$^4A_2'$	−367.471 16	
	C_{2v}	$^2B_1$	−367.460 54	6.7
		$^2A_2$	−367.460 98	6.4
	D_{3h}	$^2E''$	−367.455 70	9.7
WF_2	$D_{\infty h}$	$^3\Sigma_g^-$	−267.534 43	
		$^5\Pi_g$	−267.519 43	9.4
WF	$C_{\infty v}$	$^6\Sigma^+$	−167.569 91	
		$^4\Pi$	−167.557 19	8.0
		$^4\Delta$	−167.543 55	16.5
W	K_h	^7S	−67.638 95	
		^5D	−67.631 29	4.8
F	K_h	$^2P^o$	−99.739 49	

undergoes Jahn−Teller distortion to a pair of degenerate states in D_{2h} symmetry corresponding to the two possible choices of distortion mode. The state is labeled here as $^3B_{2g}$. WF_3 has a quartet ground state and is planar D_{3h}; the ground state is $(a_1')^1(e'')^2\ ^4A_2'$. The $(a_1')^2(e'')^1\ ^2E''$ states undergo Jahn−Teller distortion to C_{2v} symmetry, forming a $^2B_1/^2A_2$ pair at about 6−7 kcal/mol higher than the ground state. WF_2 forms sd_z hybrids to bond with the F atoms. The ground state is the linear $(\sigma_g)^2(\delta_g)^2\ ^3\Sigma_g^-$ state; the (σ_g) orbital is the equatorial s−d_z hybrid. The lowest quintet is the $(\pi_g)^2(\delta_g)^2\ ^5\Sigma_g^+$ state at about 10 kcal/mol. WF has a $(\sigma)^1(\pi)^2(\delta)^2\ ^6\Sigma^+$ ground state; again the sigma orbitals form sd_z hybrids. The lowest quartet is the $(\sigma)^2(\pi)^1(\delta)^2\ ^4\Pi$ at about 8 kcal/mol, followed by the $(\sigma)^2(\pi)^2(\delta)^1\ ^4\Delta$ at about 16 kcal/mol. The $^4\Pi$ is in fact a mixture of $(\sigma)^2(\pi)^1(\delta)^2$ and $(\sigma)^1(\pi)^1(\delta)^3$.

The cation geometries are shown in Figure 2, with the corresponding energetic data in Table 2. The HOMO for WF_6 is a t_{1g} orbital which is composed of F 2p orbitals. The cation undergoes Jahn−Teller distortion to three equivalent states with D_{4h} symmetry, here designated $^2B_{2g}$. WF_5 loses the electron which would have been in the e″ orbital in D_{3h} symmetry, and therefore the cation has the expected trigonal bipyramidal geometry with a $^1A_1'$ ground state. For WF_4, loss of an electron from the a_{1g} orbital of the ground state leaves a square planar $^2A_{1g}$ ion state. However, this state collapses to a $D_{2d}\ ^2A_1$ state—as do optimizations starting from a C_{2v} and a T_d geometry. There is also a $^2B_{2g}$ state in D_{2h} symmetry some 70 kcal/mol higher. Ionization of WF_3 leads to several potential states. From the doublet, the lowest state is the planar $D_{3h}\ ^1A_1'$ state with a doubly occupied a_1' orbital. From the quartet, removal of the a_1' electron gives a planar triplet $(e'')^2\ ^3A_2'$ state. Removal of an e″ electron from the quartet or an a_1' electron from the doublet leads to a $(a_1')^1(e'')^1\ ^3E''$ state which undergoes Jahn−Teller distortion to C_{2v} symmetry. It is this last state which is the ground state, but the other two states are only a few kilocalories per mole higher in energy and must be taken into consideration. Ionization from the ground state of WF_2 generates a $(\sigma_g)^2(\delta_g)^1\ ^2\Delta_g$ state and a $(\sigma_g)^1(\delta_g)^2\ ^4\Sigma_g^-$ linear state. The latter of these is the ground state. The $^2\Delta_g$ is higher in energy by more than 20 kcal/mol, as are the $^4\Pi_g$ and the bent doublet and quartet states. The ground state of WF^+ is the $(\sigma)^1(\pi)^1(\delta)^2\ ^5\Pi$ state. The lowest-lying excited states are the $(\sigma)^1(\pi)^2(\delta)^1\ ^5\Delta$ state and the $(\sigma)^2(\delta)^2\ ^3\Sigma_g^-$ state.

