Formation and characterization of HUF and DUF in solid argon†

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

Reactions of laser-ablated U atoms with HF and DF in condensing and solid rare gas produce HUF and DUF as the major new products based on close agreement between observed and calculated vibrational frequencies and deuterium shifts for U–H and U–F stretching modes at 1383 and 544 cm^{-1}, respectively.

Uranium fluorides have been studied extensively because they play important roles in the nuclear fuel cycle as well as in the production of uranium metal. For example, uranium hexafluoride (UF_6) is used as the feed in the two main commercial methods for uranium enrichment, which are gaseous diffusion and gaseous centrifugation.[1] Uranium tetrafluoride (UF_4) is the intermediate in the conversion of UF_6 to uranium metal using calcium[2] or magnesium.[3] The uranium metal from the UF_4 reduction can be converted into uranium powder through the formation of uranium hydride (UH_3), which is of considerable importance in the purification of uranium. When uranium metal is heated to 250–300 °C in hydrogen, the hydrogen diffuses throughout metal and form a network of brittle UH_3 along the grain boundaries.[4] The UH_3 swells and then disintegrates into powder.[5] At temperatures from 20 to 400 °C, hydrogen fluoride (HF) reacts with UH_3 to form UF_4.[6] Therefore, the formation of transient uranium hydride fluoride molecules (UH_xF_y) can be expected. Matrix-isolation infrared spectroscopy is therefore an ideal method to investigate the formation of such uranium hydride fluorides. The chemistry of molecular uranium hydrides has been investigated by this method and supported by quantum-chemical calculations. Following the successful preparation of molecular uranium fluorides and hydrides from the reaction of laser ablated U atoms with fluorine

and hydrogen,[7–10] the straightforward approach is the analogous reaction of laser ablated uranium atoms with hydrogen fluoride. To the best of our knowledge there have been no publications of mixed hydride fluorides of uranium (UH_xF_y) to date.

Here we report matrix-isolation and quantum-chemical investigations of the HUF and DUF molecules which have been prepared by uranium atom insertion reactions into the HF and DF bonds under cryogenic conditions. These experimental methods have been described previously.[7–11] Several concentrations of HF–DF in argon from 0.2 to 1.5% and DF enrichments from 40 to 70% have been used in the present experiments. These HF–DF samples were prepared in Virginia by reacting D_2 and F_2 in a stainless steel vacuum system with residual water contamination, as done for a large number of previous investigations.[12] The intense HF and DF monomer bands were observed along with weaker dimer, trimer and tetramer bands identified earlier.[12] Additional experiments with argon, neon and krypton were done at Freiburg using HF gas (Solvay), which was condensed and out gassed before dilution.

Weak absorptions at 1377.0 and 965.6 cm^{-1} have been assigned to the bifluoride $[HF_2]^-$ and $[DF_2]^-$ anions isolated in solid argon:[13] here they are probably formed by the capture of laser ablated electrons by F atoms, from dissociation of HF or DF by the hard UV light in the intense plume on the target surface from the laser ablation process, followed by F$^-$ and HF–DF combination. Higher laser energy produces more intense anion bands. However, no $[F_3]^-$ anion was observed in these experiments in contrast to those with fluorine as the reagent.[14]

The most important new absorptions in solid argon were observed at 1383.1 and 544.6 cm^{-1} for the HF reagent and at 988.3 cm^{-1} and 542.6 cm^{-1} for the DF reagent. The HF and DF associations are made because these bands follow the relative enrichments of HF and DF in the experiments. The 1383.1 and 544.6 cm^{-1} bands are clearly stronger in Fig. 1 spectra whereas the 988.3 cm^{-1} and 542.6 cm^{-1} bands are stronger with increased DF enrichment (highest DF enrichment is 70%), see Fig. 2.

