INL/CON-23-72710-Revision-0



# Impact of the Electronic Properties of Chalcogenide Ligands in their Complexation with Uranyl Nitrate Complexes

May 2023

Cristian Celis-Barros, Brittany Dawn Marie Hodges, Christopher A Zarzana, JungSoo Kim

Changing the World's Energy Future


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**Idaho National Laboratory**
**Idaho Falls, Idaho 83415**

**http://www.inl.gov**

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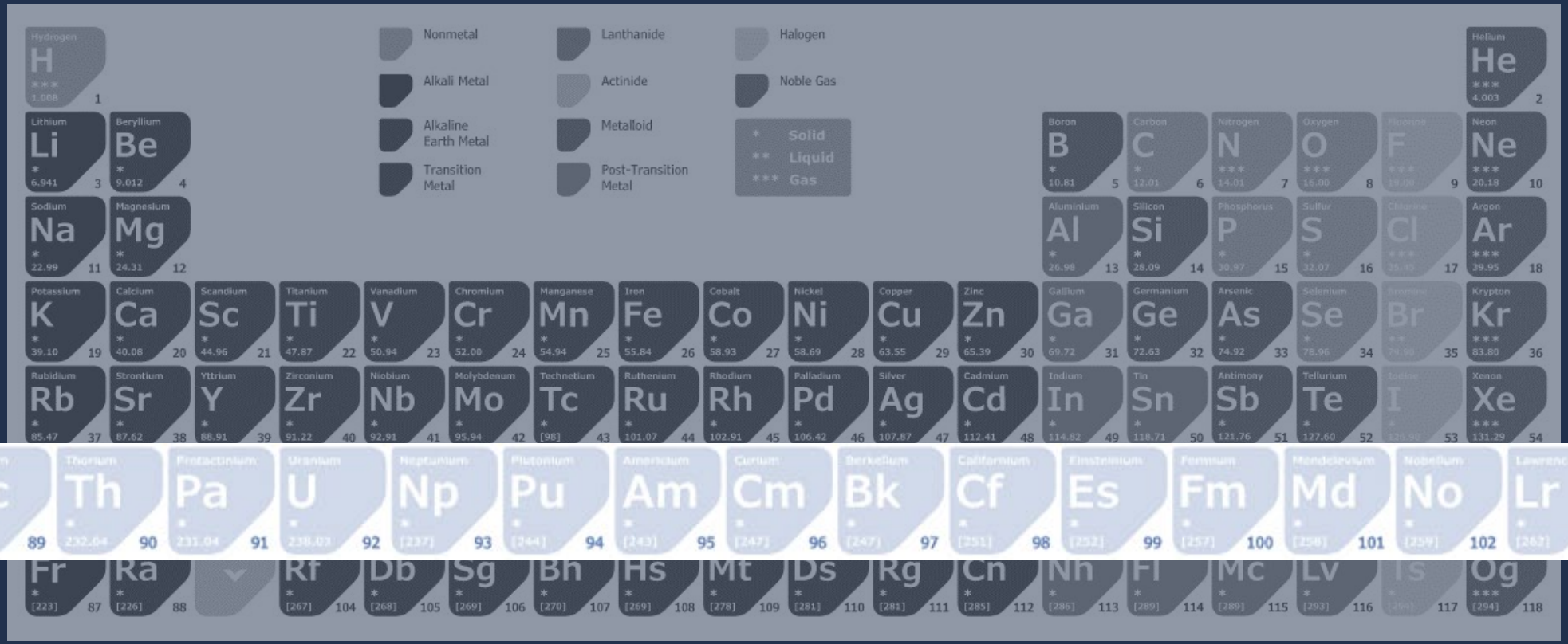
Idaho Falls
May 18th, 2023

# Impact of the Electronic Properties of Chalcogenide Ligands in their Complexation with Uranyl Nitrate Complexes

**Cristian Celis-Barros**,[a] Christopher Zarzana,[b] Brittany Hodges,[b] JungSoo Kim[b]

[a] Nuclear Science and Engineering Center, Colorado School of Mines, Golden, CO, USA

[b] Idaho National Laboratory, Idaho Falls, ID, USA

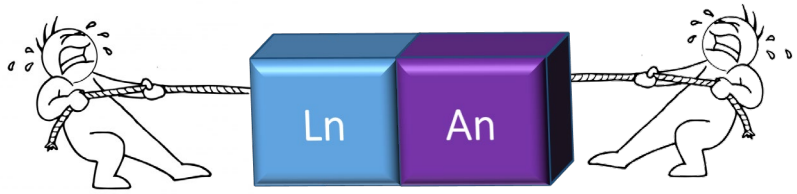



# SEPARATION LIGANDS

Rationalizing the driving forces for actinide selectivity

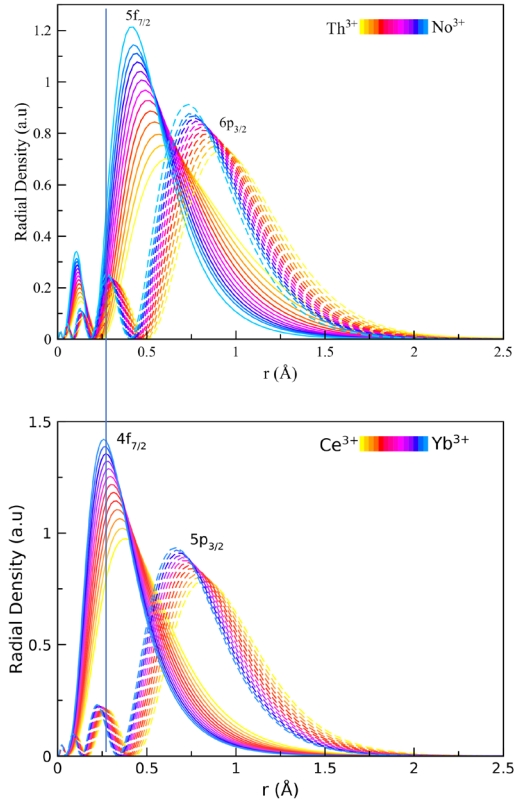
# Ln/An SEPARTION

## fundamental viewpoint




**Rationale**

- 5f orbitals radially more exposed than 4f
- 5f shell softer than 4f
- Softer-donor ligands would…
  - Enhance selectivity for actinides over lanthanides
  - Increase covalency with the metal center




HARD → SOFT(ER)