The anion geometries are shown in Figure 3, with energetic data in Table 3. The LUMO for WF_6 is a t_{2g} orbital. The anion therefore undergoes Jahn−Teller distortion to D_{4h} symmetry with a $^2B_{2g}$ ground state in a similar fashion to the cation. In WF_5, the extra electron goes in the e″ orbital to produce a $^3A_2'$ state which retains D_{3h} symmetry. There are no other low-lying states. The LUMO in the square planar ground state of WF_4 is an e_g orbital. The molecule undergoes Jahn−Teller distortion when the extra electron is placed in it, to generate a $D_{2h}\ ^2B_{2g}$ state. Addition of the extra electron to the e_g orbital in the Jahn−Teller distorted triplet state of the neutral restores D_{4h} symmetry and generates an $(a_{1g})^1(e_g)^2\ ^4A_{2g}$ state. This state is very close in energy to the doublet, and it is not possible to determine which of these is the ground state at this level of theory. In WF_3 the extra electron goes into the a_1' orbital to produce an $(a_1')^2(e'')^2\ ^3A_2'$ ground state—no other orbital occupation generates a state which is close in energy. WF_2^- has a linear quartet ground state, with the extra electron going into the unoccupied $d\pi$ orbital to produce a $(\sigma_g)^2(\pi_g)^1(\delta_g)^2\ ^4\Pi_g$ state. The lowest excited states are the $(\sigma_g)^2(\delta_g)^3\ ^2\Delta_g$ state at about 7 kcal/mol, and the $(\sigma_g)^1(\pi_g)^2(\delta_g)^2\ ^6\Sigma_g^+$ state at about 18 kcal/mol. The bent states all collapse to linear. WF^- has a $(\sigma)^2(\pi)^2(\delta)^2\ ^5\Sigma^+$ ground state. The septet corresponds to a $\sigma \rightarrow \sigma$ excitation. Addition of diffuse functions on W made little difference to the geometry but lowered the ground state energy by about 4.5 kcal/mol.

IV. Spin−Orbit Effects

Due to the large value of the spin−orbit splitting parameter relative to the excitation energies of the low-lying states in some of the species, corrections are needed in several cases. These will be discussed in the same order as in the previous subsection. The values of the spin−orbit corrections are given in Table 4.

