Heats of Formation of Krypton Fluorides from High Level Electronic Structure Calculations

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Supporting Information. Computational details and complete references, total CCSD(T) energies (Table SM-1) as a function of basis set, MP2 calculated frequencies (Table SM-2) as a function of basis set, calculated geometry parameters (Table SM-3) for KrF_2^+ and KrF_4^+, CCSD(T)/aVTZ calculated frequencies (Table SM-4) for KrF_4^+, CCSD(T) atomization and reaction energies (Table SM-5) for KrF_2^+ and KrF_4^+, and calculated energies/heats of formation (Table SM-6) of KrF_2^+ and KrF_4^+.

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Computational Methods

We have been developing a composite approach[1] to the prediction of the thermodynamic properties of molecules based on molecular orbital theory using coupled cluster methods at the CCSD(T) level. In most CCSD(T) calculations of atomization energies (or heats of formation), the largest source of error typically arises from the finite basis set approximation unless there is significant multireference character to the wavefunction. Our composite approach for predicting atomization energies makes use of the systematic convergence properties of the valence correlation consistent family of basis sets including additional diffuse functions.[2] These basis sets are conventionally denoted aug-cc-pVnZ, with n = D – 5, for the atoms for which they are available. The standard aug-cc-pVnZ basis sets were used for F. For heavier elements, the effects of relativity need to be included in the basis sets. A small core relativistic effective core potential (RECP) was used for Kr. The RECP subsumes the ($1s^2$, $2s^2$, $2p^6$) orbital space into the 10-electron core set, leaving the ($3s^2$, $3p^6$, $4s^2$, $3d^{10}$ and $4p^6$) space with 26 electrons to be handled explicitly. Of the latter, only the ($4s^2$, $4p^6$) electrons are active in our valence correlation treatment. The polarized relativistic basis sets are labeled as aug-cc-pVnZ-PP.[3] We use the shorthand notation of aVnZ to denote the combination of the aug-cc-pVnZ basis set on F and the aug-cc-pVnZ-PP basis set on Kr. Only the spherical component subset (e.g., 5-term d functions, 7-term f functions, etc.) of the Cartesian polarization functions were used. All CCSD(T) calculations were performed with either the MOLPRO-2002[4] program system on a single processor of an SGI Origin computer or the Cray XD-1 at the Alabama Supercomputer Center or with NWChem[5] and MOLPRO

on the massively parallel HP Linux cluster in the Molecular Science Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory.

For the open shell atomic calculations, we used the restricted method for the starting Hartree-Fock wavefunction and then relaxed the spin restriction in the coupled cluster portion of the calculation. This method is conventionally labeled R/UCCSD(T). Our CBS estimates use a mixed exponential/Gaussian function of the form[6]

$$E(n) = E_{CBS} + Be^{-(n-1)} + Ce^{-(n-1)^2} \qquad (1)$$

where n = 2(aVDZ), 3(aVTZ), 4(aVQZ). We did not go to larger basis sets because, for the xenon fluorides XeF^+, XeF^- and XeF_2 (except for $XeF^+ \longrightarrow Xe + F^+$ with a difference of 0.73 kcal/mol), the dissociation energies with the CBS extrapolation from eq. 1 were within 0.2 kcal/mol with a CBS extrapolation using the aVQZ and aV5Z energies.[7]

Most correlated electronic structure calculations based on molecular orbital theory are done in the frozen core approximation with the energetically lower lying orbitals, e.g., the 1s in fluorine, excluded from the correlation treatment. In order to achieve thermochemical properties within ±1 kcal/mol of experiment, it is necessary to account for core-valence correlation energy effects. Core-valence (CV) calculations were carried out with the weighted core-valence basis set cc-pwCVTZ.[8] The cc-pwCVTZ-PP basis set for Kr is based on the cc-pVTZ-PP basis set and accompanying small core RECP. For Kr, the cc-pwCVTZ-PP basis set includes up through g-functions in order to provide a consistent degree of angular correlation for the active 3d electrons.[9] Core-valence calculations for Kr involve all 26 electrons outside the RECP core, i.e. $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, and $4p^6$.