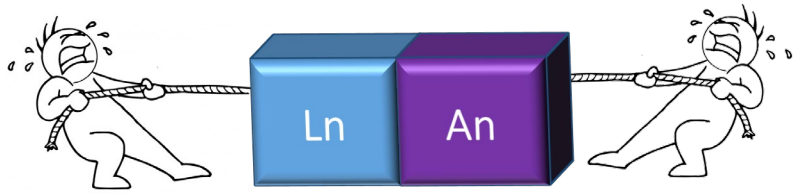
Metal center $Ln^{3+}$ $An^{3+}$

Preferred Ligand (L) LO LN LS LSe

IONIC → COVALENT

# Ln/An SEPARTION

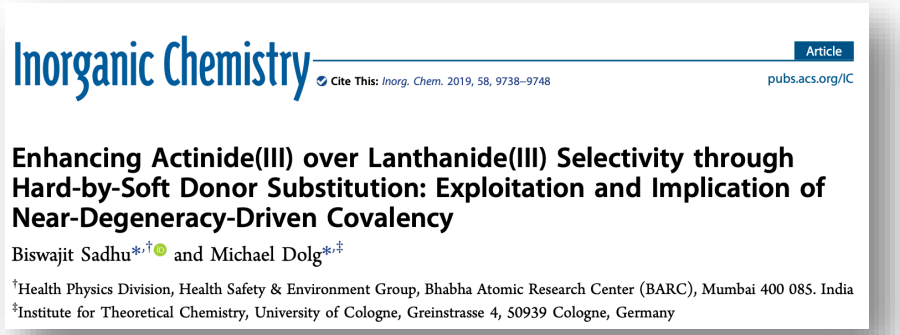
## fundamental viewpoint




**Chemical bond = electrostatic + covalency + dispersion + hyperconjugation + …**

Classical Mechanics  Quantum Mechanics

Sadhu, B., Dolg, M. *Inorganic Chemistry*, **2019**, 58, 9738-97-48.



Inorganic Chemistry  Article

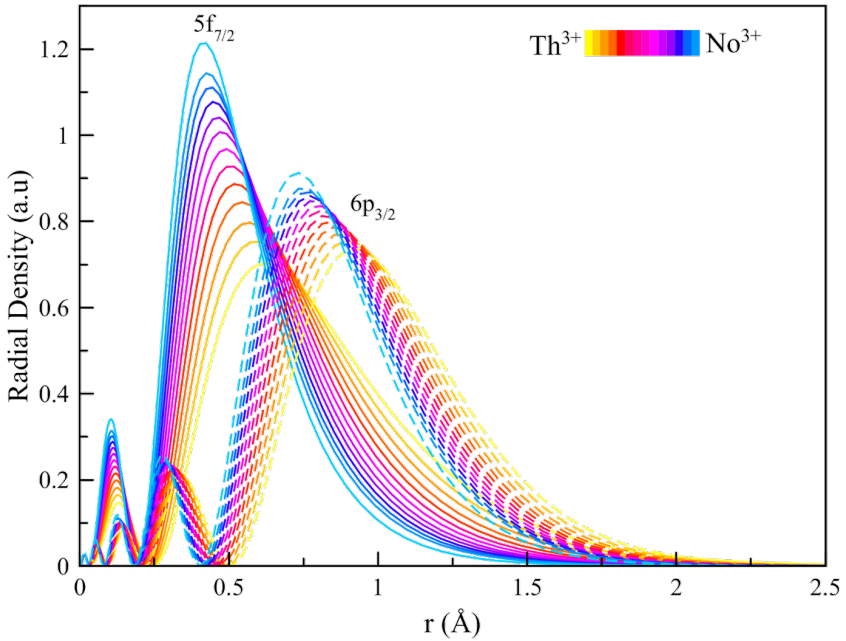
Cite This: *Inorg. Chem.* 2019, 58, 9738−9748  pubs.acs.org/IC

**Enhancing Actinide(III) over Lanthanide(III) Selectivity through Hard-by-Soft Donor Substitution: Exploitation and Implication of Near-Degeneracy-Driven Covalency**

Biswajit Sadhu*,† and Michael Dolg*,‡

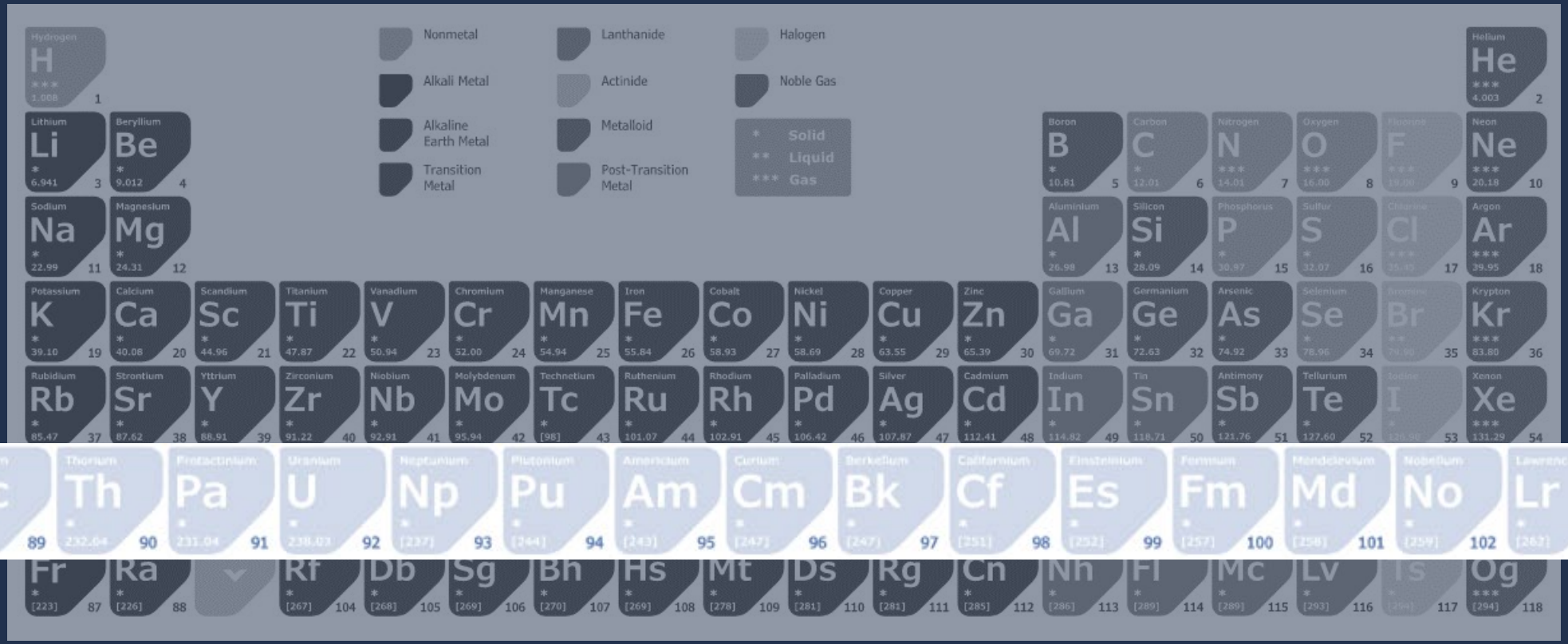
†Health Physics Division, Health Safety & Environment Group, Bhabha Atomic Research Center (BARC), Mumbai 400 085. India
‡Institute for Theoretical Chemistry, University of Cologne, Greinstrasse 4, 50939 Cologne, Germany