WF_6 needs no correction since it is a closed-shell species and has no occupied 5d orbitals. WF_5 requires only a simple diagonal shift of $(-1/2)R = -4$ kcal/mol. This is applied to the degenerate $^2E''$ state, which places it below the Jahn−Teller distorted states by 2.5 kcal/mol. Obviously there will be an interaction between the Jahn−Teller components as well, so the potential energy surface in the distortion mode will be extremely flat. The ground state with spin−orbit interaction is expected to be at the symmetric point. For WF_4 the A_g component of the $(a_g)^1(e_g)^1\ ^3E_g$ state has a diagonal shift of $(-1/2)R$, bringing it close to the ground state. A simple 2 × 2 matrix diagonalization with the planar $(a_g)^2\ ^1A_g$ state gives a ground state shift of −10.1 kcal/mol. Adding a perturbative estimate of the shift of the ^3E_g energy due to the $(e_g)^2\ ^3A_{2g}$ gives a further shift of −0.7 kcal/mol. Both the $^4A_2'$ and $^2E''$ states of WF_3 split under the double group into $E_{1/2}$ and $E_{3/2}$ states. A similar treatment as for WF_4 with these two states and a perturbative estimate for higher states gives a ground state shift of −4.8 kcal/mol for the $E_{1/2}$ component and −5.5 kcal/mol for the $E_{3/2}$ component, both of which will be thermally populated. In WF_2 and WF, the σ orbitals are essentially $5d_z$−6s hybrids, and the spin−orbit matrix elements involving these orbitals will be reduced. We have chosen a reduction of 20%. The ground state of WF_2 splits into two components with labels 0_g^+ and 1_g. The lowest interacting excited state is the $(\sigma_g)(\pi_g)(\delta_g)^2\ ^5\Pi_g$ state which has two components with $\omega = 0$ and 1. With the reduced spin−orbit matrix element, interaction with this state gives −4.2 kcal/mol for the 1_g component and −3.4 for the 0_g^+ component. Estimated interaction with the other low-lying states such as the $^3\Pi_g$ is 1 kcal/mol. In WF there are two low-lying $^4\Pi$ states with configurations $(\sigma)^2(\delta)^2(\pi)^1$ and $(\sigma)^1(\delta)^3(\pi)^1$. DFT calculations appear to mix these two, so the energy reported for the

