Multiple Bonds

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Simple $N\equiv UF_3$ and $P\equiv UF_3$ Molecules with Triple Bonds to Uranium**

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The chemical behavior of actinide elements must be understood to manage effectively the many uses of actinide materials in today's world. Considerable interest has developed in recent years in actinide (An) complexes with metal–ligand multiple bonds. Most of these investigations have centered on organometallic systems,[1] and molecular complexes containing metal nitride units have been prepared.[2–6] These compounds with $U{=}N$ linkages and organoimido ($An{=}NR$) and phosphinidene ($An{=}PR$) groups[7,8] are representative. Matrix-isolation infrared spectroscopy has contributed to the short list of uranium compounds containing triple bonds with discovery of the NUN and CUO molecules and preparation the $[NUO]^+$ cation first detected by mass spectrometry.[9–13]

The common first-row elements carbon, nitrogen, and oxygen form multiple bonds with their 2p valence orbitals, and these bonds are responsible for the chemical properties of many simple compounds, such as $HC\equiv CH$, $N\equiv N$, and $O{=}O$. However, heavier main group elements from the second, third, and fourth complete rows of the periodic table are much less inclined to form multiple bonds, and their chemistry markedly reflects this difference.[14] Although the heavier p-block elements are involved in double bonds, such triple bonds are seldom found. On the other hand f elements (lanthanides and actinides) with multiple bonds are not common, and the quest for such compounds with multiple bonds between two actinide metals and between actinide and main-group elements has evolved vigorously with computations leading the former[15–20] and synthesis the latter.[1–8]

We recently reported the first examples of uranium methylidene and methylidyne molecules using laser-ablated uranium atoms as the reagent. These species include the $CH_2{=}UH_2$, $CH_2{=}UHF$, $CH_2{=}UF_2$, $HC\equiv UF_3$, and $FC\equiv UF_3$ molecules.[21–24] Analogous methylidene complexes are important reagents in organometallic chemistry, particularly for the early transition metals.[25] Although alkylidyne complexes are not as prevalent, a number of simple Group 6 methylidyne complexes have been prepared through metal-atom reactions with methyl halides.[25,26]

Fluorine is a very important element in uranium chemistry because of its role in uranium-isotope separation using gaseous diffusion of the volatile uranium hexafluoride. Accordingly UF_6 has been the subject of considerable experimental and theoretical investigations.[27,28] The smaller UF_n molecules have been studied less often,[28,29] but fluorine has demonstrated its ability to facilitate the participation of uranium in important chemical and physical processes. The strong inductive effect of fluorine was central to the stabilization of the first uranium methylidyne complex $FC\equiv UF_3$,[24] and fluorine should be equally as useful in assisting other even heavier main-group elements to stabilize U^{VI} and to form novel triple bonds to uranium.

We report herein a combined experimental and theoretical investigation of uranium-atom reactions with NF_3 and PF_3, designed to prepare terminal uranium nitride and phosphide functional groups. Our knowledge of terminal $U\equiv N$ bonds in neutral molecules is limited to matrix-isolation studies of $U\equiv N$ and $N\equiv U\equiv N$,[9,10] and to date no terminal $U\equiv P$ species have been prepared.

Uranium atoms, laser-ablated from a solid-metal target (Oak Ridge National Laboratory, high purity, depleted of ^{235}U) were reacted with NF_3 (Matheson) and PF_3 (PCR Research Chemicals) diluted in argon during condensation on a 4 K cesium iodide window using methods described previously.[26,30–32] After reaction, ultraviolet irradiation, and annealing, infrared spectra were recorded at a resolution of $0.5\ cm^{-1}$.

Ten experiments were carried out with NF_3 using concentrations from 1.0 to 0.05% in argon and a range of laser energies in order to minimize aggregation. The major product absorptions common to experiments with other metals and NF_3 is the NF_2 radical absorbing at 932 and $1069\ cm^{-1}$, which arises from precursor photodissociation, and new bands at 999 and $873\ cm^{-1}$ for NF_2^-.[33] Infrared spectra of low energy, laser-ablated U and NF_3 (0.3%) reaction products are shown in Figure 1. The spectrum of the initial sample deposit (Figure 1a) shows four weak new bands at 938, 613, 540, and $533\ cm^{-1}$ which are marked by arrows in Figure 1b. The four bands increased five-fold on ultraviolet irradiation and acquired matching shoulders on the low energy side (Figure 1b). A second ultraviolet irradiation increased the four bands 20% in concert (Figure 1c). Annealing to 20 K increased the shoulders at the expense of the original bands and resolved them into matching three-band sets (Figure 1d