**SOMETHING MISSING from the rationale**




- Softer-donor ligands DO increase covalency
- BUT…they also decrease electrostatic interaction
- MAY lead to a weaker complex

Ligands have to ”deal” with the semi-core shells prior to interacting with the metal center




# SOFT- VS HARD-DONORS?

$[UO_2(NO_3)]$+ and chalcogenide systems

# EXPERIMENT AND THEORY

## determining bonding properties and energies

| | | |
|---|---|---|
| **EXPERIMENT** | Collision-induced dissociation | $[UO_2(TPh_3PO)(TPh_3PS)(NO_3)]^+$<br>$[UO_2(TPh_3PO)(TPh_3PSe)(NO_3)]^+$ |
| **THEORY** | Complexation free energies | $[UO_2(TPh_3PE)(NO_3)]^+ + TPh_3PE$<br>$[UO_2(Me_2E)(NO_3)]^+ + Me_2E$ |
| | Energy decomposition analysis | Pauli + Electrostatic + Orbital + Dispersion |
| | Topology of the electron density of the bond | Electron density<br>Total energy density |

# COVALENCY

## Energy decomposition analysis

Pauli + Electrostatic + Orbital + Dispersion

## Topology of the electron density of the bond

Pauli ⟶ Antisymmetrization of wave functions

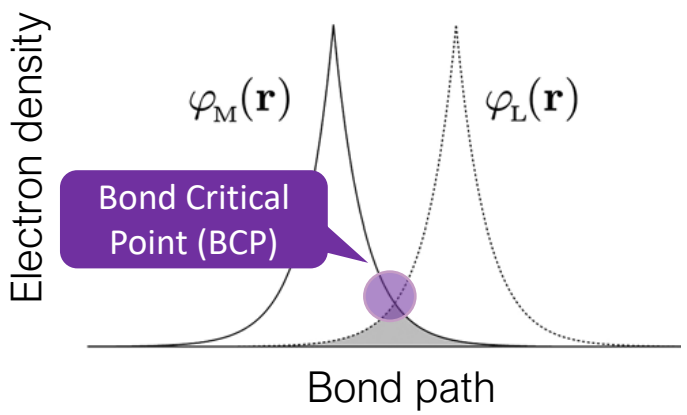
Electrostatic ⟶ Coulomb interaction between nuclei and electrons

