Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary information

## A new krypton complex – Experimental and computational investigation of the krypton sulphur pentafluoride cation, $[KrSF_5]^+$, in the gas phase

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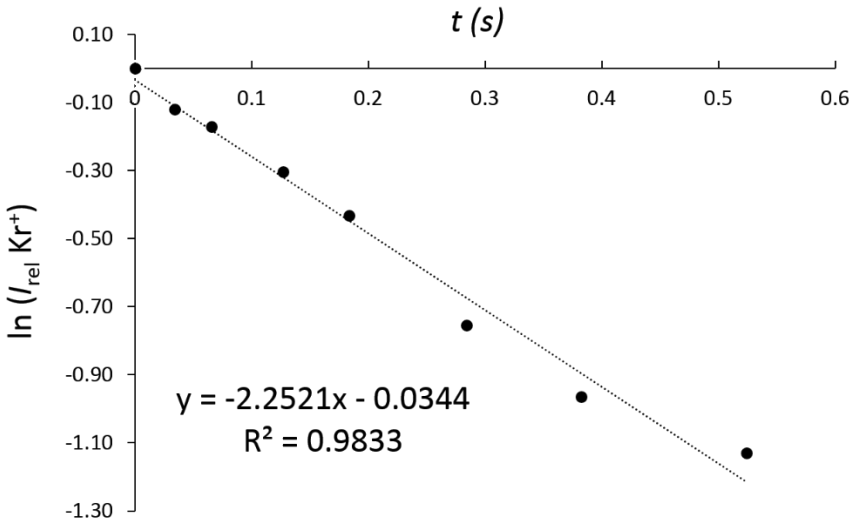


**Figure S1** – Kinetic plot for a reaction of isolated, thermalised $Kr^+$ with $SF_6$.

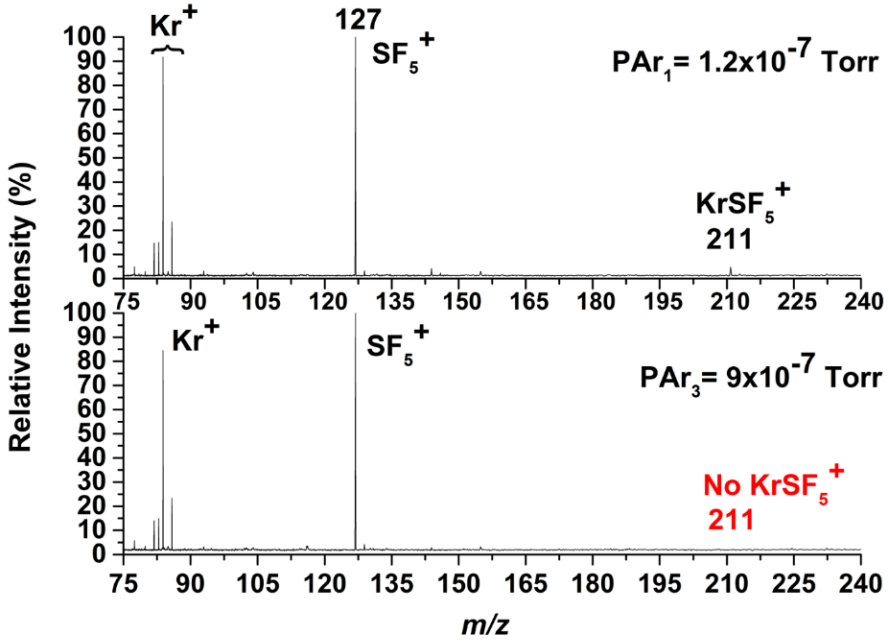


**Figure S2** – Mass spectra of a 0.5 s reaction of isolated, thermalised $Kr^+$ with $SF_6$ at two different Ar pressures.

