# Heats of Formation of $XeF_3^+$, $XeF_3^-$, $XeF_5^+$, $XeF_7^+$, $XeF_7^-$, and $XeF_8$ from High Level Electronic Structure Calculations

Daniel J. Grant, Tsang-Hsiu Wang, David A. Dixon,*,†

*Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487-0336*

Karl O. Christe

*Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089*

**Supporting Material.** CCSD(T)/aV*n*Z total energies ($E_h$) as a function of basis set (Table SM-1); CCSD(T)/awCV*n*Z total energies ($E_h$) as a function of basis set (Table SM-2); Calculated MP2 and CCSD(T) with the aVTZ basis set geometry parameters of the xenon fluoride molecules and their ions (Table SM-3); $T_1$ diagnostics calculated at the CCSD(T)/aVQZ level (Table SM-4); Calculated $F^+$ and $F^-$ affinities (Table SM-5); Calculated heats of reaction for loss of $F_2$ from the cationic, neutral and anionic xenon fluorides (Table SM-6); Calculated CCSD(T)/aVTZ and experimental geometries of the krypton fluoride molecules and their ions (Figure SM-1).

† E-mail address: dadixon@bama.ua.edu

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

| Molecule | Basis Set | Energy |
|---|---|---|
| $XeF_3^+$ ($C_{2v}$) | aVDZ | -626.736544 |
| | aVTZ | -627.058242 |
| | aVQZ | -627.162668 |
| | CBS (DTQ) | -627.222122 |
| $XeF_3$ ($C_{2v}$) | aVDZ | -627.136494 |
| | aVTZ | -627.447757 |
| | aVQZ | -627.551167 |
| | CBS (DTQ) | -627.610297 |
| $XeF_3^-$ ($C_s$) | aVDZ | -627.290996 |
| | aVTZ | -627.603399 |
| | aVQZ | -627.708918 |
| | CBS (DTQ) | -627.769436 |
| $XeF_3^-$ ($C_{2v}$) | aVDZ | -627.289741 |
| | aVTZ | -627.601554 |
| | aVQZ | -627.706878 |
| | CBS (DTQ) | -627.767285 |
| $XeF_5^+$ ($C_{4v}$) | aVDZ | -825.916031 |
| | aVTZ | -826.423761 |
| | aVQZ | -826.587511 |
| | CBS (DTQ) | -826.680627 |
| $XeF_5$ ($C_{4v}$) | aVDZ | -826.307448 |
| | aVTZ | -826.793645 |
| | aVQZ | -826.953584 |
| | CBS (DTQ) | -827.044871 |
| $XeF_7^+$ ($D_{5h}$) | aVDZ | -1025.004290 |
| | aVTZ | -1025.695687 |
| | aVQZ | -1025.916391 |
| | CBS (DTQ) | -1026.041646 |
| $XeF_7^-$ ($C_{2v}$) | aVDZ | -1025.708092 |
| | aVTZ | -1026.366555 |
| | aVQZ | -1026.584442 |
| | CBS (DTQ) | -1026.708939 |
| $XeF_7^-$ ($D_{5h}$) | aVDZ | -1025.709358 |

| | | |
|---|---|---|
| | aVTZ | -1026.365922 |
| | aVQZ | -1026.583562 |
| | CBS (DTQ) | -1026.707958 |
| $XeF_7^-$ ($C_{3v}$) | aVDZ | -1025.707895 |
| | aVTZ | -1026.366442 |
| | aVQZ | -1026.584313 |
| | CBS (DTQ) | -1026.708796 |
| $XeF_8$ ($D_{4d}$) | aVDZ | -1125.004373 |
| | aVTZ | -1125.776607 |
| | aVQZ | -1126.025515 |
| | CBS (DTQ) | -1126.167040 |

[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 Xe RECP has a 28 electron core, leaving 26 electrons to be explicitly treated.