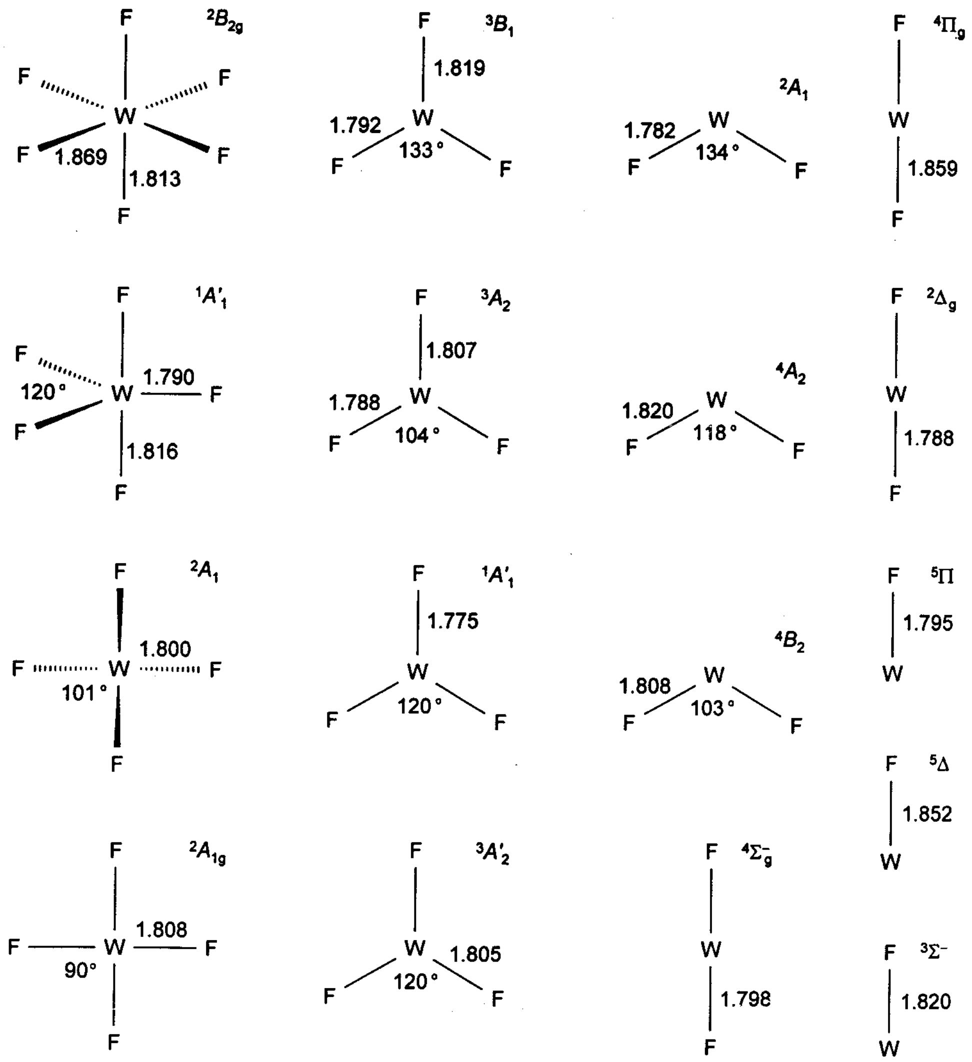

Figure 2. Geometries of singly charged tungsten fluoride cations, with bond lengths in angstroms and angles in degrees.

TABLE 2: Symmetries and Energetics of Positive Species (Total Energies in Hartrees, Relative Energies in kcal/mol)

species	mol sym	state sym	total energy	rel energy
WF_6^+	D_{4h}	$^2A_{2g}$	−666.675 25	
WF_5^+	D_{3h}	$^1A_1'$	−566.960 62	
WF_4^+	D_{2d}	$^2A_1$	−467.061 73	
	D_{4h}	$^2A_{1g}$	−467.022 56	24.6
	D_{2h}	$^2B_{2g}$	−466.950 21	73.4
WF_3^+	C_{2v}	$^3A_2$	−367.140 35	
		$^3B_1$	−367.140 30	0.03
	D_{3h}	$^1A_1'$	−367.135 78	2.9
		$^3A_2'$	−367.135 87	2.8
WF_2^+	$D_{\infty h}$	$^4\Sigma_g^-$	−267.218 12	
		$^2\Sigma_g^+$	−267.173 22	28.2
		$^4\Pi_g$	−267.157 43	38.1
		$^2\Delta_g$	−267.150 26	42.6
	C_{2v}	$^4B_2$	−267.181 76	22.8
		$^4A_2$	−267.166 61	32.3
		$^2A_1$	−267.167 33	31.9
WF^+	$C_{\infty v}$	$^5\Pi$	−167.265 21	
		$^5\Sigma^+$	−167.234 63	19.2
		$^3\Sigma^-$	−167.223 74	26.0
W^+	K_h	^6S	−67.325 94	

$^4\Pi$ state is probably to be taken as the energy of the lowest state. It is then difficult to estimate the effect of the other state. With the maximum possible interaction but with a scaled $\langle\sigma|\pi\rangle$ spin−orbit matrix element, the ground state shift is −8.9 kcal/mol for the $\Omega = 5/2$ component, which is the lowest component. The $^4\Delta$ state has only a small coupling with the $^4\Pi$ states and thus has very little influence on the ground state energy. For W atom we combine the DFT calculations with the experimental data to obtain the value reported here.

For WF_6^+ the hole is essentially in the F 2p orbitals, and since the spin−orbit splitting on F is small, it may be neglected in the molecule. WF_5^+ is similar to WF_6 in having no occupied 5d orbitals, and hence has no shift. WF_4^+ has a single electron in a d_{z^2} orbital, and has no diagonal shift. The d orbitals with which it will interact via the spin−orbit interaction are the orbitals into which the F^- ligands are donating, and the empty orbitals will also be mixed with F orbitals. Hence only a small spin−orbit shift is expected, probably about 1 kcal/mol. WF_3^+ is probably the most interesting since it has three very close-lying states which have large spin−orbit matrix elements connecting them. The lowest is the Jahn−Teller distorted $(d_0)(d_1))$ $^3E''$ state; the other two, the $(d_{+1})(d_{-1})$ $^3A_2'$ and the $(d_0)^2$ $^1A_1'$ states, are practically degenerate. Inclusion of these three states in a spin−orbit configuration interaction at the symmetric point on the assumption that they are degenerate produces a splitting of 19 kcal/mol between each state, and thus a ground state lowering of 16 kcal/mol. In contrast, the excited states of WF_2^+ are relatively high-lying and have small spin−orbit matrix elements with the ground state, so that the ground state shift is estimated at −0.5 kcal/mol. The $^5\Pi$ ground state of WF^+ splits into $\Omega = 3, 2, 1, 1, 0^+$, and 0^- components.