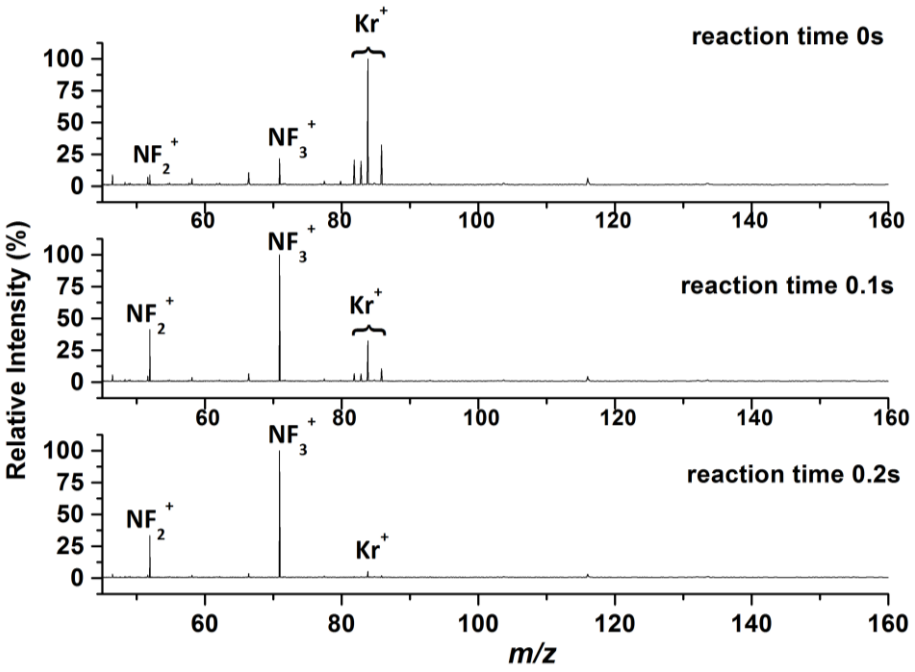


**Figure S3** – Mass spectra of the reaction of isolated, thermalised $Kr^+$ with $NF_3$.

**Table S1** – Final coordinates and energy ($E_h$, BCCD(T)) from single point energy calculations on geometry optimised structures (MP2) reported in this study.

| **$KrSF_6^+$** | | | | **$XeSF_6^+$** | | | |
|---|---|---|---|---|---|---|---|
| -3747.9 $E_h$ (-2351827.7 kcal/mol) | | | | -1324.2 $E_h$ (-830948.22 kcal/mol) | | | |
| S | -0.058078000 | -0.095547000 | 0.058321000 | S | 0.082680000 | 0.091591000 | 0.071651000 |
| F | 0.078799000 | -0.349799000 | 1.565504000 | F | -0.196430000 | -1.372323000 | -0.284224000 |
| F | 0.226768000 | 0.425211000 | -1.387679000 | F | -0.030446000 | -0.176731000 | 1.588161000 |
| F | 1.432607000 | 0.311088000 | 0.003174000 | F | -1.440671000 | 0.449177000 | 0.022462000 |
| F | 1.581896000 | -0.235605000 | 0.173545000 | F | 0.366306000 | 1.688155000 | 0.436330000 |
| F | -0.376291000 | 1.649213000 | 0.581237000 | F | 1.609435000 | -0.133914000 | 0.125384000 |
| F | 0.186319000 | -1.530270000 | -0.350957000 | F | 0.196269000 | 0.491984000 | -1.437658000 |
| Kr | 0.544679000 | 3.394709000 | -0.374871000 | Xe | -0.586170000 | 3.863968000 | -0.576030000 |
| **$KrSF_5^+$ (Conf. 1)** | | | | **$XeSF_5^+$ (Conf. 1)** | | | |
| -3648.232 Eh (-2289300.13 kcal/mol) | | | | -1224.471 Eh (-768322.76 kcal/mol) | | | |
| S | 0.001384000 | 0.563744000 | -0.036476000 | S | 0.000000000 | -0.099606000 | -0.089783000 |
| F | 0.005436000 | 0.259726000 | 1.464264000 | F | -0.000001000 | -0.338902000 | 1.385426000 |
| F | -0.002396000 | 0.854156000 | -1.540425000 | F | 0.000001000 | -1.280397000 | -1.005991000 |
| F | 1.320951000 | -0.123485000 | -0.176551000 | F | 1.531385000 | -0.097412000 | -0.099736000 |
| F | -1.291257000 | -0.172321000 | -0.179404000 | F | -1.531385000 | -0.097412000 | -0.099739000 |
| F | -0.026366000 | 2.029850000 | 0.253320000 | F | 0.000001000 | 1.308687000 | -0.591146000 |
| Kr | 0.071969000 | -3.293022000 | -0.293879000 | Xe | -0.000002000 | 0.540428000 | -4.093606000 |
| **$KrSF_5^+$ (Conf. 2)** | | | | **$XeSF_5^+$(Conf. 2)** | | | |
| -3648.231 $E_h$ (-2289299.5 kcal/mol) | | | | -1224.469 $E_h$ (-768365.89 kcal/mol) | | | |
| S | 0.001915000 | 0.348898000 | 0.121476000 | S | 0.001698000 | 0.351754000 | 0.145057000 |
| F | 0.003954000 | -0.765396000 | 1.118644000 | F | -0.003485000 | -0.753388000 | 1.152595000 |
| F | 0.011377000 | 0.043886000 | -1.341310000 | F | 0.009797000 | 0.034048000 | -1.314981000 |
| F | 1.533329000 | 0.349813000 | 0.132373000 | F | 1.533288000 | 0.352453000 | 0.155016000 |
| F | -1.529505000 | 0.348452000 | 0.112813000 | F | -1.529898000 | 0.351497000 | 0.138194000 |
| F | -0.001704000 | 1.768908000 | 0.590100000 | F | -0.001246000 | 1.775909000 | 0.601204000 |
| Kr | -0.011457000 | -0.565157000 | -4.599097000 | Xe | -0.010155000 | -0.582869000 | -4.742085000 |