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

**Table SM-2**. CCSD(T) Total Energies ($E_h$) as a Function of the Basis Set.[a,b]

| Molecule | Basis Set | Energy |
|---|---|---|
| $XeF^-$ ($C_{\infty v}$) | awCVDZ | -428.556602 |
| | awCVTZ | -429.070331 |
| | awCVQZ | -429.281393 |
| | CBS $(DTQ)_{CV}$ | -429.406318 |
| $XeF_2$ ($D_{\infty h}$) | awCVDZ | -528.101771 |
| | awCVTZ | -528.723365 |
| | awCVQZ | -528.963850 |
| | CBS $(DTQ)_{CV}$ | -529.104926 |
| $XeF_3^+$ ($C_{2v}$) | awCVDZ | -627.290432 |
| | awCVTZ | -628.027599 |
| | awCVQZ | -628.295103 |
| | CBS $(DTQ)_{CV}$ | -628.450439 |
| $XeF_3$ ($C_{2v}$) | awCVDZ | -627.688558 |
| | awCVTZ | -628.414911 |
| | awCVQZ | -628.682648 |
| | CBS $(DTQ)_{CV}$ | -628.838516 |
| $XeF_3^-$ ($C_s$) | awCVDZ | -627.842653 |
| | awCVTZ | -628.570622 |
| | awCVQZ | -628.840537 |
| | CBS $(DTQ)_{CV}$ | -628.997821 |
| $XeF_3^-$ ($C_{2v}$) | awCVDZ | -627.841391 |
| | awCVTZ | -628.568832 |
| | awCVQZ | -628.838574 |
| | CBS $(DTQ)_{CV}$ | -628.995760 |
| $XeF_4$ ($D_{4h}$) | awCVDZ | -727.355872 |
| | awCVTZ | -728.196262 |
| | awCVQZ | -728.496113 |
| | CBS $(DTQ)_{CV}$ | -728.669737 |
| $XeF_5^+$ ($C_{4v}$) | awCVDZ | -826.552488 |
| | awCVTZ | -827.523179 |
| | awCVQZ | -827.854095 |
| | CBS $(DTQ)_{CV}$ | -828.044199 |
| $XeF_5$ ($C_{4v}$) | awCVDZ | -826.941706 |

| | | |
|---|---|---|
| | awCVTZ | -827.888068 |
| | awCVQZ | -828.216991 |
| | CBS $(DTQ)_{CV}$ | -828.406594 |
| $XeF_5^-$ ($D_{5h}$) | awCVDZ | -827.157465 |
| | awCVTZ | -828.103578 |
| | awCVQZ | -828.434351 |
| | CBS $(DTQ)_{CV}$ | -828.625215 |
| $XeF_6$ ($O_h$) | awCVDZ | -926.599019 |
| | awCVTZ | -927.658496 |
| | awCVQZ | -928.019200 |
| | CBS $(DTQ)_{CV}$ | -928.226368 |
| $XeF_6$ ($C_{3v}$) | awCVDZ | -926.587101 |
| | awCVTZ | -927.656393 |
| | awCVQZ | -928.018669 |
| | CBS $(DTQ)_{CV}$ | -928.226558 |
| $XeF_6$ ($C_{2v}$) | awCVDZ | -926.582604 |
| | awCVTZ | -927.654675 |
| | awCVQZ | -928.016872 |
| | CBS $(DTQ)_{CV}$ | -928.224611 |
| $XeF_7^+$ ($D_{5h}$) | awCVDZ | -1025.718973 |
| | awCVTZ | -1026.921037 |
| | awCVQZ | -1027.313874 |
| | CBS $(DTQ)_{CV}$ | -1027.537817 |
| $XeF_7^-$ ($C_{2v}$) | awCVDZ | -1026.424880 |
| | awCVTZ | -1027.590504 |
| | awCVQZ | -1027.982763 |
| | CBS $(DTQ)_{CV}$ | -1028.207584 |
| $XeF_7^-$ ($D_{5h}$) | awCVDZ | -1026.425424 |
| | awCVTZ | -1027.589245 |
| | awCVQZ | -1027.981130 |
| | CBS $(DTQ)_{CV}$ | -1028.205761 |
| $XeF_7^-$ ($C_{3v}$) | awCVDZ | -1026.424753 |
| | awCVTZ | -1027.590427 |
| | awCVQZ | -1027.982717 |
| | CBS $(DTQ)_{CV}$ | -1028.207557 |
| $XeF_8$ ($D_{4d}$) | awCVDZ | -1125.759749 |