Two adjustments to the total atomization energy (TAE = ΣD_0) are necessary in order to account for relativistic effects in atoms and molecules. The first correction lowers the sum of the atomic energies (decreasing TAE) by replacing energies that correspond to an average over the available spin multiplets with energies for the lowest multiplets as most electronic structure codes produce only spin multiplet averaged wavefunctions. The atomic spin-orbit corrections are $\Delta E_{SO}(F) = 0.39$ kcal/mol, $\Delta E_{SO}(F^+) = 0.48$ kcal/mol, and $\Delta E_{SO}(Kr^+) = 5.12$ kcal/mol from the tables of Moore.[10] A second relativistic correction to the atomization energy accounts for molecular scalar relativistic effects, ΔE_{SR}. We evaluated ΔE_{SR} by using expectation values for the two dominant terms in the Breit-Pauli Hamiltonian, the so-called mass-velocity and one-electron Darwin (MVD) corrections from configuration interaction singles and doubles (CISD) calculations. The quantity ΔE_{SR} was obtained from CISD wavefunctions with an aVTZ basis set at the CCSD(T)/aVTZ geometry. The CISD(MVD) approach generally yields ΔE_{SR} values in good agreement (±0.3 kcal/mol) with more accurate values from, for example, Douglass-Kroll-Hess calculations, for most molecules. A potential problem arises in computing the scalar relativistic corrections for the molecules in this study as there is the possibility of "double counting" the relativistic effect on Kr when applying a MVD correction to an energy which already includes most of the relativistic effects via the RECP. Because the MVD operators mainly sample the core region where the pseudo-orbitals are small, we assume any double counting to be small.

Optimized bond lengths and harmonic frequencies for the diatomic molecular ions KrF^+ and KrF^- were obtained from a 5^{th} degree Dunham fit of the potential energy surface.[11] For the polyatomic molecules KrF_2, KrF_4, and KrF_6, numerical geometry

optimizations were performed with a convergence threshold on the gradient of approximately $10^{-4}E_h$/bohr or smaller. Geometries were optimized at the aVDZ, aVTZ, and aVQZ levels for KrF^+, KrF^-, and KrF_2 and the first two basis sets were used in the KrF_3^+, KrF_4, KrF_5^+, and KrF_6 optimizations. The geometry obtained with the aVTZ basis set was then used for the aVQZ calculations for the latter two molecules. The zero point energies (ΔE_{ZPE}) for the diatomics included anharmonic corrections ($\omega_e x_e$) and were calculated at the CCSD(T)/aVQZ level. For the polyatomic molecules, we calculated the harmonic frequencies at the CCSD(T) level with the aVDZ and aVTZ basis sets. For KrF_2, the experimental values[12,13,14,15] of the frequencies are known and the zero point energy for KrF_2 was calculated as the average of the CCSD(T)/aVTZ value and the experimental value following previous work.[16] This yields a scaling factor of 0.988 as compared to the CCSD(T)/aVTZ results and this scaling factor was used for the other polyatomic molecules.

By combining our computed ΣD_0 values given by the following expression

$$\Sigma D_0 = \Delta E_{elec}(CBS) - \Delta E_{ZPE} + \Delta E_{CV} + \Delta E_{SR} \qquad (2)$$

with the known[17] heats of formation at 0 K for the elements, $\Delta H_f^0(Kr) = 0$ kcal/mol and $\Delta H_f^0(F) = 18.47 \pm 0.07$ kcal/mol, we can derive ΔH_f^0 values for the molecules under study. Heats of formation at 298 K were obtained by following the procedures outlined by Curtiss *et. al.*.[18]

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Table SM-1. CCSD(T) Total Energies (E_h) as a Function of the Basis Set.[a,b]