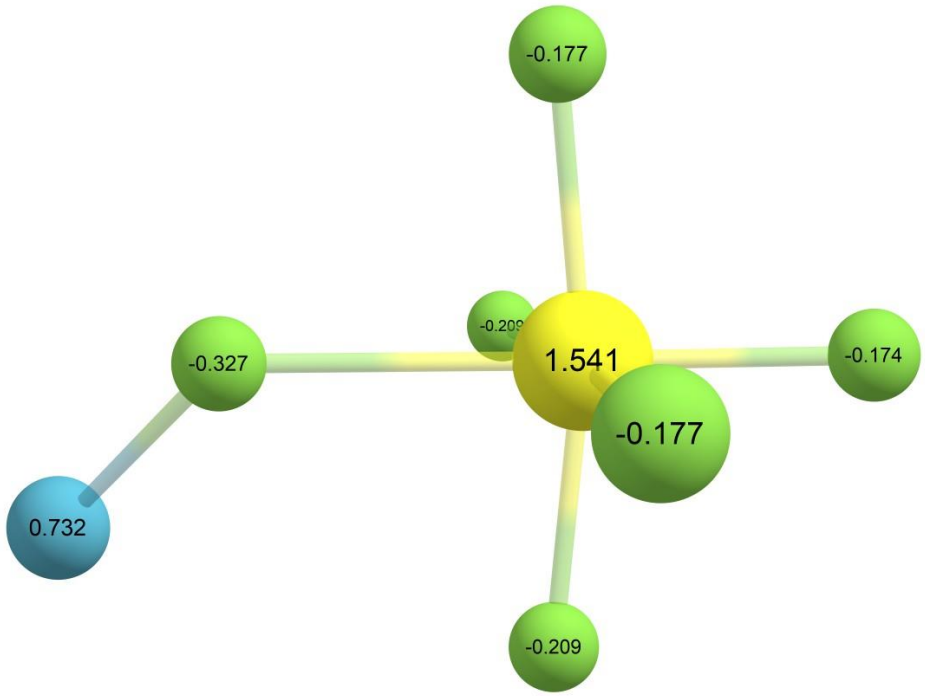


**Figure S4** – Mulliken charges in $[KrSF_6]^+$ computed at the MP2/def2-TZVPP level.

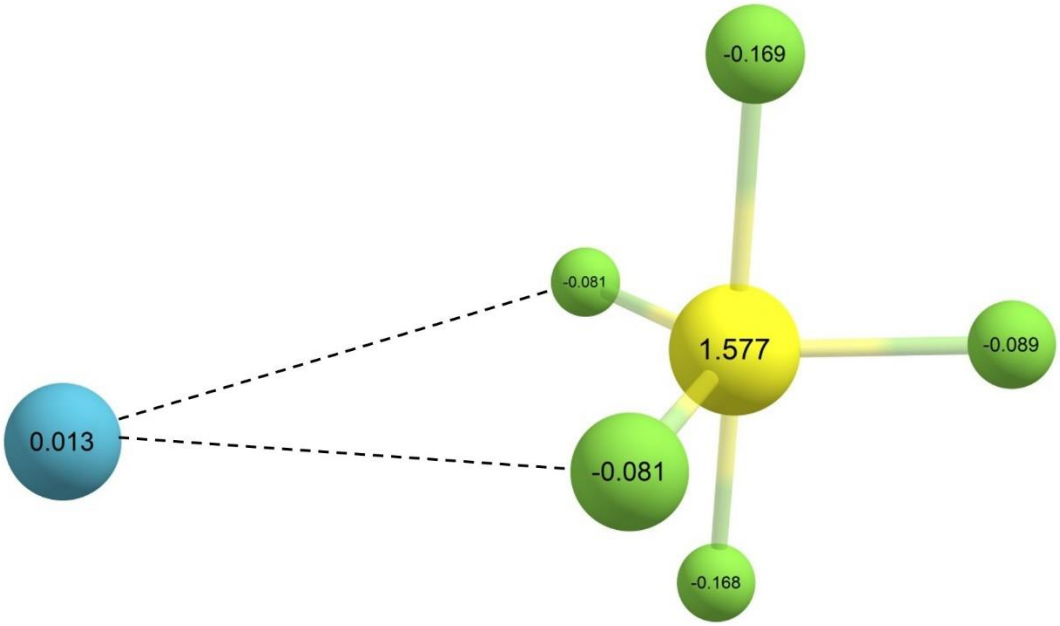


**Figure S5** – Mulliken charges in $[KrSF_5]^+$ (Conformer 1) computed at the MP2/def2-TZVPP level.

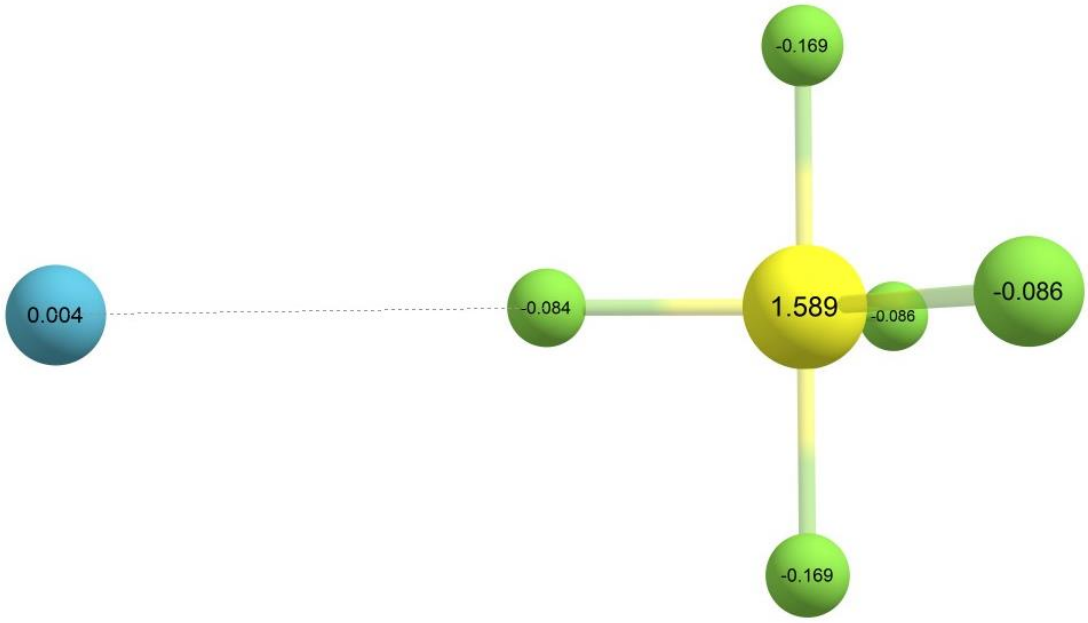


**Figure S6** – Mulliken charges in $[KrSF_5]^+$ (Conformer 2) computed at the MP2/def2-TZVPP level.

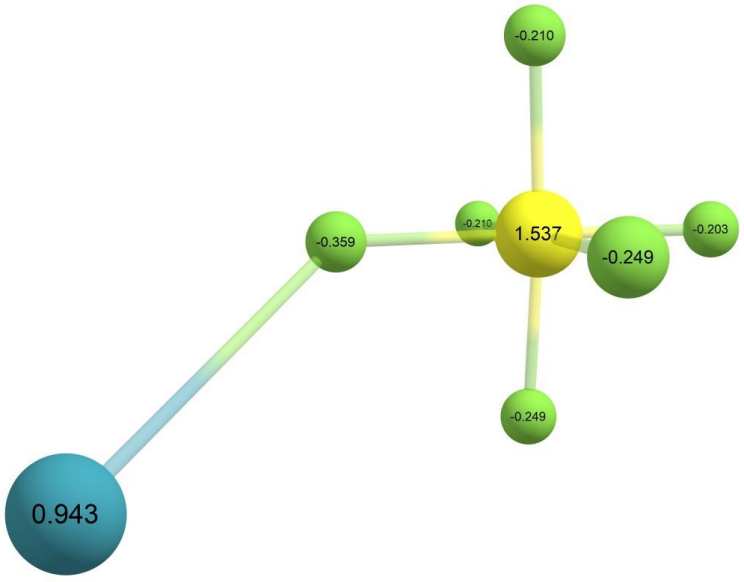


**Figure S7** – Mulliken charges in $[XeSF_6]^+$ computed at the MP2/def2-TZVPP level.

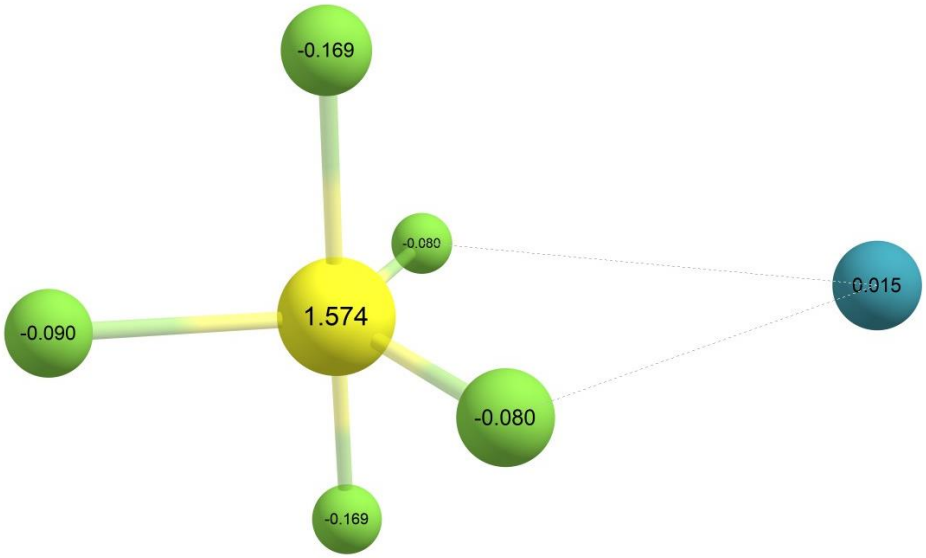