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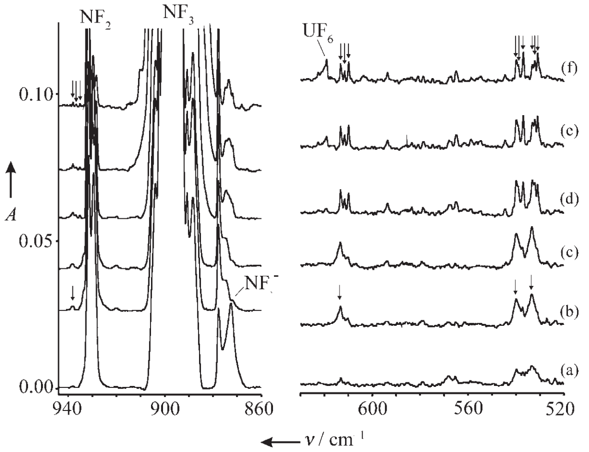

Figure 1. Infrared spectra for U-atom reaction products with NF_3 in the 940–860 and 630–480 cm^{-1} regions, arrows indicate key absorptions, see text for details; for clarity the *y* axis of spectra (b)–(f) has been vertically shifted. a) spectrum after co-deposition of laser-ablated U and NF_3 at 0.3 % in argon at 4 K for 60 min, b) after 240–380 nm irradiation for 20 min, c) after 240–380 nm irradiation for 20 min more, d) after annealing to 20 K, e) after annealing to 30 K, and f) after annealing to 35 K.

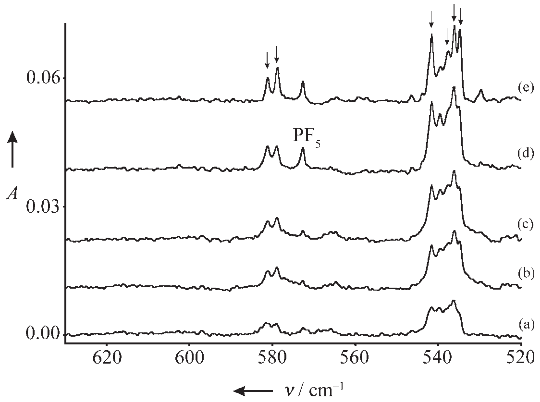

Figure 2. Infrared spectra for U-atom reaction products with PF_3 in the 630–520 cm^{-1} regions; arrows indicate key absorptions, see text for details; for clarity the *y* axis of spectra (b)–(e) has been vertically shifted. a) spectrum after co-deposition of laser-ablated U and PF_3 at 0.4 % in argon at 4 K for 60 min, b) after annealing to 20 K, c) after >290 nm irradiation for 20 min, d) after >220 nm irradiation for 20 min, and e) after annealing to 30 K.

and marked by arrows in Figure 1 f), and produced a weak band due to UF_6 (619 cm^{-1}; marked in Figure 1 f). Further annealing to 30 and 35 K continued these trends and markedly increased the UF_6 absorption (Figure 1 e and f). The 938 cm^{-1} band clearly tracks with the 613, 540, and 533 cm^{-1} bands, and the observation of similar red-shifted satellite structures for these four bands associates them with a common product species. The UF_6 band was observed in earlier U and F_2 reactions,[29] but not in our subsequent investigations with the less reactive PF_3 precursor. The UF_6 peak increased more relative to the new product absorptions on using higher reagent concentration. It is clear that uranium fluorides are also products of the U and NF_3 reaction.

Five investigations with U at different laser energies and PF_3 in different concentrations produced the representative spectra shown in Figure 2. Absorptions common to ablation experiments with other heavy metals and PF_3 include the PF_2 radical at 830 cm^{-1} (not shown) which decreased on annealing, and PF_5 at 1017 and 573 cm^{-1}, which increased on annealing.[33] Clearly some F atoms are produced on photodissociation of PF_3, but not enough to form uranium fluorides. New absorption peaks (marked by arrows in Figure 2 e) were observed at 581, 579, 542, 538, 536 and 535 cm^{-1}. These bands sharpened on annealing. Near-UV irradiation increased these absorptions and the very weak 1051 cm^{-1} NUN band,[10] which shows that U atoms undergo further reactions even with trace N_2 impurity.