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|---|---|
| awCVTZ | -1127.062694 |
| awCVQZ | -1127.486749 |
| CBS $(DTQ)_{CV}$ | -1127.728299 |

[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 Xe RECP has a 28 electron core, leaving 26 electrons to be explicitly treated.

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

**Table SM-3**. Calculated MP2 and CCSD(T) with the aVTZ Basis Set Geometry Parameters of the Xenon Fluoride Molecules and their Ions. Bond Distances in Å and Bond Angles in Degrees.

| Molecule | Method | $R_e$ (Å) | ∠FXeF (deg) |
|---|---|---|---|
| $XeF^+$ | MP2 | 1.8674 | |
| | CCSD(T) | 1.8830 | |
| | expt.[a] | 1.872(17) | |
| $XeF_3^+$ ($C_{2v}$)[b] | MP2 | 1.8830/1.8380 | 83.3 |
| | CCSD(T) | 1.8907/1.8528 | 83.0 |
| | expt.[c] | 1.88(1)/1.83(1) | 81.0(1) |
| $XeF_3$ ($C_{2v}$)[b] | MP2 | 1.8534/3.3811 | 89.9 |
| | CCSD(T) | 1.9743/2.3221 | 90.2 |
| $XeF_3^-$ ($C_s$)[d] | MP2 | 2.4921/2.0596/1.9911 | 120.4/73.1 |
| | CCSD(T) | 2.5098/2.0729/2.0021 | 121.0/72.4 |
| $XeF_3^-$ ($C_{2v}$)[b] | MP2 | 2.1129/2.1726 | 145.2 |
| | CCSD(T) | 2.0195/2.6613 | 93.8 |
| $XeF_5^+$ ($C_{4v}$)[b] | MP2 | 1.8111/1.8439 | 82.8 |
| | CCSD(T) | 1.8202/1.8491 | 82.6 |
| | expt.[e] | 1.813(7)/1.843(8) | 79.2(4)ax-eq |
| $XeF_5$ ($C_{4v}$)[b] | MP2 | 3.6967/1.9498 | 89.9 |
| | CCSD(T) | 2.2276/1.9348 | 89.4 |
| $XeF_7^+$ ($D_{5h}$)[f] | MP2 | 1.8337/1.8899 | 180.0/72.0 |
| | CCSD(T) | 1.8074/1.8661 | 180.0/72.0 |
| $XeF_7^-$ ($C_{2v}$)[g] | MP2 | 1.9879/1.9945/2.0255 | 78.8/143.2 |
| | CCSD(T) | 1.9641/1.9815/2.0341 | 78.2/142.9 |
| | expt.[h] | 1.842/1.890/2.189 | |
| $XeF_7^-$ ($D_{5h}$)[f] | MP2 | 1.9781/2.0160 | 180.0/72.0 |
| | CCSD(T) | 1.9708/2.0078 | 180.0/72.0 |
| $XeF_7^-$ ($C_{3v}$)[g] | MP2 | 2.0312/2.0086/1.9865 | 74.9/130.9 |
| | CCSD(T) | 2.0441/2.0046/1.9667 | 75.4/131.3 |
| | expt.[h] | 2.100/1.932/1.970 | |

| | | | |
|---|---|---|---|
| $XeF_8$ ($D_{4d}$)[i] | MP2 | 1.8952 | 73.1/77.9 |
| | CCSD(T) | 1.8984 | 73.0/78.0 |
| $KrF_3^-$ ($C_{2v}$)[b] | MP2 | 1.8899/2.5941 | 93.6 |
| | CCSD(T) | 1.8989/2.6020 | 93.5 |
| $KrF_5^-$ ($D_{5h}$) | MP2 | 1.9942 | 72.0 |
| | CCSD(T) | 1.9772 | 72.0 |
| $KrF_7^-$ ($D_{5h}$)[f] | MP2 | 1.8771/1.9972 | 180.0/72.0 |
| | CCSD(T) | 1.9186/2.0133 | 180.0/72.0 |