**Figure S8** – Mulliken charges in $[XeSF_5]^+$ (Conformer 1) computed at the MP2/def2-TZVPP level.

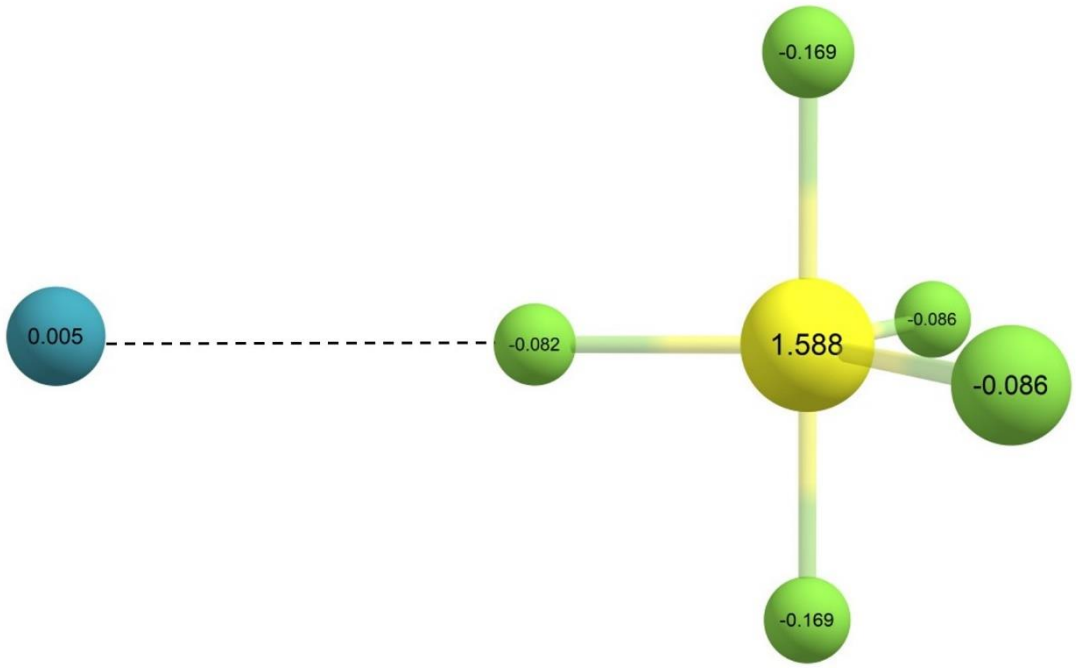


**Figure S9** – Mulliken charges in $[XeSF_5]^+$ (Conformer 2) computed at the MP2/def2-TZVPP level.

**Table S2** – Enthalpies and Gibbs energies of reaction (kcal/mol) computed by MP2 and BCCD(T) methods for $Ng^+ + SF_6$ [a]

| Reaction | MP2[b] | | | | BCCD(T)[c] | | | |
|---|---|---|---|---|---|---|---|---|
