INL/CON-24-76430-Revision-2

Gas-Phase Coordination of Phosphine-Chalcogenides to the Uranyl Cation

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Changing the World's Energy Future

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Idaho National Laboratory

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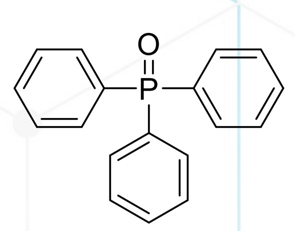
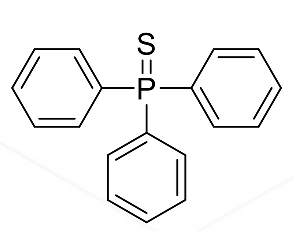
The uranyl asymmetric stretch (ν_3) is not always correlated with density-based measures of equatorial bond covalency.

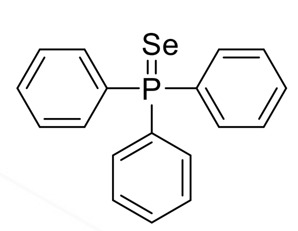
Background

Understanding the fundamentals of bonding in the uranyl cation ($[UO_2]^+$) is important for development of improved processes for separation and disposal of used nuclear fuel. The covalency of axial U=O bonds and the equatorial U—ligand bonds are often used to study uranyl bonding. As covalency cannot be directly observed, the degree of covalency must be inferred from other observables. One proposed observable is the uranyl asymmetric stretch (ν_3), as prior work has reported a correlation between the gas-phase ν_3 frequency and metrics of covalency calculated with density functional theory (DFT): lower calculated frequencies were correlated with larger electron densities and the Laplacian of the electron density calculated at bond critical points using the quantum theory of atoms in molecules (QTAIM). Both calculated quantities have been used as measures of bond covalency.

This work compares the ν_3 frequency measured with IR ion spectroscopy with measures of equatorial bond covalency calculated with DFT and QTAIM for uranyl nitrate complexes with triphenylphosphine chalcogenide (oxide, sulfide, and selenide) ligands.


triphenylphosphine oxide


triphenylphosphine sulfide


triphenylphosphine selenide

Methods

Infrared Ion Spectroscopy of Homogeneous-Ligand Complexes

The gas-phase infrared frequency of the asymmetric uranyl stretch (ν_3) of homogeneous-ligand complexes ($[UO_2NO_3(Ph_3PE)_2]^+$, E=O,S, and Se) was measured using the quadrupole ion trap MS for IR ion spectroscopy user station at the FELIX laboratory at Radboud University.

Density Functional Theory

Structures of homogeneous complexes were optimized using the B3LYP functional with the ECP60MDF effective core potential and associated basis set for uranium and the Def2-TZVPP basis set for all other atoms. Single point energies and frequencies were calculated for the optimized geometries using the PBE functional and the TZ2P basis set.

Measured Uranyl v3 Frequencies

Species	Experimental ν_3
$[UO_2NO_3(Ph_3PO)_2]^+$	951 cm^{-1}
$[UO_2NO_3(Ph_3PS)_2]^+$	959 cm^{-1}
$[UO_2NO_3(Ph_3PSe)_2]^+$	953 cm^{-1}

Uranyl ν_3 Frequencies
O ~ Se < S

Calculated Density-Based Measured of Bond Covalency

Bond	Electron Density (e/Å3)	Laplacian of Electron Density
U—O=P(Ph)$_3$	0.551	0.312
U—S=P(Ph)$_3$	0.316	0.0851
U—Se=P(Ph)$_3$	0.289	0.0653

Density-Based Measures of Covalency
O > S > Se

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