Orbital ⟶ Covalency through orbital mixing

Dispersion ⟶ Non-bonding attractive forces

Electron density

Total energy density




Orbital overlap

Accidental degeneracy

Electrostatic

**Total energy density**

**H(r)** = G(r) + V(r)

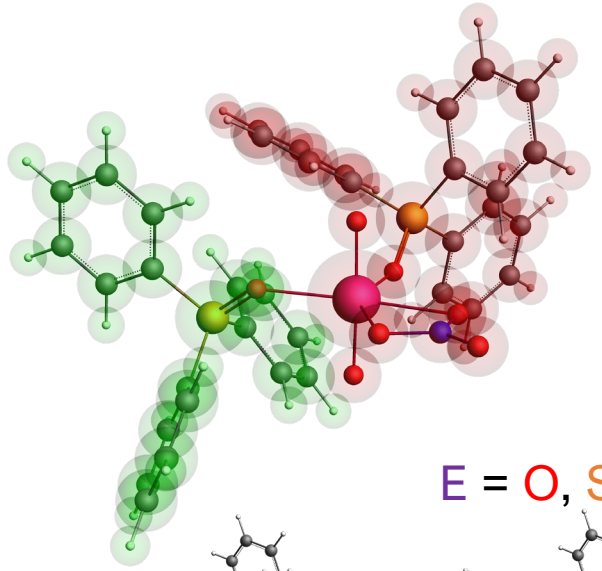
**Kinetic energy density**

**Potential energy density**

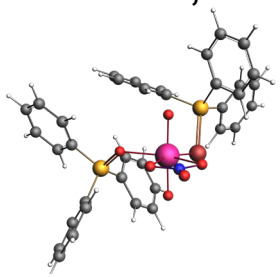
# MOLECULAR SYSTEMS

## Triphenyl phosphine chalcogenide

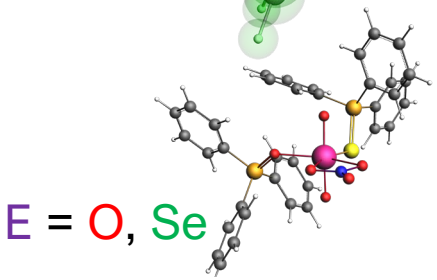
$[UO_2(TPh_3PE)_2(NO_3)]^+$



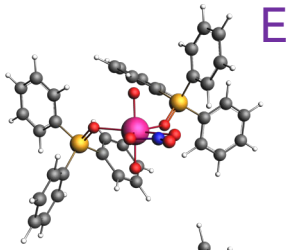
E = O, S



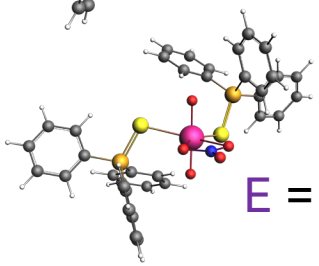
E = O, Se



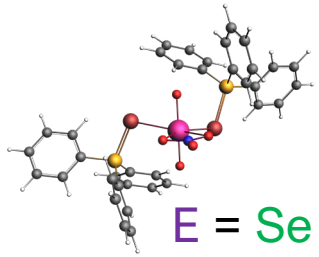
E = O



E = S

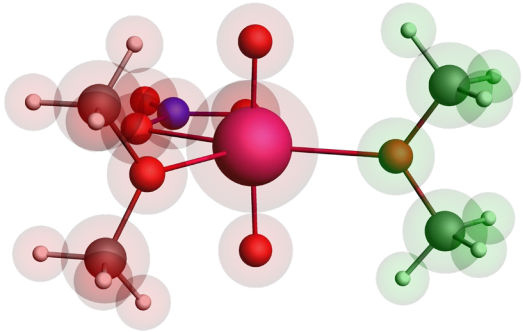


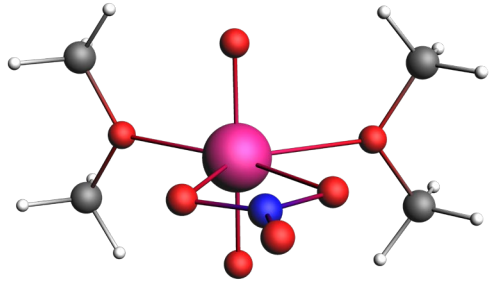
E = Se



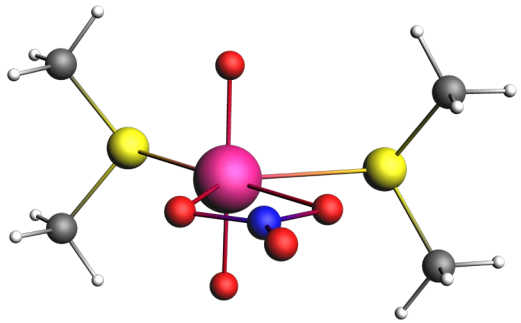
## Dimethyl chalcogenide

$[UO_2(Me_2E)_2(NO_3)]^+$

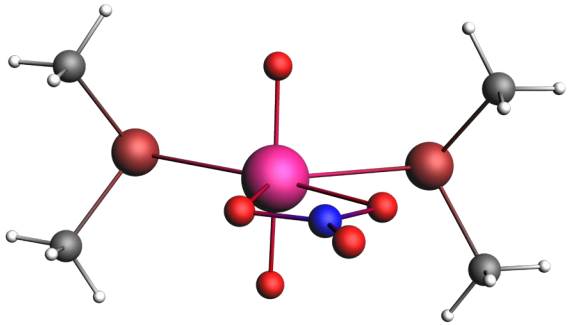




E = O



E = Se

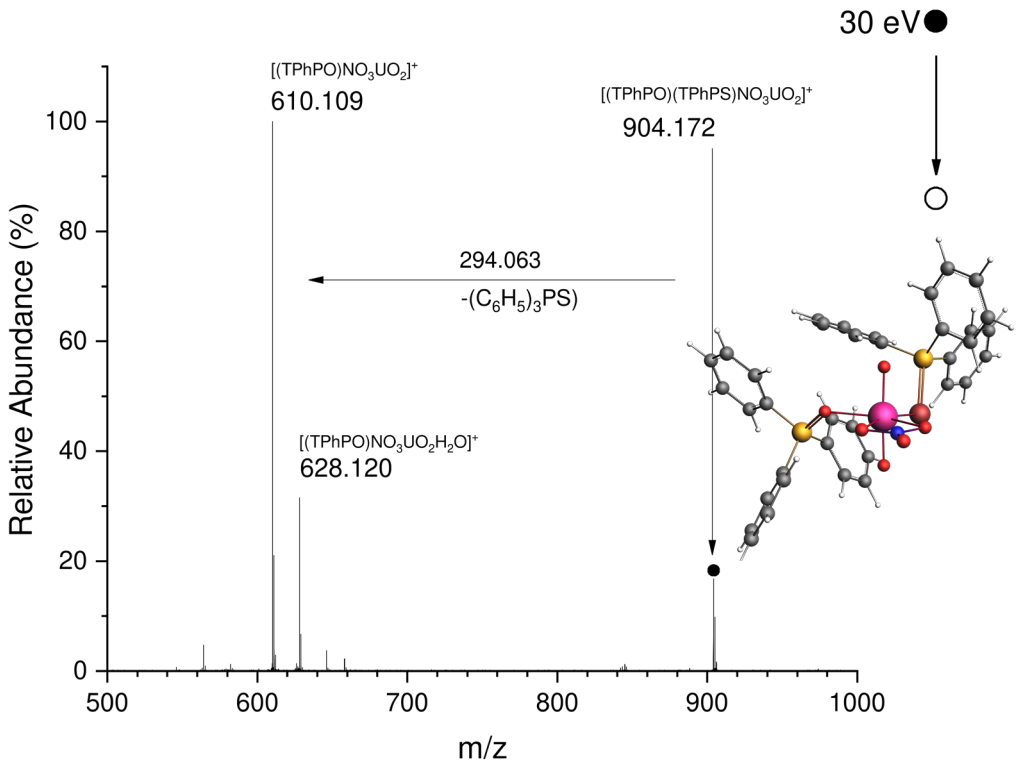


E = S

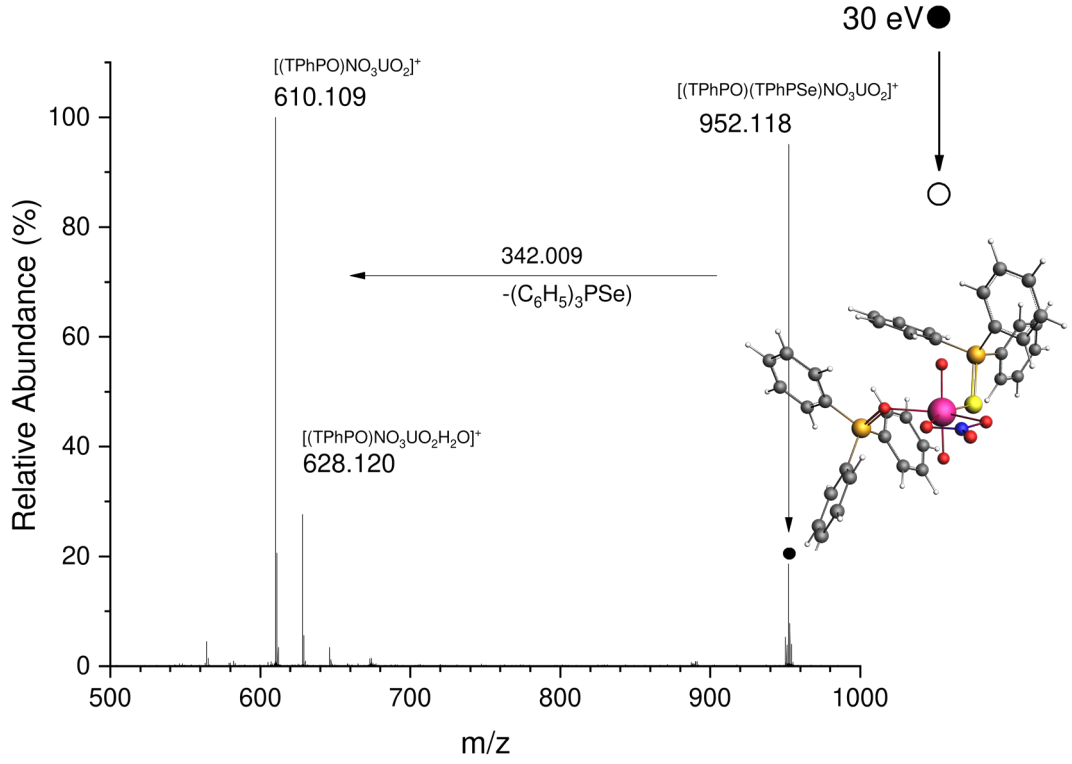