| | ΔH | | ΔG | | ΔH | | ΔG | |
| | Conf. 1 | Conf. 2 | Conf. 1 | Conf.2 | Conf. 1 | Conf.2 | Conf. 1 | Conf.2 |
| $Kr^+ + SF_6 \rightarrow KrSF_6^+$ | -17.4 | -17.4 | 12.9 | 12.9 | -18.0 | -18.0 | 12.3 | 12.3 |
| $KrSF_6^+ \rightarrow Kr\cdots SF_5^+ + F$ | 16.4 | 17.4 | -17.8 | -17.9 | 15.0 | 16.0 | -19.1 | -19.3 |
| $Kr\cdots SF_5^+ \rightarrow Kr + SF_5^+$ | 4.1 | 3.1 | -15.3 | -15.2 | 3.2 | 2.2 | -16.3 | -16.1 |
| $Kr^+ + SF_6 \rightarrow Kr + SF_5^+ + F$ | 3.1 | 3.1 | -20.2 | -20.2 | 0.2 | 0.2 | -23.1 | -23.1 |
| $Xe^+ + SF_6 \rightarrow XeSF_6^+$ | -9.8 | -9.8 | 20.0 | 20.0 | -11.7 | -11.7 | 18.1 | 18.1 |
| $XeSF_6^+ \rightarrow Xe\cdots SF_5^+ + F$ | 47.1 | 48.3 | 13.5 | 13.5 | 46.4 | 47.5 | 12.7 | 12.7 |
| $Xe\cdots SF_5^+ \rightarrow Xe + SF_5^+$ | 4.7 | 3.5 | -14.8 | -14.8 | 3.7 | 2.6 | -15.6 | -15.6 |
| $Xe^+ + SF_6 \rightarrow Xe + SF_5^+ + F$ | 42.0 | 42.0 | 18.7 | 18.7 | 38.4 | 38.4 | 15.2 | 15.2 |

[a] ΔH and ΔG were computed at T = 298.15 K and the entropy was corrected for a pressure of $10^{-7}$ Torr ($S_2 = S_1 - R\ln(P_2/P_1)$).