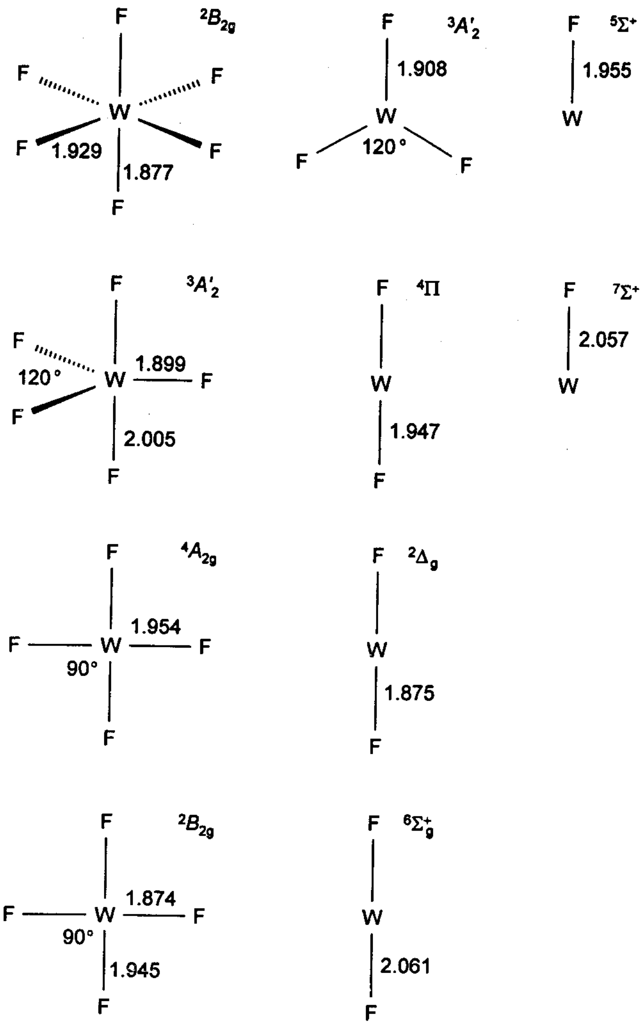

Figure 3. Geometries of singly charged tungsten fluoride anions, with bond lengths in angstroms and angles in degrees.

TABLE 3: Symmetries and Energetics of Negative Species (Total Energies in Hartrees, Relative Energies in kcal/mol)

species	mol sym	state sym	total energy	rel energy
WF$_6^-$	D_{4h}	$^2B_{2g}$	−667.341 16	
WF$_5^-$	D_{3h}	$^3A_2'$	−567.395 44	
WF$_4^-$	D_{2h}	$^2B_{2g}$	−467.479 84	
	D_{4h}	$^4A_{2g}$	−467.477 18	1.7
WF$_3^-$	D_{3h}	$^3A_2'$	−367.521 10	
WF$_2^-$	$D_{\infty h}$	$^4\Pi_g$	−267.584 94	
		$^2\Delta_g$	−267.572 91	7.5
		$^6\Sigma_g^+$	−267.556 62	17.8
WF$^-$	$C_{\infty v}$	$^5\Sigma^+$	−167.617 02	
		$^7\Sigma^+$	−167.582 17	21.9
W$^-$	K_h	^6S	−67.683 81	
F$^-$	K_h	^1S	−99.870 37	

Interaction with the $(\pi)^2(\delta)^2$ $^5\Sigma^+$ and $(\sigma)^2(\delta)^2$ $^3\Sigma^-$ states gives a ground state of $^5\Pi_1$ at −8.2 kcal/mol relative to the $^5\Pi$. The next component is the $^5\Pi_{0+}$ at −4.9 kcal/mol. The ground state of W$^+$ is the d^5 ^{6}S state which has no first-order spin−orbit splitting.