Our previous investigations of metal-atom reactions with fluorocarbons have shown that C–F bond insertion occurs followed by one, two, or three F-atom transfers to give the more stable products.[23,24,34] Such was the case with CF_4 to give the final $FC{\equiv}UF_3$ methylidyne. The driving force was the formation of exceedingly strong U–F bonds at the expense of C–F bonds that though strong, are less so.[28,35] This situation is even more dramatic for the NF_3 and PF_3 precursors which have weaker fluorine bonds, as summarized in Reactions (1) and (2).

$$U + NF_3 \rightarrow F_2N{-}UF \rightarrow FN{=}UF_2 \rightarrow N{\equiv}UF_3 \qquad (1)$$

$$U + PF_3 \rightarrow F_2P{-}UF \rightarrow FP{=}UF_2 \rightarrow P{\equiv}UF_3 \qquad (2)$$

Calculations were performed with density functional (DFT, PW91) and wave function (CASSCF/CASPT2) methods[36,37] to support the above reaction mechanism, to identify the new molecules, and to explore their bonding and structure. The details of these theoretical methods are summarized in the Supporting Information. The first quintet insertion product, F_2N-UF, failed to converge, but the NF-UF_2 imine is +345 kJ mol^{-1} higher in energy than the final nitride product (quoted energies from PW91 density functional calculations). Furthermore, the strongest U–F stretching mode calculated (PW91) for $NF{=}UF_2$ at 528 cm^{-1} is clearly lower than the strongest observed absorptions. However, the four new product bands observed at 938, 613, 540, and 533 cm^{-1} correlate nicely with the U≡N and U–F stretching vibrations computed for the final nitride product $N{\equiv}UF_3$, as shown in Table 1. First, the N≡U stretching mode at 938 cm^{-1} is bracketed by the DFT (976 cm^{-1}) and CASPT2 (921 cm^{-1}) theoretical values. The isolated UN molecule absorption was observed at 1001 cm^{-1} in solid argon.[8] Second, the symmetric U–F stretching mode observed at 613 cm^{-1} is calculated at 634 cm^{-1} for the C_{3v} molecule at the CASPT2 level and at 603 cm^{-1} with DFT. Third, the degenerate U–F stretching mode calculated at 548 cm^{-1} by CASPT2 is split at 541 and 533 cm^{-1} using DFT, and the observed solid-argon-matrix band is split at 540 and 533 cm^{-1}. The calculated frequencies are harmonic and are expected to be slightly higher than observed values, particularly in solid argon. The general agreement between calculated and observed frequencies substantiates the present observation of the $N{\equiv}UF_3$ molecule. The molecule may be distorted slightly by the argon matrix to

Table 1: Observed and calculated frequencies of the N≡UF$_3$ and P≡UF$_3$ molecules in the singlet ground electronic states with C_{3v} or C_s structures.[a]

Approximate Description	N≡UF$_3$					P≡UF$_3$				
	obs	calcd(CA)	int	calcd(PW)	int	obs	calcd(CA)	int	calcd(PW)	int
N≡U str, a$_1$,a′	938	921	71	976	110					
U-F str, a$_1$,a′	613	634	171	603	98	581	619	259	600	166
U-F str, e, a″	540	548	454	541	155	542	560	430	557	140
U-F str, a′	533			533	141	536			548	140
P≡U str, a′						n.o.[b]	404	26	374	11
F-U-F bend, a$_1$, a′		143	20	148	8		148	19	128	10
F-U-F bend, e, a“		135	30	135	5		111	12	124	2
F-U-F bend, a′				119	17				103	9
P-U-F bend, e, a″		22i	118	82	39		25	54	62	13
P-U-F bend, a′				51	34				34	14

[a] Frequencies and intensities (int) are in cm^{-1} and km mol^{-1}, respectively. Observed in an argon matrix. Frequencies and intensities computed with CASPT2 (CA) or PW91 (PW) methods in the harmonic approximation. Symmetry notations are first for C_{3v} from CASSCF and second for C_s from PW91. [b] Not observed because it falls below the instrument limit.

facilitate a bonding interaction of the first argon atom with the uranium metal center.[38]

We have found the N≡UF$_3$ molecule to be extremely difficult to preserve in these experiments and dilute samples were required to trap the isolated product in solid argon. In fact, the red-shifted satellites that increase in intensity on annealing are most likely to be due to (N≡UF$_3$)–(NF$_3$) complexes in two different orientations. We note a dramatic increase in UF$_6$ absorption intensity on the final annealing at the expense of both N≡UF$_3$ and NF$_3$ and propose the highly exothermic (995 kJ mol^{-1}) mechanism given in Reaction (3) to explain the favorable reaction of N≡UF$_3$ under these conditions.