This is confirmed by experiments with neat HF diluted in argon, which are illustrated in Fig. 3. The 1383.1 and 554.6 cm^{-1} bands are cleanly observed for the HF reaction product. Although there

[a] *Albert-Ludwigs Universität Freiburg, Institut für Anorganische und Analytische Chemie, Albertstrasse 21, 79104 Freiburg, Germany. E-mail: sriedel@psichem.de; Web: www.psichem.de; Fax: +49-7612036001; Tel: +49-7612038717*

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

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

† Electronic supplementary information (ESI) available: Computational details, spectra of HUF in neon and krypton, spectra of laser-ablated U with fluorine in different rare gases. See DOI: 10.1039/c3cc41379a
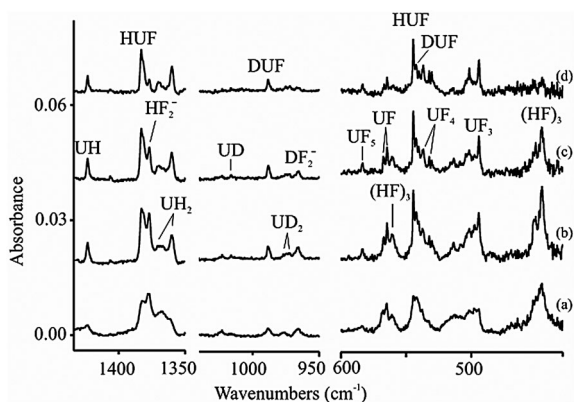
Fig. 1 Infrared spectra of laser-ablated U atom and HF–DF mixture (60% HF) reaction products in solid argon: (a) U + 0.5% HF–DF deposition for 50 min; (b) after annealing to 27 K; (c) after annealing to 34 K; and (d) after annealing to 39 K. DF enrichment is best followed by the relative intensities of the 988 cm^{-1} DUF and 1383 cm^{-1} HUF bands.
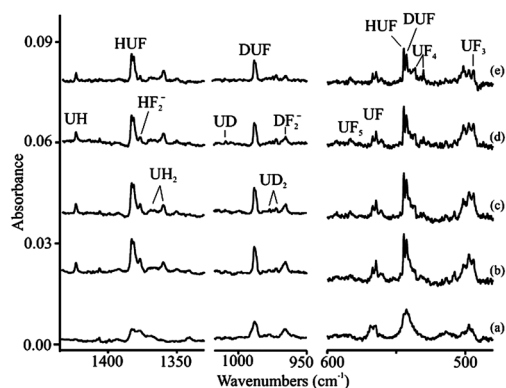

Fig. 2 Infrared spectra of laser-ablated U atom and HF–DF mixture (70% DF) reaction products in solid argon: (a) U + 0.5% HF–DF deposition for 50 min; (b) after annealing to 27 K; (c) after annealing to 31 K; (d) after annealing to 36 K; (e) after annealing to 39 K.

appears to be a broad absorption underlying the 544 cm^{-1} band in these experiments, Fig. 3 shows how well the two bands track on sequential annealing cycles. Annealing to 23 K increased the product bands, as before, and higher annealing as well as full mercury arc irradiation (220–900 nm) decreased them. Based on the lower product yield, the laser energy delivered to the U sample was less in the Fig. 3 spectra. Spectra for neon and krypton matrix experiments are shown in the ESI.†

If these two bands can be assigned to the anticipated HUF reaction product, there must be appropriate deuterium counterparts in the mixed HF–DF spectra presented in Fig. 1 and 2 where the 1383.1 and 988.3 cm^{-1} band profiles match, and their frequency ratio, 1.400, is appropriate for an observed (anharmonic) U–H vibrational mode.[7,8] This is in line, for example, with the observed antisymmetric stretching fundamental of UH_2 observed in solid argon at 1370.7 cm^{-1}, which shifts to 978.7 cm^{-1} for UD_2 with a frequency ratio of 1.401.[7] Note how close the UH_2 and UD_2 bands are to the above new product absorptions. A 1360.0 cm^{-1} band and its 972.3 cm^{-1} DF counterpart appeared on annealing to 27 K, increased on
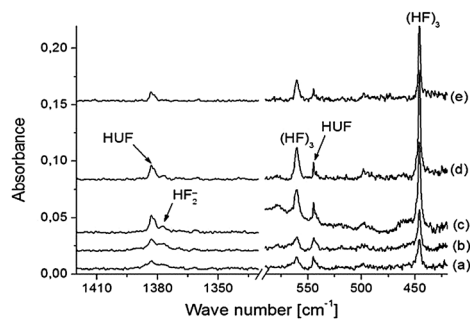