For WF$_6^-$ the extra electron is in the t$_{2g}$ orbital which undergoes Jahn−Teller distortion. In the double group, the t$_{2g}$ orbital splits into a doubly degenerate γ_7 and a quadruply degenerate γ_8 representation. The former is lower in energy, and has equal weight of the three t$_{2g}$ orbitals so it does not Jahn−Teller distort. The spin−orbit shift is −8 kcal/mol, and given that the Jahn−Teller energy is about 2 kcal/mol, the overall shift relative to the unperturbed state is −6 kcal/mol. WF$_5^-$ has no diagonal shift, and the interacting excited states will be higher in energy and have reduced matrix elements because of mixing with the F 2p orbitals. The ground state energy is therefore not corrected. In WF$_4^-$, both the ^{4}A$_{2g}$ and ^{2}E$_g$ split into E$_{1/2g}$ and E$_{3/2g}$ components. The ^{2}E$_g$ is approximately 2 kcal/mol higher than the ^{4}A$_{2g}$ at the symmetric point, and the lowest E$_{1/2g}$ and E$_{3/2g}$ states then lie at approximately −7.2 and −6.6 kcal/mol relative to the ^{4}A$_{2g}$ state. An extra shift of −1 kcal/mol due to neglected states is added to these totals. WF$_3^-$ has higher lying excited states and the spin−orbit shift is therefore small, estimated by perturbation arguments to be −1 kcal/mol. For WF$_2^-$ the ground $(\sigma_g)^2(\delta_g)^2(\pi_g)$ $^4\Pi$ state interacts with the $(\sigma_g)^2(\delta_g)^3$ $^2\Delta$ state and the $(\sigma_g)^1(\delta_g)^2(\pi_g)^2$ $^6\Sigma_g^+$ state. The ground state has $\Omega = 5/2$ and lies at −7.0 kcal/mol. WF$^-$ has a $\sigma^2\delta^2\pi^2$ $^5\Sigma^+$ ground state which has no near-lying states with which it can interact, and the spin−orbit shift is likely to be small. The ground state of W$^-$ is the d^{5}s^2 ^{6}S state which has no first-order spin−orbit splitting.

TABLE 4: Spin−Orbit Corrections to Ground State Energies in kcal/mol[a]

species	neutral	cation	anion
WF$_6$	0.0	0.0	−6.0
WF$_5$	−2.5	0.0	0.0
WF$_4$	−10.8	−1.0	−6.5
WF$_3$	−5.5	−16.1	−1.0
WF$_2$	−5.2	−0.5	−7.0
WF	−8.9	−8.2	−2.0
W	−13.2	0.0	0.0
F	−0.4		0.0

[a] These figures include geometric changes due to Jahn−Teller distortion.

TABLE 5: Ionization Potentials and Electron Affinities in eV[l]

species	IP	+SO	expt[a]	EA	+SO	expt
WF$_6$	14.9	14.9		3.2	3.5	3.5(1),[d] 3.4(2),[e] 3.7(2)[f]
WF$_5$	9.3	9.4	10.0(1), 14.9[b]	2.5	2.4	<3.5,[e] >1.8(3),[g] 1.25[h]
WF$_4$	9.3	9.7	9.9(1)	2.1	1.9	2.6,[h] >2.3(1)[i]
WF$_3$	9.0	8.5	9.0(2)	1.4	1.2	
WF$_2$	8.6	8.8	9.0(3)	1.4	1.5	
WF	8.3	8.3	8.5(10)	1.5	1.2	
W	8.5	9.1	7.98[c]	1.2	0.7	0.817(4)[j]
F				3.56	3.54	3.4012[k]

[a] Reference 4. [b] Reference 10. [c] Reference 18. [d] Reference 6. [e] Reference 5. [f] Reference 9. [g] Reference 19. [h] Reference 8. [i] Reference 7. [j] Reference 20. [k] Reference 21. [l] The columns labeled IP and EA give the property without spin−orbit effects; the columns labeled +SO give the property with spin−orbit effects included.