$$F_3N + N{\equiv}UF_3 \rightarrow N{\equiv}N + UF_6 \qquad (3)$$

The N≡UF$_3$ molecule contains a strong uranium–nitrogen triple bond with a calculated length of 1.76 Å (CASPT2) or 1.75 Å (PW91). The C_{3v} symmetry structure converged by CASSCF/CASPT2 is given in Figure 3. The degenerate N-U-F bending frequency is imaginary (i22 cm^{-1}), and a distorted structure is found 19 cm^{-1} lower in energy. PW91 also finds an imaginary degenerate bending frequency (i13 cm^{-1}): geometry optimization in C_s symmetry leads to a true minimum that is distorted from C_{3v} geometry, but which lies only 17 cm^{-1} lower in energy. Vibrational frequencies of the N≡UF$_3$ molecule are given in Table 1: it is important to note that the stretching frequencies are almost identical for the C_{3v} and C_s structures. Hence, both DFT and the CASSCF/CASPT2 methods predict a slightly distorted molecule to be the global minimum, but the energy gain compared to the C_{3v} structure is minute.

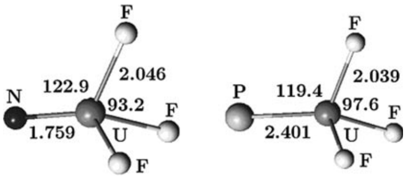

Figure 3. Structures of N≡UF$_3$ and P≡UF$_3$ in C_{3v} symmetry calculated at the CASSCF/CASPT2 level of theory. Bond lengths [Å] and angles [°].

The active molecular orbitals that contribute to this triple bond are shown in Figure 4. The natural orbital occupation numbers for the σ- and π-bonding and antibonding orbitals add to give a strong triple bond in N≡UF$_3$ with an effective bond order of 2.78. Recent characterization of the HC≡UF$_3$ molecule with a 2.56 bond order using the same level of theory[24] indicated that N≡UF$_3$ has the strongest triple bond to uranium yet prepared in a ternary molecule. The bonding-orbital occupancy is higher and the antibonding orbital occupancy lower for N≡UF$_3$ than for HC≡UF$_3$. Thus, it appears that nitrogen valence orbitals are particularly favorable for forming strong multiple bonds to uranium.

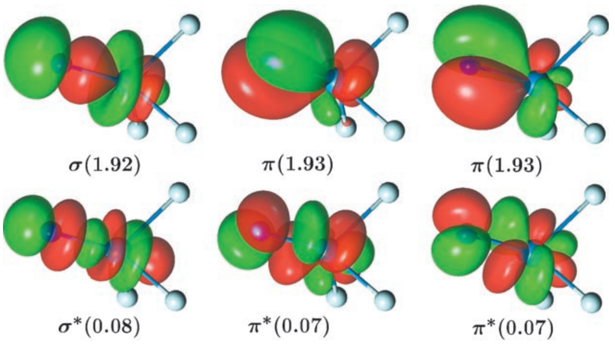

Figure 4. Active molecular orbitals in N≡UF$_3$. Contour line 0.05 e au^{-3}. Natural orbital occupation numbers given below the orbital.

For the reaction with PF$_3$ [Reaction (2)] the first and second intermediate species are +184 and +50 kJ mol^{-1} higher than the final phosphide product. Although we find two sets of bands for assignment to P≡UF$_3$, which may be due to the isolated molecule and a complex with PF$_3$, there appears to be no reaction of product with the more stable PF$_3$ molecule as no UF$_6$ is detected in this system. In Table 1 the observed and calculated frequencies for P≡UF$_3$ are compared; the correlation again substantiates our assignments.

The P≡UF$_3$ molecule has a weak uranium–phosphorus triple bond with a calculated bond length of 2.38 Å (PW91) or 2.40 Å (CASPT2; Figure 3). The natural orbital occupation numbers (Figure 5) give an effective bond order of 2.4 corresponding to a considerably weaker triple bond than in N≡UF$_3$. The terminal U≡P bond is expected to be weaker than the terminal U≡N bond as the more diffuse phosphorus orbitals are less effective in forming multiple bonds than nitrogen atomic orbitals.[14] The U≡N and U≡P bond energies can be estimated as the energy of the atom reaction with UF$_3$, where UF$_3$ has a C_s structure with U−F bond lengths of 2.055 and 2.074 Å. These CASSCF/CASPT2 calculations are approximate without ZPE or spin-orbit correction. Nevertheless, the difference between the U≡N and U≡P bond energies is striking. While the U≡N bond is strong (460 kJ mol^{-1}), the U≡P bond is much weaker (176 kJ mol^{-1}).