# COLLISION INDUCED DISSOCIATION

**Chris Zarzana, Brittany Hodges, JungSoo Kim - INL**

$[UO_2(TPh_3PO)(TPh_3PS)(NO_3)]^+$




$[UO_2(TPh_3PO)(TPh_3PSe)(NO_3)]^+$

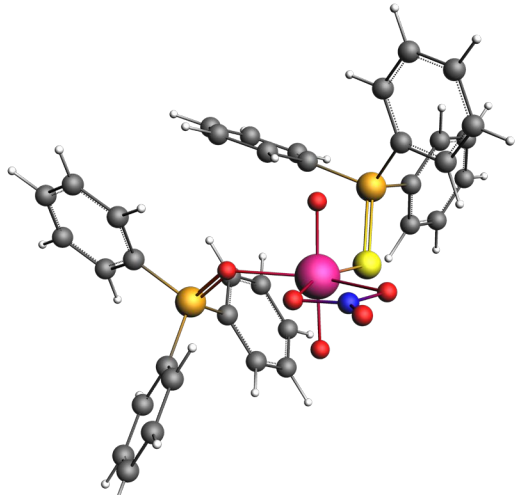


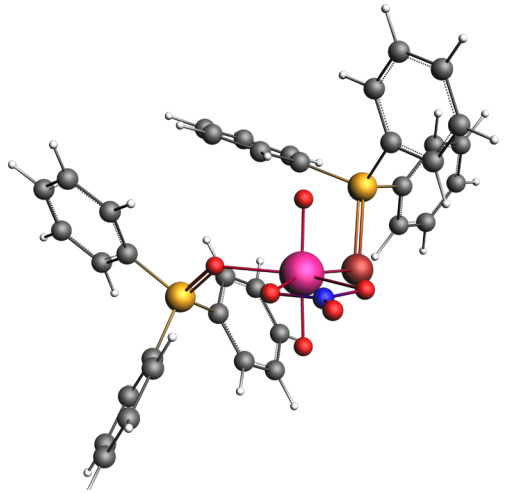
# COMPLEXATION FREE ENERGIES

$[UO_2(TPh_3PO)(TPh_3PS)(NO_3)]^+_{(g)} \longleftarrow [UO_2(TPh_3PO)(NO_3)]^+_{(g)} + TPhe_3PS_{(g)}$

$[UO_2(TPh_3PO)(TPh_3PSe)(NO_3)]^+_{(g)} \longleftarrow [UO_2(TPh_3PO)(NO_3)]^+_{(g)} + TPhe_3PSe_{(g)}$

| | ΔH | -ΔTS | ΔG |
|---|---|---|---|
| $[UO_2(TPh_3PO)\ (TPh_3PO)(NO_3)]^+$ | -50.2 | 16.2 | -34.0 |
| $[UO_2(TPh_3PO)\ (TPh_3PS)(NO_3)]^+$ | -45.0 | 16.4 | -28.6 |
| $[UO_2(TPh_3PO)\ (TPh_3PSe)(NO_3)]^+$ | -46.5 | 16.4 | -30.0 |

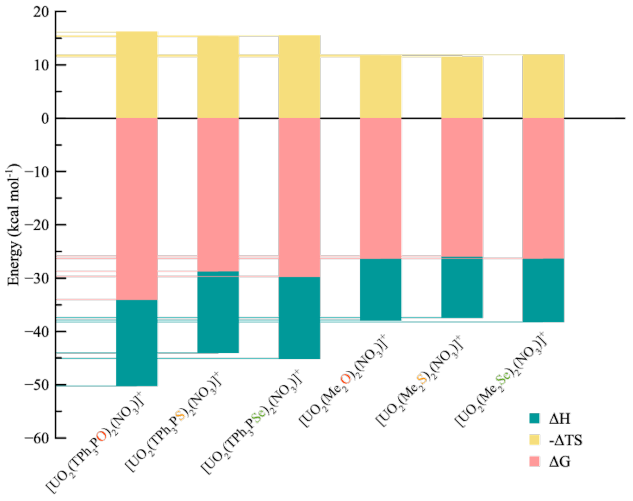




# COMPLEXATION FREE ENERGIES

$[UO_2(TPh_3PE)_2(NO_3)]^+_{(g)} \leftarrow [UO_2(TPh_3PE)(NO_3)]^+_{(g)} + TPhe_3PE_{(g)}$

$[UO_2(Me_2E)_2(NO_3)]^+_{(g)} \leftarrow [UO_2(Me_2E)(NO_3)]^+_{(g)} + Me_2E_{(g)}$