Fig. 3 Infrared spectra of laser-ablated U atom and HF reaction products in solid argon: (a) U + 0.15% HF deposition for 50 min; (b) after annealing to 15 K; (c) after annealing to 23 K; (d) after annealing to 30 K; (e) after annealing to 38 K.

annealing into the 30's K, then decreased on annealing to 39 K. The HF–DF frequency ratio identifies a U–H/U–D stretching mode, and the position suggests an antisymmetric U–H_2/U–D_2 stretching mode. These bands are very close to weaker matrix site bands at 1360.6 and 972.5 cm^{-1} previously assigned to UH_2 and UD_2.[7] These molecules can be made here from H and D atoms photodissociated from the precursor by the laser ablation plume.

We expect a very small deuterium shift for the U–F stretching mode and the split band at 544.6, 542.6 cm^{-1} attracts our attention. This feature tracks with the sum of the above 1383.1 and 988.3 cm^{-1} bands on annealing cycles taking in to account the extra broad underlying absorption near 540 cm^{-1}. The 542.6 cm^{-1} band is stronger with the highest DF enrichment, and the 544.6 cm^{-1} band is stronger with the highest HF enrichment, and of course, it is the only sharp feature observed with the HF reagent (Fig. 3). Higher annealing to 36 and 39 K (Fig. 2d and e) decreases all of these bands slightly. At the same time the HF and DF monomer bands decrease while the dimer, trimer, and tetramer bands first increase then decrease giving way to broad, weak bands near 3200 and 2400 cm^{-1} for higher HF clusters.[12] No extra satellite bands appear on any of the new product bands on annealing, and the weak anion bands decrease, as observed previously. In addition weak bands appear at 537.0, 532.4, and 530.4 cm^{-1} on annealing. These three bands agree precisely with stronger bands observed in F_2 experiments, which have been assigned to UF_4.[9] Note that our new band at 544.6 cm^{-1} is very close to these matrix site split U–F stretching modes for UF_4. The sharp new bands at 564.9 and 567.7 cm^{-1} are probably due to the UF diatomic molecule, which is expected to have a fundamental frequency above 550 cm^{-1}.[15]

Additional confirmation of the HUF formation here comes from B3LYP/RSC/aug-cc-pVTZ (denoted as RSC/aVTZ), CASPT(2) and CCSD(T) calculations which have recently been used for the description of OUF_2 and $OThF_2$.[16] Computational details can be
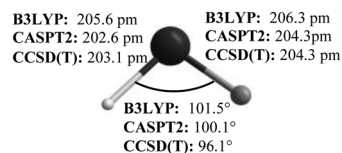

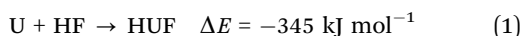**Fig. 4** Optimized structure of HUF at different levels of theory.

Table 1 Calculated and observed vibrational frequencies of HUF in cm^{-1} (intensities in km mol^{-1}) compared with UH$_2$ and UF$_2$ and calculated thermochemistry of HUF in kJ mol^{-1}

	Stretching mode	B3LYP RSC/ aVTZ[a]	B3LYP RSC/ aVTZ[b]	CCSD(T) RSC/ aVTZ[a]	CCSD(T) RSC/ aVTZ[c]	Ar	Reaction	B3LYP RSC/ aVTZ
HUF[d]	U–F	548.3 (148)	543.8	568.7 (150)	564.2	544.6[e]	HUF → U +HF	345
	U–H	1426.4 (401)	1349.6	1454.4 (406)	1377.6	1383.1[e]	HUF → UF + H	229
DUF	U–F	546.1 (132)	541.0	567.7	562.6	542.6	HUF → UH + F	626
	U–D	1011.5 (201)	972.1	1031.3	992.2	988.3	UF → U + F	673[f,g]
UH$_2$	U–H sym.	1452.4 (339)	1393.3	1480.0 (411)	1420.1	1406.1[7]	U + HF → UF + H	−115
	U–H asym.	1395.6 (651)	1329.7	1438.0 (460)	1372.1	1370.7[7]	U + HF → UH + F	281
UD$_2$	U–D sym.	1029.0 (171)	999.2	1050.4	1020.6	1003.5[7]	UF + HF → HUF$_2$	−300
	U–D asym.	989.9 (329)	956.6	1021.8	988.5	978.7[7]	HUF + F → HUF$_2$	−628
UF$_2$	U–F sym.	552.6 (87)	547.0	567.5 (104)	561.9	—	HUF + H → FUH$_2$	−267
	U–F asym.	526.7 (152)	518.0	513.5 (114)	504.8	—	2HUF → UH$_2$ + UF$_2$	10