[b] Basis set def2-TZVPP. [c] Basis set cc-pVTZ.

**Table S3** – Thermochemical calculations for $HXF_n^+ \rightarrow XF_{n-1}^+ + HF$ (X = S, n = 6; X = N, n = 3; X = Si, n = 4)

| **Reaction** | **ΔH (kcal/mol)** [ $\Delta H = AE(XF_{n-1}^+/XF_n) + PA(XF_n) + \Delta_fH^o(HF) - \Delta_fH^o(F) - \Delta_fH^o(H^+)$ ] | |
|---|---|---|
| $HSF_6^+ \rightarrow SF_5^+ + HF$ (X = S, n = 6) | -5.2 ± 4.8 | |
| $HNF_3^+ \rightarrow NF_2^+ + HF$ (X = N, n = 3) | 10.6 ± 1.9 | |
| $HSiF_4^+ \rightarrow SiF_4^+ + HF$ (X = Si, n = 4) | 24.9 ± 4.6 | |
| **Data (kcal/mol)[a]** | **$AE(XF_{n-1}^+/XF_n)$** | **$PA(XF_n)$** |
| **X = S** | 308.6 ± 4.4[b] | 137.5 ± 1.9[c] |
| **X = N** | 326.0 ± 0.2[d] | 135.9 ± 1.9[c] |
| **X = Si** | 374.0 ± 4.2[e] | 102.2 ± 1.9[c] |
| **$\Delta_fH^o(HF)$** | -65.14 ± 0.19[f] | |
| **$\Delta_fH^o(F)$** | 19.97 ± 0.07[f] | |
| **$\Delta_fH^o(H^+)$** | 367.17 ± 0.01[f] | |

[a] T = 298.15 K.

[b] E. R. Fisher, B. L. Kickel and P. B. Armentrout, *J. Chem. Phys.*, 1992, **97**, 4859-4870; converted to 298.15 K considering a difference of -0.94 kcal/mol between $\Delta_fH^o(SF_5^+)$ [298.15 K] and $\Delta_fH^o(SF_5^+)$ [0 K] in ref. f.

[c] E. P. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data*, 1998, **27**, 413-656.

[d] J. Berkowitz, J. P. Greene, J. Foropoulos Jr. and O. M. Nesković, *J. Chem. Phys.*, 1984, **81**, 6166-6175; in the absence of data for $NF_2^+$ in ref. f, converted to 298.15 K considering a difference of +0.8 kcal/mol between $\Delta_fH^o(PF_2^+)$ [298.15 K] and $\Delta_fH^o(PF_2^+)$ [0 K] in ref. f.

[e] B. L. Kickel, E. R. Fisher and P. B. Armentrout, *J. Phys. Chem.*, 1993, **97**, 10198-10203; converted to 298.15 K considering a difference of +0.23 kcal/mol between $\Delta_fH^o(SiF_3^+)$ [298.15 K] and $\Delta_fH^o(SiF_3^+)$ [0 K] in ref. f.

[f] M. W. Chase, Jr., Ed., *NIST-JANAF Thermochemical Tables, 4th ed., J. Phys. Chem. Ref. Data Monogr. 9*, AIP and ACS, New York, USA, 1998.