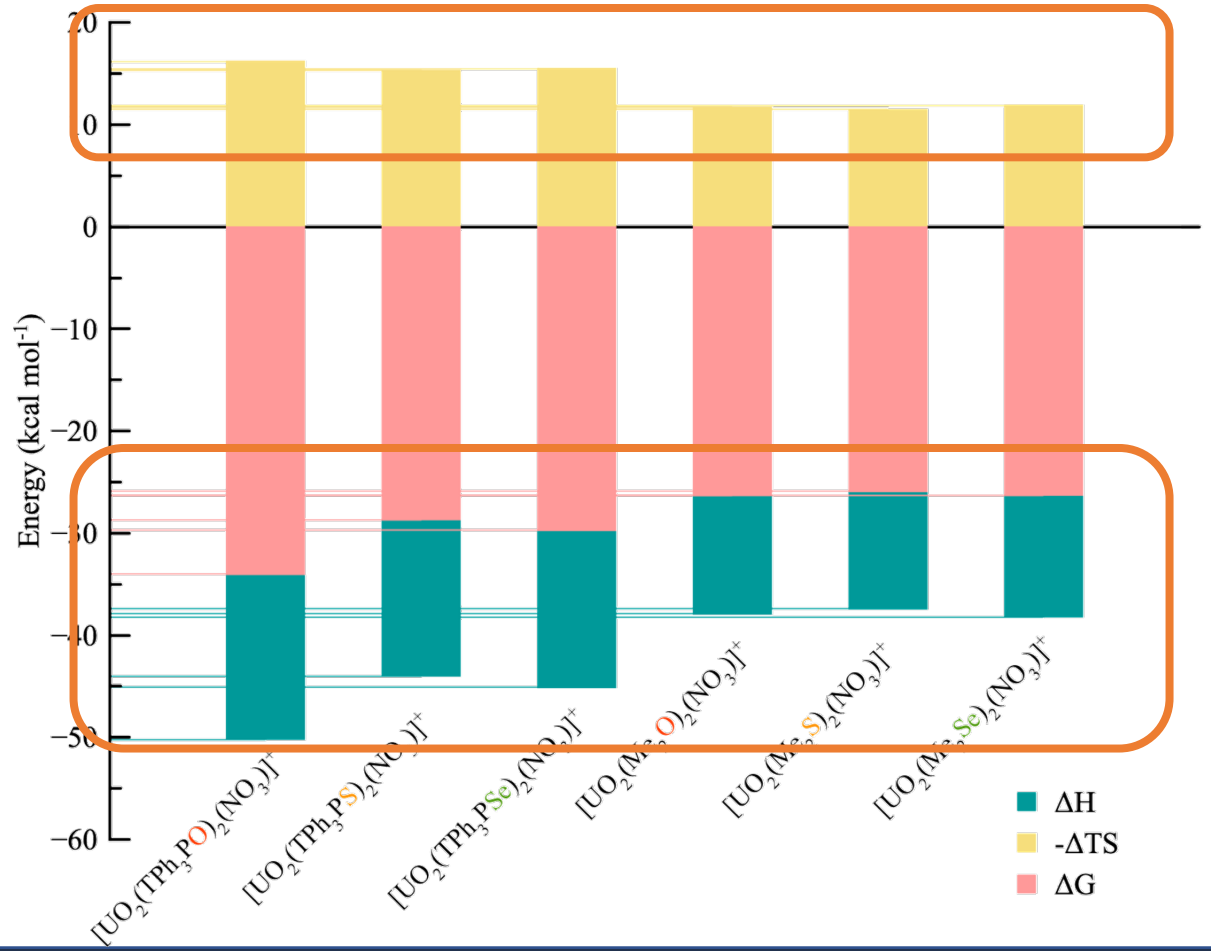



| | ΔH | -ΔTS | ΔG |
|---|---|---|---|
| $[UO_2(TPh_3PO)_2(NO_3)]^+$ | -50.2 | 16.2 | -34.0 |
| $[UO_2(TPh_3PS)_2(NO_3)]^+$ | -44.0 | 15.3 | -28.7 |
| $[UO_2(TPh_3PSe)_2(NO_3)]^+$ | -45.1 | 15.5 | -29.7 |
| $[UO_2(Me_2O)_2(NO_3)]^+$ | -37.9 | 11.7 | -26.3 |
| $[UO_2(Me_2S)_2(NO_3)]^+$ | -37.4 | 11.5 | -25.9 |
| $[UO_2(Me_2Se)_2(NO_3)]^+$ | -38.2 | 11.9 | -26.3 |

# COMPLEXATION FREE ENERGIES

$[UO_2(TPh_3PE)_2(NO_3)]^+_{(g)} \leftarrow [UO_2(TPh_3PE)(NO_3)]^+_{(g)} + TPhe_3PE_{(g)}$

$[UO_2(Me_2E)_2(NO_3)]^+_{(g)} \leftarrow [UO_2(Me_2E)(NO_3)]^+_{(g)} + Me_2E_{(g)}$

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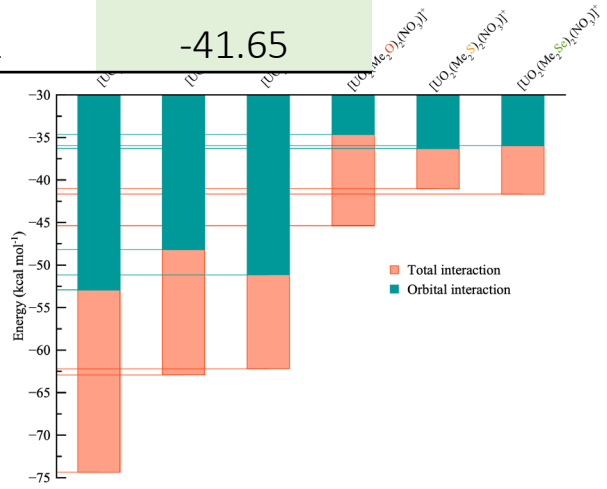
| $[UO_2(Me_2S)_2(NO_3)]^+$ | -37.4 | 11.5 | -25.9 |
| $[UO_2(Me_2Se)_2(NO_3)]^+$ | -38.2 | 11.9 | -26.3 |

# ENERGY DECOMPOSITION

$[UO_2(TPh_3PE)_2(NO_3)]^+_{(g)} \leftarrow [UO_2(TPh_3PE)(NO_3)]^+_{(g)} + TPhe_3PE_{(g)}$

$[UO_2(Me_2E)_2(NO_3)]^+_{(g)} \leftarrow [UO_2(Me_2E)(NO_3)]^+_{(g)} + Me_2E_{(g)}$

| | Pauli | Electrostatic | Steric | Orbital | Dispersion | Total |
|---|---|---|---|---|---|---|
| $[UO_2(TPh_3PO)_2(NO_3)]^+$ | 73.38 | -82.42 | -9.04 | -52.91 | -12.41 | -74.36 |
| $[UO_2(TPh_3PS)_2(NO_3)]^+$ | 63.38 | -66.01 | -2.63 | -48.19 | -12.08 | -62.90 |
| $[UO_2(TPh_3PSe)_2(NO_3)]^+$ | 66.33 | -68.63 | -2.30 | -51.15 | -8.75 | -62.19 |
| $[UO_2(Me_2O)_2(NO_3)]^+$ | 45.59 | -53.48 | -7.89 | -34.67 | -2.81 | -45.37 |
| $[UO_2(Me_2S)_2(NO_3)]^+$ | 44.37 | -46.39 | -2.02 | -36.28 | -2.72 | -41.02 |
| $[UO_2(Me_2Se)_2(NO_3)]^+$ | 42.88 | -45.66 | -2.78 | -35.97 | -2.91 | -41.65 |



# ENERGY DECOMPOSITION

$[UO_2(TPh_3PE)_2(NO_3)]^+_{(g)} \leftarrow [UO_2(TPh_3PE)(NO_3)]^+_{(g)} + TPhe_3PE_{(g)}$