It is clear from these results that no account of the energetics of the tungsten fluorides can hope to be quantitatively correct without the inclusion of spin−orbit effects. The planar d^2 systems show particularly large ground state shifts, and many of the other species show shifts greater than 5 kcal/mol.

V. Ionization Potentials and Electron Affinities

Computed ionization potentials (IP) and electron affinities (EA) in eV of the various species are given in Table 5, along with the available experimental data.[4−10,18−21] The larger IP of WF$_6$ reflects the fact that the electron is coming out of the F 2p orbitals, whereas for all other species the electron is removed from a W 5d orbital. The photoelectron value for WF$_5$ reported by Vovna et al.[10] is similar to the IP of WF$_6$, and therefore

TABLE 6: Equilibrium Bond Dissociation Energies in kcal/mol[a]

	neutral			cation			anion		
species	SF	SO	total	SF	SO	total	SF	SO	total
WF_6	113.8	-2.9	110.9	15.6	-0.4	15.2	129.4	$+5.6$	135.0
WF_5	103.1	-8.7	94.4	100.0	-1.4	98.6	110.5	-6.9	103.6
WF_4	118.1	$+4.9$	123.0	114.1	-15.4	98.7	137.6	$+5.1$	142.7
WF_3	123.6	-0.1	123.5	114.7	$+15.0$	129.7	123.4	-4.4	117.0
WF_2	141.2	-4.1	137.1	133.9	-8.1	125.8	143.3	$+4.6$	147.9
WF	125.0	-4.7	120.3	125.4	$+7.8$	133.2	121.6	$+1.6$	123.2
sum	724.8	-15.6	709.2	603.7	-2.5	601.2	765.8	$+3.6$	769.4

[a] The columns labeled SF give the spin-free value, columns labeled SO give the spin−orbit correction.

TABLE 7: Bond Dissociation Energies and Enthalpies in kcal/mol for $WF_n \rightarrow WF_{n-1} + F$ and Total Atomization Energy and Enthalpy of WF_6[a]

WF_6	WF_5	WF_4	WF_3	WF_2	WF	atomization	description
114	103	118	124	141	125	725	ΔE_e spin free
111	94	123	124	137	120	709	ΔE_e with spin−orbit
109	93	121	122	136	120	701	$\Delta E_0 = \Delta H°$ at 0 K
110	94	122	123	136	121	705	$\Delta H°$ at 298 K
112	96	125	126	140	123	723	$\Delta H°$ scaled at 0 K
112	97	126	127	141	125	729	$\Delta H°$ scaled at 298 K
121	106	120	120	132	130	729	exptl $\Delta H°$ (298 K)

[a] Experimental data are derived from Hildenbrand and the JANAF compilation.

must be regarded as coming from the F 2p orbitals, not the W 5d orbital. The values obtained here are in general agreement with the appearance potentials reported by Hildenbrand,[4] and display the same general trend. The electron affinities are in reasonable agreement with the available experiment. For W^- it was necessary to add diffuse s and d functions to the basis set to obtain reasonable results; without them the EA was smaller by 0.6 eV. Similarly, the EA of WF increases by 0.2 eV when the diffuse functions are added to W. The EA of WF_5 given by De Wall et al.[8] is probably too low to be correct, if the value for WF_4 is accepted.