[a] Bartlett, N.; Gennis, M. Gibler, D. D.; Morrell, B. K.; Zalkin, A. *Inorg. Chem.* **1973**, *12*, 1717.

[b] Bond distance corresponds to $r(Xe\text{-}F_a)$ and $r(Xe\text{-}F_e)$ in the $C_{2v}$ or $C_{4v}$ structures. Angle corresponds to $\angle F_aXeF_e$. The long $Xe\text{-}F_a$ distances in $XeF_3$ and $XeF_5$ at the MP2 level are due to the fact that they are unbound with respect to $XeF_2$ and $XeF_4$ respectively.

[c] McKee, D. E.; Zalkin, A.; Bartlett, N. *Inorg. Chem.* **1973**, *8*, 1713.

[d] Bond distances correspond to $r(Xe\text{-}F_1)$, $r(Xe\text{-}F_2)$ and $r(Xe\text{-}F_3)$. See Figure 1.

[e] Leary, K.; Templeton, D. H.; Zalkin, A.; Bartlett, N. *Inorg. Chem.* **1973**, *12*, 1726.

[f] Bond distances correspond to $r(Xe\text{-}F_a)$ and $r(Xe\text{-}F_e)$ in the $D_{5h}$ structure.

[g] Bond distances correspond to $r(Xe\text{-}F_1)$, $r(Xe\text{-}F_2)$, and $r(Xe\text{-}F_3)$. Angles correspond to $\angle F_1XeF_2$ and $\angle F_1XeF_3$. See Figure 1.

[h] Ellern, A.; Mahjoub, A-R.; Seppelt, K. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1123.

[i] First $\angle FXeF$ angles is between adjacent F atoms on the same square face, while the second is between F atoms on separate planes.

**Table SM-4**. $T_1$ Diagnostics Calculated at the CCSD(T)/aVQZ Level.

| **Molecule** | $T_1$ **Diagnostics** |
|---|---|
| $XeF_3^+$ ($C_{2v}$) | 0.018 |
| $XeF_3$ ($C_{2v}$) | 0.034 |
| $XeF_3^-$ ($C_s$) | 0.030 |
| $XeF_3^-$ ($C_{2v}$) | 0.018 |
| $XeF_5^+$ ($C_{4v}$) | 0.018 |
| $XeF_5$ ($C_{4v}$) | 0.031 |
| $XeF_7^+$ ($D_{5h}$) | 0.016 |
| $XeF_7^-$ ($C_{2v}$) | 0.018 |
| $XeF_7^-$ ($D_{5h}$) | 0.018 |
| $XeF_7^-$ ($C_{3v}$) | 0.018 |
| $XeF_8$ ($D_{4d}$) | 0.015 |

**Table SM-5**. Calculated $F^+$ (FPA) and $F^-$ (FA) Affinities in kcal/mol at 0 K.

| **Molecule** | **FPA** | **FA** |
|---|---|---|
| Xe | 1651.1 | 6.3 |
| $XeF_2$ | 155.3 | 19.9 |
| $XeF_4$ | 172.7 | 59.1 |
| $XeF_6$ | 132.5 | 75.0 |
| Kr | 119.7[a] | 3.8[a] |
| $KrF_2$ | 104.5[a] | 16.8[a] |
| $KrF_4$ | 100.1[a] | 35.5[a] |
| $KrF_6$ | | 45.2[a] |

[a] Dixon, D. A.; Wang, T-H.; Grant , D. J.; Peterson , K. A.; Christe, K. O., *Inorg. Chem.* **2007**, *46*, 10016. The heats of formation of $F^+$ and $F^-$ are 420.2 and -59.96 kcal/mol respectively.

