Electronic Supplementary Material (ESI) for Chemical Communications


# Supporting Information

# Formation and Characterization of HUF and DUF in Solid Argon

**Thomas Vent-Schmidt,[a] Rodney Dale Hunt,[b] Lester Andrews*[a,c] and Sebastian Riedel*[a]**

[a] *Albert-Ludwigs Universität Freiburg, Institut für Anorganische und Analytische Chemie, Albertstrasse 21, 79104 Freiburg, Germany. Fax: 0049-7612036001; Tel:0049-7612038717 E-mail: sriede@psichem.de; WWW: www.psichem.de*

[b] *Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6223 E-mail:huntrd@ornl.gov*

[c] *University of Virginia, Department of Chemistry, Charlottesville, VA, USA.22904-4319 E-mail: lsa@virginia.edu*

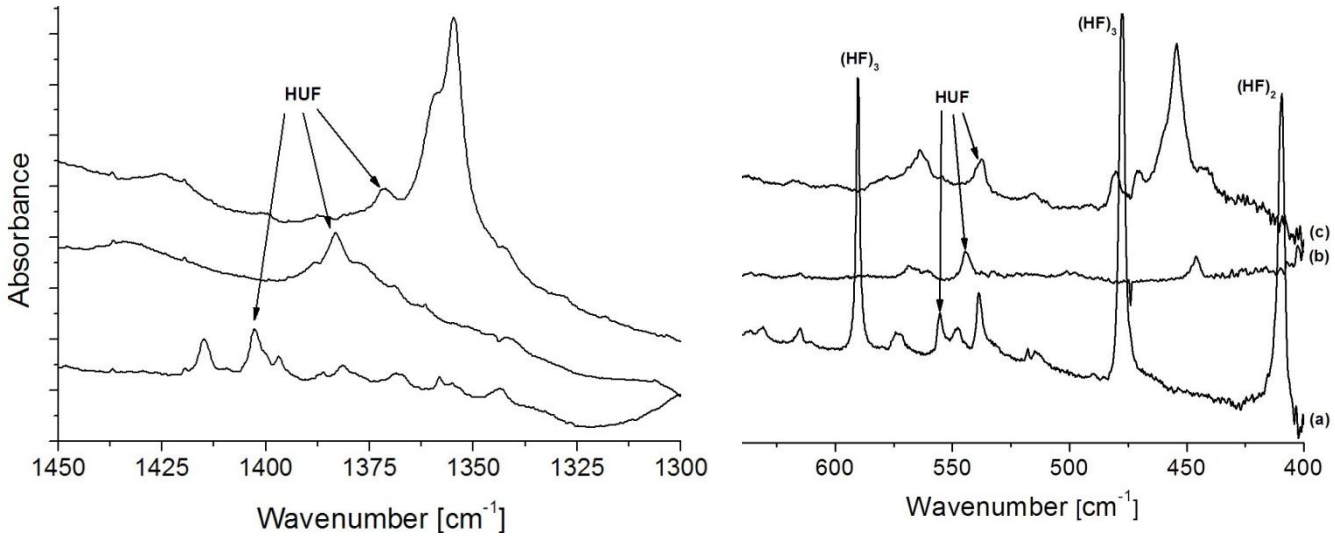


**Figure S1**. Matrix-isolation experiments with different matrix gases. (a) U + 0.5% HF in Neon (b) U + 0.15% HF in Argon (c) U + 0.5% HF in Krypton. HF Dimer/Trimer bands were assigned according to reference 8.