$[UO_2(Me_2E)_2(NO_3)]^+_{(g)} \leftarrow [UO_2(Me_2E)(NO_3)]^+_{(g)} + Me_2E_{(g)}$

| | Pauli | Electrostatic | Steric | Orbital | Dispersion | Total |
|---|---|---|---|---|---|---|
| $[UO_2(TPh_3PO)_2(NO_3)]^+$ | 73.38 | -82.42 | -9.04 | -52.91 | -12.41 | -74.36 |
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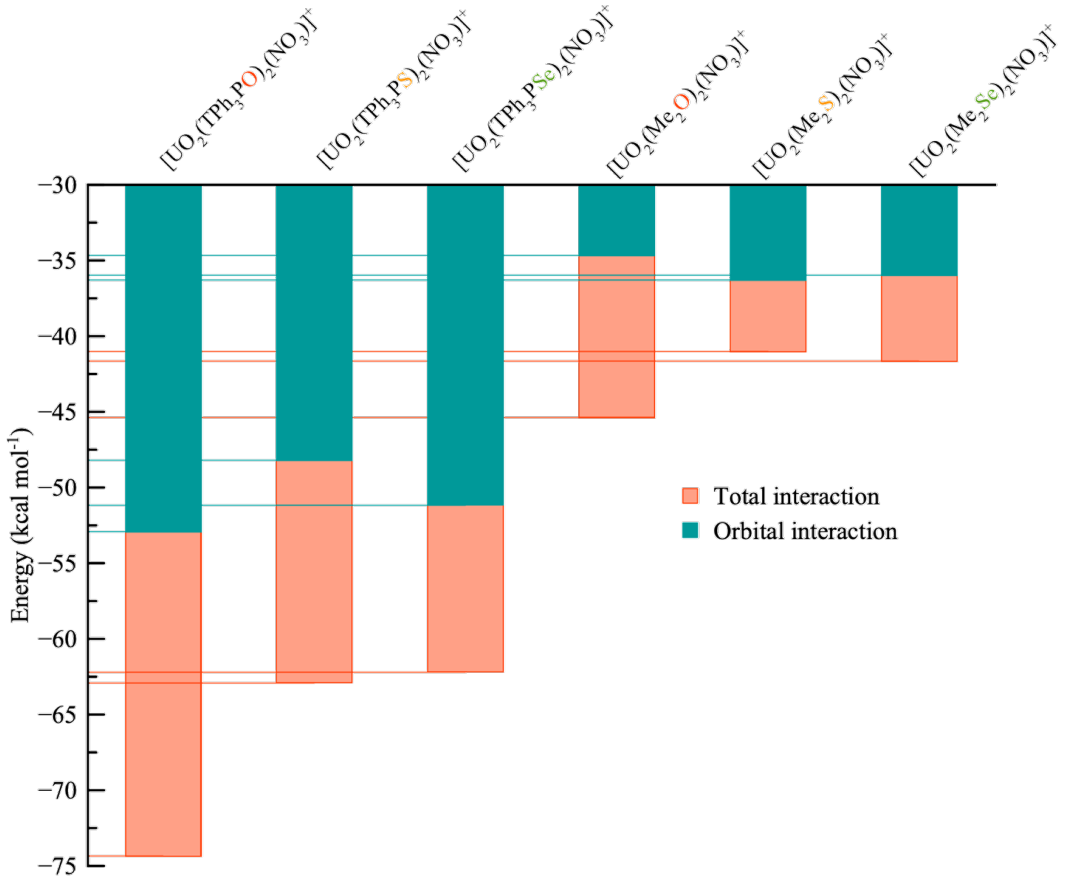
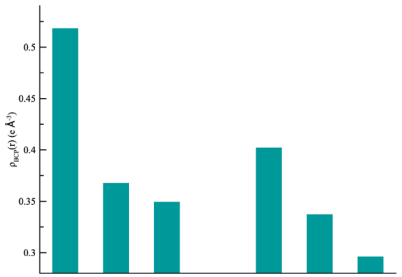
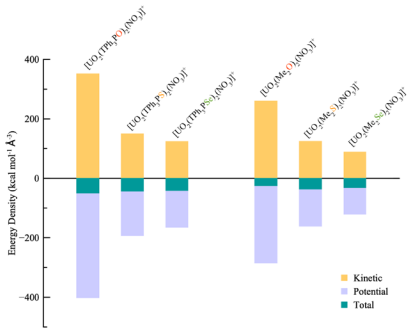
| $[UO_2(Me_2S)_2(NO_3)]^+$ | 44.37 | -46.39 | -2.02 | -36.28 | -2.72 | -41.02 |
| $[UO_2(Me_2Se)_2(NO_3)]^+$ | 42.88 | -45.66 | -2.78 | -35.97 | -2.91 | -41.65 |