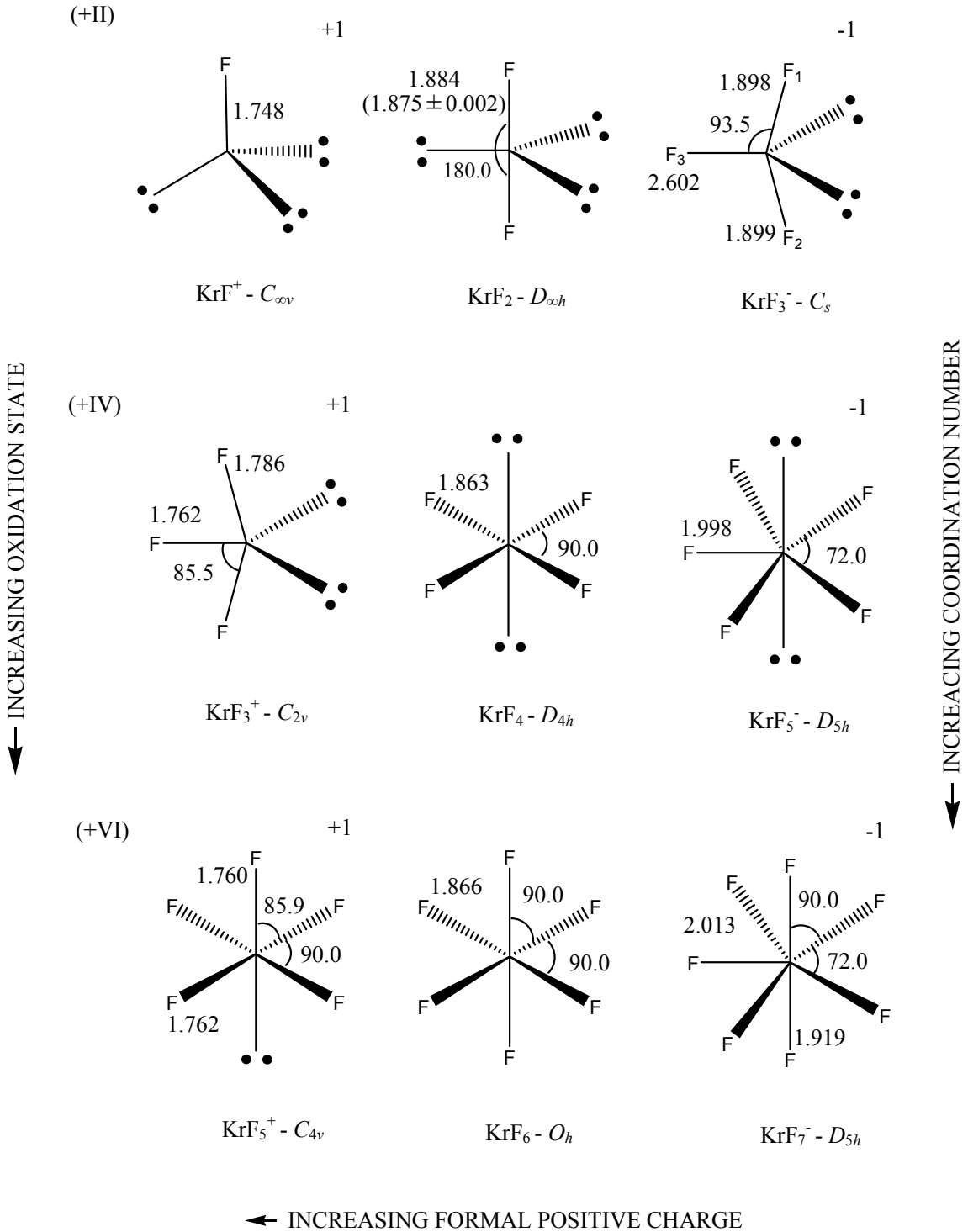
**Table SM-6**. Calculated Heats of Reaction for Loss of $F_2$ from the Cationic, Neutral and Anionic Xenon Fluorides in kcal/mol at 0 K.