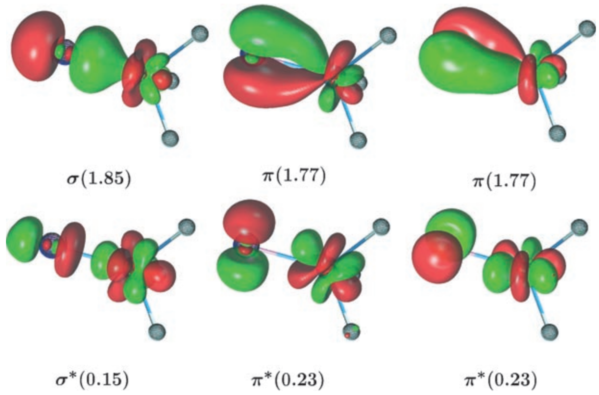

Figure 5. Active molecular orbitals in P≡UF$_3$. Contour line 0.05 e au^{-3}. Natural orbital occupation numbers given below the orbital.

Why is the U≡N bond so much stronger than the U≡P bond? The explanation is found, in part, in the character of the U^{3+} moiety. It is the 5f orbitals on this ion that are mainly used to form the bond, and they are quite contracted and hard. Therefore a more balanced covalent bond can be formed with a hard ligand such as nitrogen. The softer 3p orbitals of P do not have the same ability to form a strong bond with U^{3+}. It is interesting to look at the charges of the atoms in the two cases. The U≡P bond is slightly more ionic than the U≡N bond (Mulliken charges −0.29(P) and −0.25(N)) while the charges on F are the same in both cases. The total occupation of the U 5f orbitals is 2.21 for P≡UF$_3$ and 2.14 electrons for N≡UF$_3$. Also the U 6d orbitals participate in the bonding with a total population of 1.34 electrons (in P≡UF$_3$) and 1.43 electrons (in N≡UF$_3$), thus, slightly larger in the nitrogen compound, which is another indication of a less-ionic bond in this case. The very strong uranium–nitrogen bond is also found in the molecule NUN[9,10] in which the stabilization energy relative to U + N$_2$ has been estimated to be about 250 kJ mol^{-1}.[39] Adding the bond energy of N$_2$ yields a bond strength of about 580 kcal mol^{-1} per bond in NUN.

The U−N bond lengths in our present system, 1.75 Å (PW91) and 1.76 Å (CASPT2), and those determined earlier for N≡U≡N, 1.73 Å,[40] can also be compared to those measured for the larger complexes prepared by Evans, et al. in the 2.01–2.07 Å double-bond range, the first U^{VI} organometallic complex reported by the Burns group, 1.95 Å, and the shorter 1.85 Å N−U−N distances of Hayton, et al.[1,4,6] Our computed double-bond length for FN=UF$_2$ is 0.20 Å longer than our triple-bond length for N≡UF$_3$. Likewise the phosphinidene complexes of Burns et al.[8] with U−P bonds 2.74 Å and 2.79 Å and U=P bond lengths of 2.56 Å are longer than the 2.38 Å (PW91) and 2.40 Å (CASPT2) values calculated by us for P≡UF$_3$. Clearly, the N≡UF$_3$ and P≡UF$_3$ molecules reported herein represent uranium–Group 15 triple bonds as shown by the molecular orbital analysis, although the U≡P bond is weak. A final comparison with terminal W≡N and W≡P bond lengths of 1.67 Å and 2.12 Å in analogous organometallic complexes[41,42] shows that the triple-bond lengths computed herein for uranium are 5 and 13 % longer than their tungsten analogues. We see that the U≡P bond is clearly weaker in comparison than W≡P, which is in marked contrast to U≡N in comparison with W≡N. This situation is further supported by compiled triple-bond radii,[43] which predict a U≡N length (1.72 Å) that is 2 % shorter than our computed value but a U≡P length (2.12 Å) that is 12 % shorter than our CASPT2 value.

As for the uranium methylidyne systems,[24] macroscopic synthetic sources of terminal U≡N and U≡P triple bonds have not yet been found. This matrix-isolation work shows that with the assistance of strongly electronegative ligands such as F, the U^{VI} oxidation state can be stabilized and terminal triple bonds can be formed with N and reasonably well with the heavier analogue P. Comparison of the nitride and phosphide triple bonds to uranium demonstrates that U 5f orbitals bond more effectively with the smaller nitrogen ligand.

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