System	Basis Set	Energy
Kr	aVDZ	-462.319290
	aVTZ	-462.396565
	aVQZ	-462.419593
	CBS	-462.432483
Kr^+	aVDZ	-461.809476
	aVTZ	-461.883438
	aVQZ	-461.901693
	CBS	-461.911469
F	aVDZ	-99.550035
	aVTZ	-99.627772
	aVQZ	-99.652846
	CBS	-99.667104
F^+	aVDZ	-98.920996
	aVTZ	-98.993187
	aVQZ	-99.015250
	CBS	-99.027665
F^-	aVDZ	-99.668634
	aVTZ	-99.749538
	aVQZ	-99.777073
	CBS	-99.792887
KrF^+	aVDZ	-561.420088
	aVTZ	-561.580929
	aVQZ	-561.627820
	CBS	-561.653946
KrF^-	aVDZ	-561.992845
	aVTZ	-562.152028
	aVQZ	-562.202854
	CBS	-562.231701
KrF_2	aVDZ	-661.443116
	aVTZ	-661.687037
	aVQZ	-661.763778
	CBS	-661.807208

KrF_2^+ ($^2\Pi$, $D_{\infty h}$)	aVDZ	-660.952851
	aVTZ	-661.193284
	aVQZ	-661.266935
	CBS	-661.308395
KrF_2^+ ($^2\Pi$, $D_{\infty h}$, Vertical)	aVDZ	-660.952549
	aVTZ	-661.192504
	aVQZ	-661.266074
	CBS	-661.307497
KrF_2^+ ($^2\Sigma^+$, $D_{\infty h}$)	aVDZ	-660.943752
	aVTZ	-661.182253
	aVQZ	-661.254801
	CBS	-661.295582
KrF_2^+ ($^2\Sigma^+$, $D_{\infty h}$, Vertical)	aVDZ	-660.941210
	aVTZ	-661.179649
	aVQZ	-661.252282
	CBS	-661.293124
KrF_2^+ ($^2\Pi$, $C_{\infty v}$)	aVDZ	-660.978923
	aVTZ	-661.217732
	aVQZ	-661.289960
	CBS	-661.330514
KrF_3	aVDZ	-760.993140
KrF_3^+	aVDZ	-760.510127
	aVTZ	-760.841404
	aVQZ	-760.943369
	CBS	-761.000824
KrF_4	aVDZ	-860.545751
	aVTZ	-860.956770
	aVQZ	-861.087599
	CBS	-861.161807
KrF_4^+	aVDZ	-860.047733
	aVTZ	-860.459738
	aVQZ	-860.588327
	CBS	-860.660984
KrF_5	aVDZ	-960.095788
KrF_5^+	aVDZ	-959.600972
	aVTZ	-960.107668

	aVQZ	-960.264895
	CBS	-960.353632
KrF_6	aVDZ	-1059.634775
	aVTZ	-1060.210360
	aVQZ	-1060.394066
	CBS	-1060.498321

[a] Dissociation is with respect to RCCSD(T) atoms for closed shell atoms and R/UCCSD(T) for open shell atoms. Symmetry equivalencing of the p_x, p_y and p_z orbitals was not imposed in the atomic calculations. The Kr RECP has a 10 electron core, leaving 26 electrons to be explicitly treated.

[b] CBS values from Eq. 1 (see text) obtained with the aVnZ basis sets with n = D, T, Q.

Table SM-2. MP2 Calculated Frequencies (cm^{-1})

Molecule	Symmetry	aVDZ	aVTZ
KrF_2	σ_u^+	620.5	622.9
	σ_g^+	466.1	484.1
	π_u	227.9	241.3
KrF_3^+	a_1	650.5	675.0
		513.8	546.9
		233.6	256.3
	b_1	227.5	242.0
	b_2	694.4	709.0
		340.8	373.0
KrF_4	a_{1g}	430.4	465.4
	b_{2g}	397.2	422.3
	b_{1g}	216.4	233.0
	a_{2u}	280.7	305.6
	b_{1u}	161.3	172.5
	e_u	629.0	638.8
		204.0	212.1
KrF_5^+	a_1	570.6	615.5
		516.5	557.2
		341.8	378.1
	b_1	290.3	322.8
	b_2	505.4	541.9
		213.4	235.1
	e	683.1	702.4
		359.5	403.4
		236.5	254.7
KrF_6	a_{1g}	392.4	449.1
	e_g	319.3	365.3
	t_{2g}	207.3	222.9
	t_{1u}	632.7	660.4
		265.5	277.1

t_{2u}	162.0	169.0

Table SM-3. Calculated Geometry Parameters for KrF_2^+ and KrF_4^+.