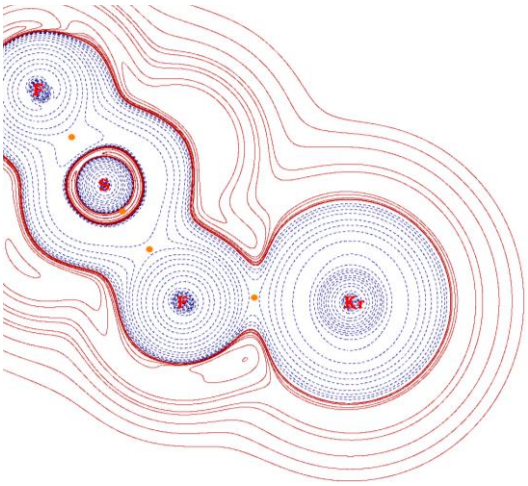

**Figure S10** – Energy density map of the $[KrSF_6]^+$ species with (3,+1) Hamiltonian critical points signalled as orange dots.

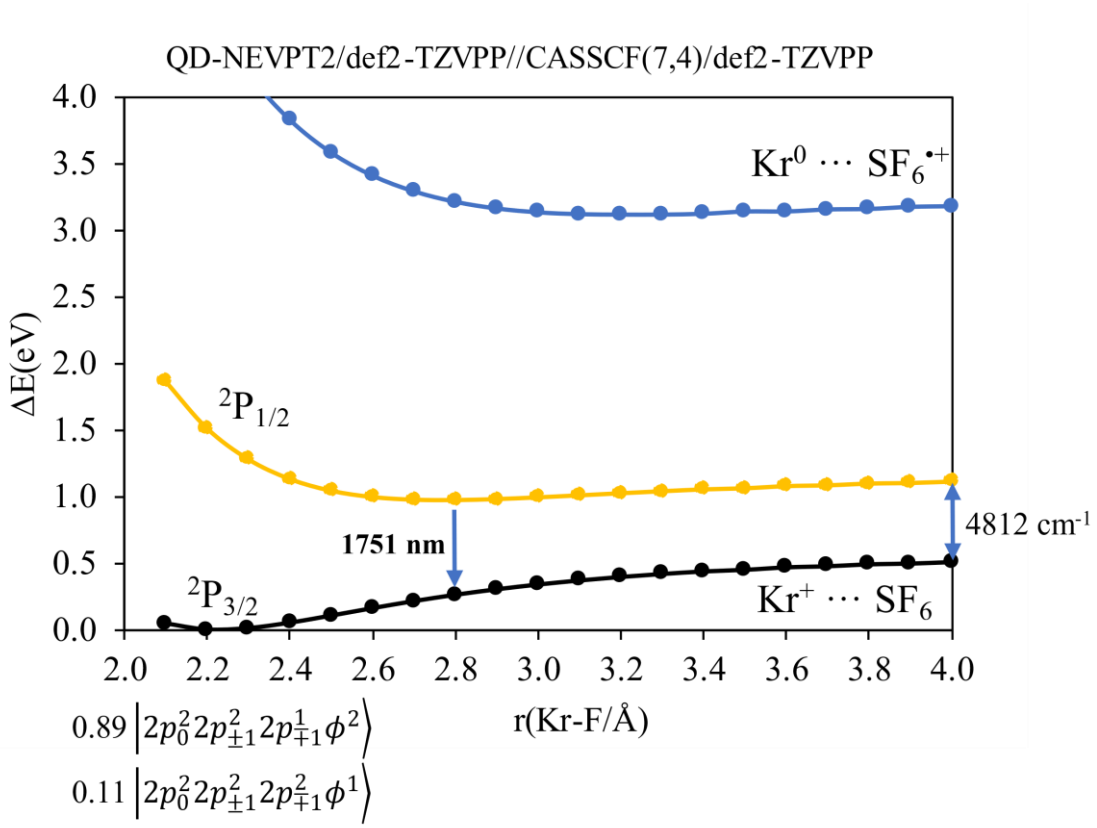


**Figure S11** – Potential energy surface map along with the Kr-F distance coordinate in $[KrSF_6]^+$ including spin-orbit coupling. The dissociation limit agrees with the experimentally determined value of 5370.1 $cm^{-1}$ (E. B. Saloman, *J. Phys. Chem. Ref. Data*, 2007, **36**, 215-386). The minimum in the "$^2P_{1/2}$" surface lies at 2.8 Å. A localised basis set was used throughout allowing for the determination of the extent of charge transfer at the equilibrium bond distance using two valence bond like configurations.