Inorganic Chemistry
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Combined Triple and Double Bonds to Uranium: The $N\equiv U=N-H$ Uranimine Nitride Molecule Prepared in Solid Argon

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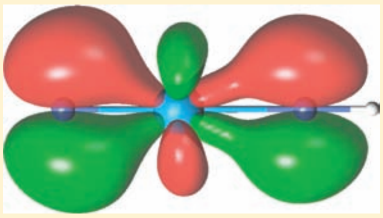


ABSTRACT: Reactions of laser-ablated U atoms with N_2 and H_2 mixtures upon codeposition in excess argon at 5 K gave strong NUN and weak UN infrared absorptions and new bands at 3349.7, 966.9, 752.4, and 433.0 cm^{-1} for the unusual new U(V) molecule $N\equiv U=N-H$, uranimine nitride, containing both triple and double bonds. This identification is based on D and ^{15}N isotopic substitution and comparison with frequencies computed by density functional theory for the $^2\Delta$ ground state NUNH. Calculated bond lengths are compared to those of the $^1\Sigma_g^+$ ground state of U(VI) uranium dinitride $N\equiv U\equiv N$, the $^2\Phi$ ground state of the isoelectronic nitride oxide $N\equiv U=O$, and the ^3A ground state of the U(IV) uranimine dihydride $HN=UH_2$ molecule, which have all been prepared in solid argon matrices. Mulliken bond orders based on the CASSCF orbitals for $N\equiv U=N-H$ are 2.91, 2.19, and 1.05, respectively. Here, the terminal nitride is effectively a triple bond, just as found for $N\equiv U\equiv N$. The solid argon matrix is a convenient medium to isolate reactive terminal uranium nitrides for examination of their spectroscopic properties.

INTRODUCTION

Multiple bonding between uranium and main group elements is of considerable research importance, owing to interest in the behavior of 5f electrons as well as nuclear fuels and waste remediation.[1−10] Several ligand-supported imido ($U=NX$), $N-U-N$, and $U-N-U$ molecular linkages,[1−7] as well as uranium carbene complexes, have been prepared.[8,9] Evidence has been presented recently for a transient terminal uranium nitride complex following photolysis of uranium azide complexes.[10] In addition, solid uranium nitrides and carbides are of potential importance as nuclear fuel materials.[11−13]

The $U\equiv N$ diatomic molecule, prepared first from a nitrogen discharge in the presence of uranium metal,[14] has only been observed to date in solid argon matrices.[14,15] The nitrogen analog to the uranyl dication, $N\equiv U\equiv N$, was also prepared in this discharge work and later through the insertion of laser-ablated U atoms into dinitrogen during condensation with excess argon.[16] It was also shown that near UV excitation of U atoms in these experiments increased the yield of $N\equiv U\equiv N$ through more reaction with N_2 in solid argon.[16] Upon condensation of U atoms and pure dinitrogen, the $N\equiv U\equiv N$ molecule so formed is complexed extensively to extra dinitrogen molecules.[17,18] Subsequently, a variety of simple new uranium-bearing molecules such as $HN=UH_2$, $N\equiv U=O$, $N\equiv UF_3$, $CH_2=UH_2$, and $U\equiv C$ containing multiple bonds to uranium have been identified in matrix isolation experiments and characterized through quantum chemical calculations.[19−23] The linear uranium dinitride molecule $N\equiv U\equiv N$, which was the first terminal uranium nitride formed by photolysis,[16] has fully developed triple bonds based on early SCF and recent CASPT2 calculations.[24,25] Although NUN is isoelectronic with the common UO_2^{2+} uranyl dication,[24] and a stable species in its own right, we wanted to examine the reactivity of NUN with other abundant materials such as hydrogen in order to prepare other derivatives of this stable molecule under matrix isolation conditions. Hence, the reaction of laser ablated U atoms and N_2/H_2 mixtures in condensing excess argon has been investigated, and we found that some of the NUN produced reacts with H atoms to give the linear uranimine nitride molecule NUNH. The formation and isolation of a stable molecule like NUNH in solid argon suggests that it will be possible to prepare more ligand stabilized derivatives of terminal uranium nitrides on a macroscopic scale.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Laser-ablated U atoms were reacted with N_2/H_2 mixtures (Matheson, 0.3 to 0.6% of each reagent) in argon during condensation at 5 K using methods described in our previous papers.[16,26,27] The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused onto a rotating uranium target (Oak Ridge National Laboratory, high purity, depleted of ^{235}U). The uranium target was filed to remove surface oxide and immediately placed in the vacuum