Molecule	**Method /Basis Set**	**r_e (Å)**
KrF_2^+ ($^2\Pi$, $D_{\infty h}$)	CCSD(T)/aVDZ	1.9223
	CCSD(T)/aVTZ	1.8841
	CCSD(T)/aVQZ	1.8747
KrF_2^+ ($^2\Sigma^+$, $D_{\infty h}$)	CCSD(T)/aVDZ	1.9223
	CCSD(T)/aVTZ	1.8841
	CCSD(T)/aVQZ	1.8747
KrF_2^+ ($^2\Pi$, $C_{\infty v}$)[a]	CCSD(T)/aVDZ	1.7906/2.5485
	CCSD(T)/aVTZ	1.7498/2.5207
	CCSD(T)/aVQZ	1.7420/2.4932
KrF_4^+ (C_{4v})[b]	CCSD(T)/aVDZ	1.8678 (89.12°)
	CCSD(T)/aVTZ	1.8096 (89.03°)

[a] First distance is the Kr-F^+ bond and the second distance is the weakly associated Kr···F bond.
[b] The angle is ∠F-Kr-F.

Table SM-4. CCSD(T)/aVTZ Calculated Frequencies (cm^{-1}) for KrF_4^+

Molecule	**Symmetry**	**aVTZ**
KrF_2^+ ($^2\Pi$, $C_{\infty v}$)	σ	638.1
		153.9
	π	97.6
KrF_4^+	a_1	465.2
		432.2
		279.6
	b_1	550.6
		231.3
	b_2	550.7
		230.2
	a_2	270.7

Table SM-5. CCSD(T) Atomization and Reaction Energies in kcal/mol.[a]

Molecule	**CBS**	ΔE_{ZPE}	ΔE_{CV}	ΔE_{SR}	ΔE_{SO}	ΣD_0 **(0K)**
KrF_2^+ ($^2\Pi$, $D_{\infty h}$) + $e^- \longrightarrow$ Kr + 2F·	-287.58		-0.91	0.34	-0.78	-288.93
KrF_2^+ ($^2\Pi$, $D_{\infty h}$, Vertical) + $e^- \longrightarrow$ Kr + 2F·	-288.15		-0.93	0.31	-0.78	-289.55
KrF_2^+ ($^2\Sigma^+$, $D_{\infty h}$) + $e^- \longrightarrow$ Kr + 2F·	-295.62		-0.78	0.13	-0.78	-297.05
KrF_2^+ ($^2\Sigma^+$, $D_{\infty h}$, Vertical) + $e^- \longrightarrow$ Kr+ 2F·	-297.17		-0.58	0.14	-0.78	-298.38
KrF_2^+ ($^2\Pi$, $C_{\infty v}$) + $e^- \longrightarrow$ Kr + 2F·	-273.70	1.41	-0.65	0.17	-0.78	-276.37
KrF_4^+ + $e^- \longrightarrow$ Kr + 4F·	-276.05	4.30	-1.77	0.54	-1.56	-283.14

[a] See text for description of column headings.

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Table SM-6. Calculated Energies/Heats of Formation (kcal/mol) at 0 K.

Molecule	**$\Delta E/\Delta H_f$**
KrF_2^+ ($^2\Pi$, $D_{\infty h}$)[a,b]	325.9
KrF_2^+ ($^2\Pi$, $D_{\infty h}$, Vertical)[a]	326.5
KrF_2^+ ($^2\Sigma^+$, $D_{\infty h}$)[a,b]	334.0
KrF_2^+ ($^2\Sigma^+$, $D_{\infty h}$, Vertical)[a]	335.3
KrF_2^+ ($^2\Pi$, $C_{\infty v}$)	313.3[c]
KrF_4^+	357.0[d]

[a] ΔE.

[b] ZPE not included. ZPE corrections will be less than 2 kcal/mol.

[c] $\Delta H_f(298\ K) = 313.7$ kcal/mol

[d] $\Delta H_f(298\ K) = 357.2$ kcal/mol