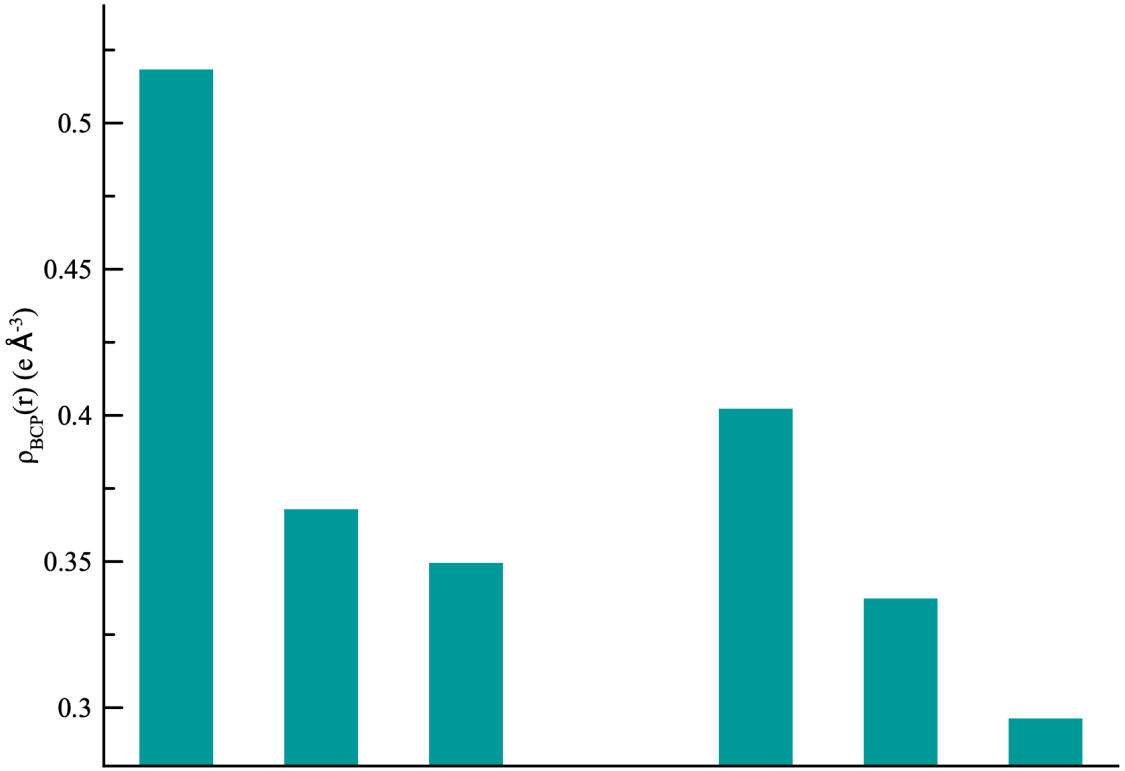
# TOPOLOGICAL ANLAYSIS - QTAIM

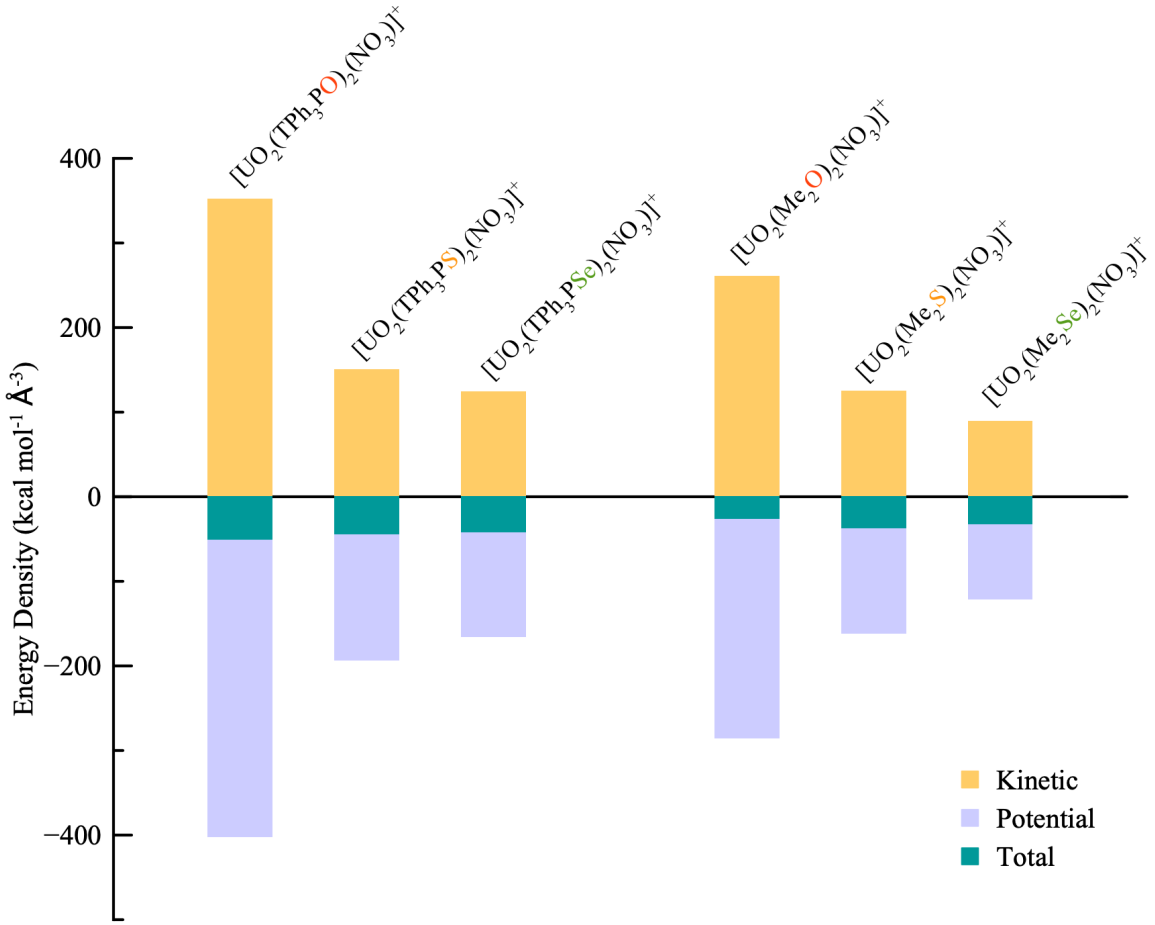
| | ρ(r) | G(r) | V(r) | H(r) |
|---|---|---|---|---|
| $[UO_2(TPh_3PO)_2(NO_3)]^+$ | 0.5181 | 351.57 | -401.26 | -49.69 |
| $[UO_2(TPh_3PS)_2(NO_3)]^+$ | 0.3675 | 149.74 | -193.07 | -43.33 |
| $[UO_2(TPh_3PSe)_2(NO_3)]^+$ | 0.3492 | 124.16 | -165.23 | -41.07 |
| $[UO_2(Me_2O)_2(NO_3)]^+$ | 0.4019 | 260.18 | -285.27 | -25.09 |
| $[UO_2(Me_2S)_2(NO_3)]^+$ | 0.3370 | 124.61 | -161.37 | -36.76 |
| $[UO_2(Me_2Se)_2(NO_3)]^+$ | 0.2960 | 89.20 | -120.72 | -31.52 |



# TOPOLOGICAL ANLAYSIS - QTAIM



# LIGAND POLARIZABILITY

## Average Localized Ionization Energies (ALIEs)

$$\bar{I}(\boldsymbol{r}) = \frac{\sum_i \rho_i(\boldsymbol{r})|\varepsilon_i|}{\rho(\boldsymbol{r})}$$

Quantification of how loosely bound electrons are → Inversely proportional to LOCAL POLARIZABILITY

| | ALIE (kcal/mol) | | |
|---|---|---|---|
| | E1 | E2 | E3 |
| TPh3P=O | 207.5 | 207.6 | 207.6 |
| TPh3P=S | 163.3 | 163.7 | 163.9 |
| TPh3P=Se | 148.6 | 149.1 | 149.3 |
| $Me_2O$ | 227.6 | 227.8 | |
| $Me_2S$ | 165.6 | 165.6 | |
| $Me_2Se$ | 153.8 | 154.0 | |

| | Mulliken charge |
|---|---|
| | q(E) |
| TPh3P=O | -0.839 |
| TPh3P=S | -0.566 |
| TPh3P=Se | -0.669 |
| $Me_2O$ | -0.546 |
| $Me_2S$ | -0.012 |
| $Me_2Se$ | -0.076 |

# SUMMARY AND OVERLOOK

TPh3P=O

- More negatively charged oxygen atom
- More polarizable than O atom in dimethyl ether
- Increased coulomb and covalent interactions

- HSAB theory is ONLY part of the equation for rational design of ligands
- Expand this work to different chalcogenide ligands and trivalent transU actinides


# Acknowledgments


- Christopher Zarzana
- Britanny Hodges
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