VI. Bond Dissociation Energies

Table 6 shows the computed equilibrium bond dissociation energies (BDEs) and total atomization energies for the tungsten fluorides. The size of the spin−orbit effect is shown in columns 3, 6, and 9. The BDEs of WF_4 and WF_2 involve a change in the total spin and therefore must involve a spin−orbit avoided crossing which could produce a barrier in the dissociation channel. The very small value of the BDE for WF_6^+ can be explained in terms of the differences in IP between WF_6 and WF_5 as discussed above. Ionization of WF_6 with only a small amount of excess energy is likely to produce fragmentation. Removal of the second and third F atoms from WF_6^+ is relatively easier than the remaining three, which require an extra 30 kcal/mol for each F. In contrast, the anion WF_6^- is particularly strongly bound. There is an alternation in the bond strengths of the WF_n^- anions with n, with the even numbers having a higher BDE.

Experimental data are available for several species. For the neutral systems, an accurate value can be deduced for WF from the JANAF data,[3] and values for WF_n, $n = 3-6$, have been reported by Hildenbrand.[4] The value for WF_2 can be derived from these. The theoretical data for the neutral systems with the zero-point and thermal corrections are presented in Table 7 along with these experimental data. Since the final theoretical numbers are underestimated, a scaling factor has been introduced which adjusts the total atomization energy to the experimental value. The BDEs of WF_6 and WF_5 are obviously too small by about 10 kcal/mol, even after scaling, whereas the unscaled BDEs of WF_4 and WF_3 are close to the experimental values. The BDE of WF_2 is somewhat too high and that of WF too low, suggesting that, if anything, the effect of spin−orbit coupling may have been underestimated. Nonetheless, even an adjustment of 5 kcal/mol would not bring the BDE of WF close enough to experiment, although it would improve the BDE of WF_2. No such easy explanation can be found for WF_6 and WF_5, however. The experimental errors in the derived heats of formation are of the order of 2−3 kcal/mol, so the differences are definitely outside the experimental errors.

For the positive ions, estimates of the experimental BDEs may be obtained by use of the IP data from Hildenbrand.[4] The values for WF_5, WF_4, and WF_3 are 103, 100, and 120 kcal/mol, which compare reasonably well with the theoretical values of 99, 99, and 130 kcal/mol, given that the thermal and zero-point energies approximately cancel and that the errors due to the IP data are 5, 7, and 12 kcal/mol.

It is for the negative ions that there is more disagreement among the experimental data. The heat of formation of WF_6^- is -490 ± 5 kcal/mol. Using $\Delta H_f° = -337$ kcal/mol from Thynne and Harland[7] for WF_5^- and $\Delta H_f° = -306$ kcal/mol from DeWall and Neuert[8] for WF_4^-, the BDEs of WF_6^- and WF_5^- are 172 and 50 kcal/mol, respectively. This suggests that the Thynne and Harland heat of formation is too high, and should be adjusted downward by perhaps 40 kcal/mol to -377 kcal/mol. The enthalpy change for the reaction $WF_6^- \rightarrow WF_4^- + 2F$ is the sum of these two BDEs, 222 kcal/mol, which is in reasonable accord with the theoretical estimate of 239 kcal/mol. However, using the electron affinity for WF_4 from DeWall and Neuert and the heat of formation of WF_4 from Hildenbrand, a value of -286 kcal/mol is obtained for $\Delta H_f°$ (WF_4^-). This brings the reaction energy above to 242 kcal/mol which happens to be close to the theoretical estimate. The atomization enthalpy, $WF_6^- \rightarrow W^- + 6F$, is calculated using the experimental electron affinities to be 791 kcal/mol. Again, the theoretical numbers underestimate this value, in this case by more than 20 kcal/mol.

VII. Conclusions

The bond dissociation energies of the neutral and singly charged anionic and cationic tungsten fluorides have been calculated using density functional theory with the B3LYP functional and the Hay/Wadt relativistic effective core potential for W, with an estimate of spin−orbit effects. Spin−orbit effects are large for some molecules and cannot be neglected if accurate thermochemistry is required. Density functional theory performs moderately well, but the maximum errors are disappointingly large, at around 10 kcal/mol. It is possible but not likely that changes in the basis set, the functional, or the core potential will dramatically improve these figures.

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