| **Reaction** | **$\Delta H_{rxn}$** |
|---|---|
| $XeF_3^+ \rightarrow XeF^+ + F_2$ | 14.8 |
| $XeF_5^+ \rightarrow XeF_3^+ + F_2$ | 37.8 |
| $XeF_5^+ \rightarrow XeF^+ + 2F_2$ | 52.6 |
| $XeF_7^+ \rightarrow XeF_5^+ + F_2$ | -24.1 |
| $XeF_7^+ \rightarrow XeF_3^+ + 2F_2$ | 13.7 |
| $XeF_7^+ \rightarrow XeF^+ + 3F_2$ | 28.5 |
| $XeF_2 \rightarrow Xe + F_2$ | 24.6 |
| $XeF_4 \rightarrow Xe + F_2$ | 20.4 |
| $XeF_4 \rightarrow Xe + 2F_2$ | 45.0 |
| $XeF_6 \rightarrow Xe + F_2$ | 16.1 |
| $XeF_6 \rightarrow Xe + 2F_2$ | 36.5 |
| $XeF_6 \rightarrow Xe + 3F_2$ | 61.0 |
| $XeF_8 \rightarrow Xe + F_2$ | -22.3 |
| $XeF_8 \rightarrow Xe + 2F_2$ | -6.2 |
| $XeF_8 \rightarrow Xe + 3F_2$ | 14.2 |
| $XeF_8 \rightarrow Xe + 4F_2$ | 38.7 |
| $XeF_3^- \rightarrow XeF^- + F_2$ | 38.2 |
| $XeF_5^- \rightarrow XeF_3^- + F_2$ | 59.6 |
| $XeF_5^- \rightarrow XeF^- + 2F_2$ | 97.8 |
| $XeF_7^- \rightarrow XeF_5^- + F_2$ | 31.9 |
| $XeF_7^- \rightarrow XeF_3^- + 2F_2$ | 91.5 |
| $XeF_7^- \rightarrow XeF^- + 3F_2$ | 129.7 |

**Figure Captions**

**Figure SM-1.** Calculated CCSD(T)/aVTZ and experimental geometries in parenthesis of the krypton fluoride molecules and their ions (bond lengths in angstroms and bond angles in degrees. The structures for $KrF^+$, $KrF^-$, $KrF_2$, $KrF_3^+$, $KrF_4$, $KrF_5^+$, and $KrF_6$ taken from Dixon, D. A.; Wang, T-H.; Grant , D. J.; Peterson , K. A.; Christe, K. O., *Inorg. Chem.* **2007**, *46*, 10016. Experimental geometry for $KrF_2$ from Murchinson, C.; Reichman, S.; Anderson, D.; Overend, J.; Schreiner, F. *J. Am. Chem. Soc.* **1968**, *90*, 5690.

**Figure SM-1.**


(+II)
+1
-1
F
1.748
1.884
(1.875 ± 0.002)
F
180.0
F
1.898
F1
93.5
F3
2.602
1.899
F2
KrF+ - C∞v
KrF2 - D∞h
KrF3- - Cs
INCREASING OXIDATION STATE
INCREACING COORDINATION NUMBER
(+IV)
+1
-1
F
1.786
1.762
F
85.5
F
1.863
F
F
90.0
F
F
1.998
F
F
72.0
F
F
KrF3+ - C2v
KrF4 - D4h
KrF5- - D5h
(+VI)
+1
-1
F
1.760
F
85.9
F
F
90.0
F
F
1.762
1.866
F
90.0
F
F
90.0
F
F
2.013
F
F
90.0
F
F
72.0
F
F
1.919
F
KrF5+ - C4v
KrF6 - Oh
KrF7- - D5h
INCREASING FORMAL POSITIVE CHARGE