[a] Harmonic frequencies. [b] Anharmonic frequencies. [c] Anharmonicity calculated at DFT level. [d] CASPT(2) harmonic frequencies are U–F 563.9 cm^{-1} (191) and U–H 1490.1 cm^{-1} (677). [e] Neon: 555.5/1402.8 cm^{-1}, Krypton: 537.5/1371.6 cm^{-1}. [f] Experimental value from ref. 19: 648 kJ mol^{-1}. [g] Computed value at B3LYP level of ref. 20: 673 kJ mol^{-1}.

found in the ESI.† The quintet ground state structure is shown in Fig. 4: the triplet state is 20 kJ mol^{-1} higher in energy.

Table 1 compares calculated and observed frequencies for some species of interest. The harmonic frequencies, cm^{-1} (intensities, km mol^{-1}) calculated for HUF are 1426.4(401), 548.3(148), 308.4(63) and for DUF are 1011.5(201), 546.1(132), 225.5(33). The 1426.4/1011.5 ratio, 1.410, is larger than our observed 1.400 ratio owing to a small cubic anharmonicity in the U–H stretching mode. Including anharmonicity based on B3LYP calculations the computed ratio is 1.388. The calculated 543.8 cm^{-1} U–F stretching frequency is fortunately close to the 544.6 cm^{-1} observed argon matrix value, and the calculated DUF shift of 2.2 cm^{-1} for this mode matches our observed shift, which helps to characterize this new molecule and first uranium hydride fluoride. Several calculated energies are of interest. First, for the primary reaction, ignoring spin orbit coupling for U, the energy is exothermic 345 kJ mol^{-1} at DFT level. The addition of a second HF is also favorable, but the addition of another HF is slightly endothermic. Additional thermochemistry data is given in Table 1.

$$U + HF \rightarrow HUF \quad \Delta E = -345 \text{ kJ mol}^{-1} \quad (1)$$

$$HUF + HF \rightarrow H_2UF_2 \quad \Delta E = -278 \text{ kJ mol}^{-1} \quad (2)$$

$$H_2UF_2 + HF \rightarrow H_3UF_3 \quad \Delta E = 28 \text{ kJ mol}^{-1} \quad (3)$$

The CCSD(T) U–H distance of 203.1 is close enough to the sum of recently reported single-bond covalent radii, 170 + 32 = 202 pm. In contrast, the U–F bond length of 204.3 is between the sum of the single-bond radii, 170 + 64 = 234 pm,[17] and the sum of the double-bond radii, 134 + 59 = 193 pm.[18] Our intermediate U–F distance might indicate some π bonding, but the B3LYP orbitals instead suggested considerable ionic character for the U–F bond (NPA charges U: 1.24, F: −0.71).

Based on our extensive work with laser ablated U reacting with F$_2$ and H$_2$,[7–10] we expect laser ablated U atoms to react with HF during condensation in excess argon, and the new 1383 and 544 cm^{-1} product bands support this conclusion. It is interesting to note that further reaction occurs on annealing into the 20–29 K range and these product bands increase and sharpen. Hence reaction (1) proceeds with little or no activation energy. The demise of these product bands on annealing into the

30–41 K range could be due to reaction (2), and possible evidence is found only for the strongest calculated modes for H$_2$UF$_2$ (antisymmetric U–H$_2$ modes calculated at 1523 and 1528 cm^{-1}) in a weak doublet band observed at 1487.5–1485.7 cm^{-1} (not shown). This is very close to the 1483.6–1481.7 cm^{-1} doublet observed for UH$_4$ in solid argon.[7]

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