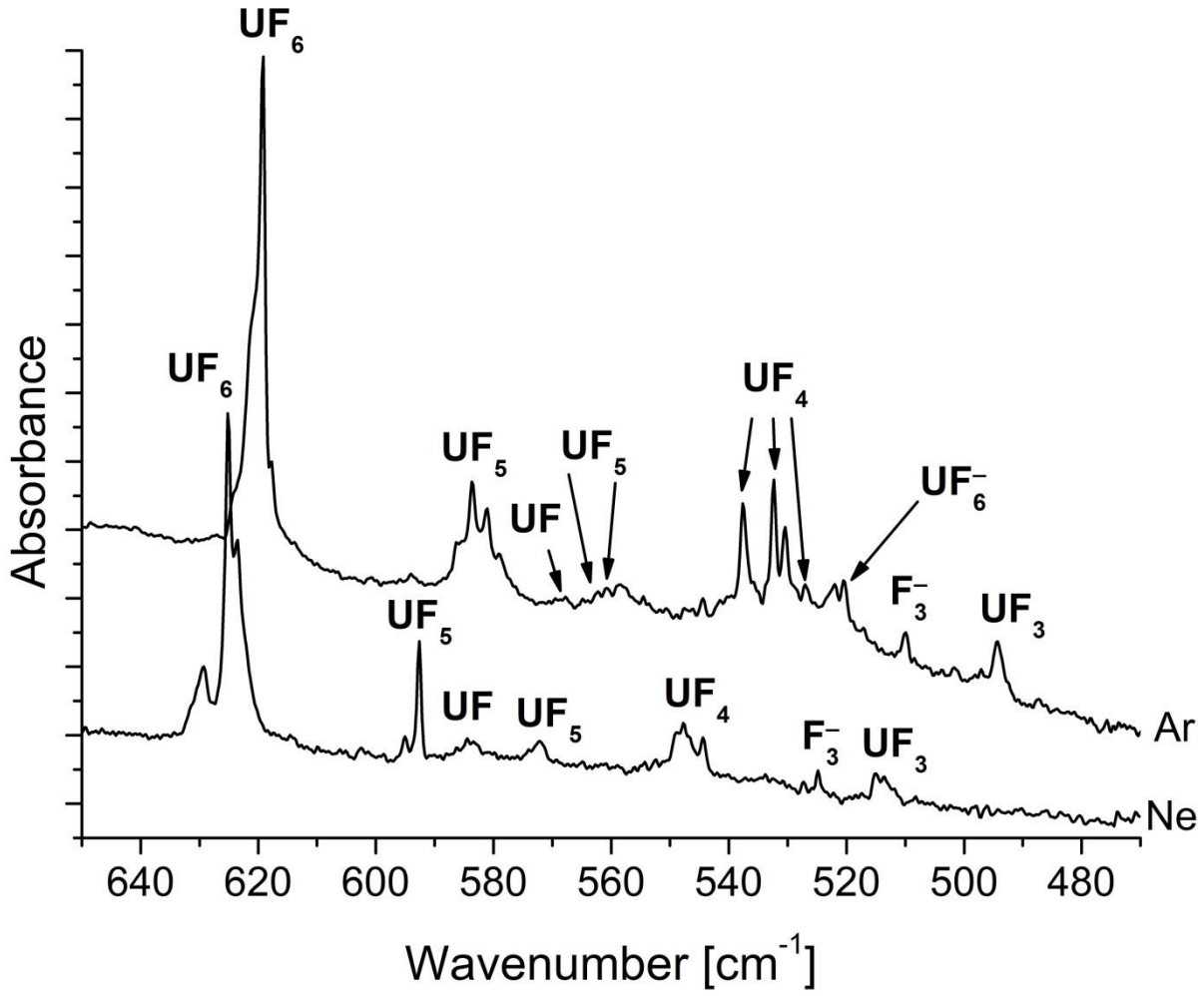


**Figure S2.** Matrix-isolation experiments of laser ablated uranium atoms under excess of fluorine in neon and argon matrices.

**Table S1.** Experimental and computed frequencies of uranium fluorides[a]

| Molecule | Neon | Argon | Krypton | B3LYP[b] | CCSD(T)[b] | Literature |
|---|---|---|---|---|---|---|
| UF | 583.3<br>584.5 | 564.9,<br>567.7 | - | 573.4 | - | 597 (calc.)[9]<br>576 (calc.)[10] |
| $UF_2$ | - | - | - | 552.6 (87)<br>526.7 (152) | 567.5 (104)<br>513.5 (114) | 554, 529 (calc.)[10] |
| $UF_3$ | 515.1,<br>513.6 | 494.5 | 491.1,<br>493.4 | - | - | 496 (Ar)[11]<br>543,534,528 (calc.)[10] |
| $UF_4$ | 547.6,<br>546.7,<br>549.1,<br>544.4 | 537.6,<br>532.4,<br>530.5,<br>527.0 | Several bands in 518-538 region | - | - | 550,545,540,537,533 (Ne)[12]<br>538,533,531 (Ar)[12]<br>535, 530 (Kr)[12] |
| $UF_5$ | 592.8,<br>595.4,<br>572.4 | 583.7,<br>586.3,<br>581.3,<br>579.1,<br>561.0,<br>562.9 | Several bands in 574-588 region | - | - | 584 (Ar)[13]<br>561 (Ar)[13]<br>570-610 (bulk)[13] |
| $UF_6$ | 625.1,<br>623.6,<br>629.6 | 619.1 | 620.9,<br>618.8 | - | - | 619.3 (Ar)[13]<br>625.5 (Gas)[13] |

[a]Values in $cm^{-1}$. [b]SDD/aVTZ basis; Intensities in parenthesis in km $mol^{-1}$.

## Computational Details

Structures have been fully optimized (by relaxing all parameters) at density functional theory level using the Gaussian09 program package[1] with the B3LYP hybrid functional[1-3] and Dunning's correlation consistent triple-ζ basis set[4] for fluorine and hydrogen and the 60 electron core SDD pseudopotential for uranium[5].

All possible spin multiplicities have been considered. The wave function stability has been checked using the keyword 'stable' as implemented in the Gaussian09 version. Structure optimizations at coupled-cluster level (CCSD(T)) using the CFOUR program suite[6] have been performed for the ground states within the restrictions of their respective point groups for $UH_2$, HUF and $UF_2$.

Structure optimization and frequency calculations for HUF at CASPT2 level have been performed with the MOLPRO 2006.1 program release.[7] In the case of HUF ($C_1$ symmetry) we used the seven 5f-orbitals as active space. Harmonic and anharmonic frequency calculations at DFT (B3LYP) level and harmonic frequencies at CCSD(T) and CASPT(2) level were executed for stationary points on the potential energy surface for both $^1H$ and $^2H$ isotopes.

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