Received: February 16, 2011
Published: March 15, 2011

Table 1. Observed and Calculated Frequencies for NUNH Isotopic Molecules in the $^2\Delta$ Ground State[a]

	$^{14}NU^{14}NH$					$^{14}NU^{14}ND$					$^{15}NU^{15}NH$					$^{15}NU^{15}ND$		
approx. mode	obs[b]	B3LYP[c]	int[c]	BPW91[d]	int[c]	obs[b]	B3LYP[c]	int[c]	BPW91[d]	int[c]	obs[b]	B3LYP[c]	int[c]	BPW91[d]	int[c]	obs[b]	B3LYP[c]	BPW91[d]
N−H str., σ	3349.7	3530.8	38	3433.3	18	2489.2	2590.4	64	2518.9	40	3342.1	3522.3	34	3425.0	15	2477.6	2577.9	2506.7
N≡U str., σ	966.9	1035.4	359	993.1[e]	316	966.5	1035.4	359	992.9	310	936.5	1002.6	342	961.7[e]	302	936.0	1002.5	961.5
U═N str., σ	752.4	784.9	304	771.7[e]	246	742.4	758.3	283	745.5	230	731.3	761.4	283	748.5[e]	228	722.3	737.4	724.9
UNH def., π	433.0	425.1	190 × 2	463.8	169 × 2		321.7	129 × 2	353.5	117 × 2	431.0	423.1	186 × 2	461.4	165 × 2		319.0	350.2
NUN def., π		96.3[f]	65 × 2	89.0	47 × 2		93.7	61 × 2	91.2	50 × 2		93.5	61 × 2	89.5	47 × 2		91.1	86.8

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Observed in an argon matrix. [c] Frequencies computed with B3LYP/6-311++G(3df, 3pd). [d] Frequencies computed with BPW91/6-311++G(3df,3pd). [e] Frequencies computed with BPW91 for 15-U-14-H are 961.9 and 771.2 cm^{-1} and for 14-U-15-H are 992.9 and 748.9 cm^{-1}. [f] CASPT2 frequencies (intensities) with no symmetry imposed: 3548 (41), 1020 (384), 787 (283), 519 (112), 303 (1590), and 79 (73).

chamber. Deuterium gas and $^{15}N_2$ (Cambridge Isotopic Laboratories, 98+%) were used as received. Isotopically scrambled dinitrogen was prepared by tesla coil discharge of $^{14}N_2$ and $^{15}N_2$ for 20 min at 10−15 Torr of pressure in a Pyrex bulb with a stainless steel valve. FTIR spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 750 machine with 0.1 cm^{-1} accuracy using a HgCdTe range B detector.

Quantum chemical calculations were performed using the Gaussian 09 program system with the hybrid B3LYP and pure BPW91 density functionals, the 6-311++G(3df,3pd) basis for H and N, and the SDD pseudopotential for U [30 electron core][28−32] as performed for previous uranium-bearing molecules.[12,23,24] Additional wave function based calculations were done using CASSCF/CASPT2 and the ANO-RCC-VTZP basis with the MOLCAS 7.2 software in order to describe the multiconfigurational nature of NUN and NUNH and to analyze the U−N bonding in detail.[33−35] The active space employed to describe NUN is composed of 12 electrons in 12 orbitals (12,12). This contains two σ bonding/antibonding pairs and two sets of π bonds (in total, four π bonding orbitals and four π* antibonding orbitals). In NUNH, one electron in a H 1s orbital is added, resulting in an active space of (13,13). The same bonding and antibonding orbitals are present in NUNH as in NUN with the addition of one nonbonding orbital localized on uranium.

RESULTS AND DISCUSSION

Infrared spectra of laser ablated uranium atom reaction products with nitrogen/hydrogen mixtures in excess argon will be presented and compared to density functional calculations of product vibrational frequencies. Multiple bonding in the new NUNH molecule will be discussed.

Infrared Spectra. First, the infrared spectra of laser ablated uranium atom reaction products with nitrogen in excess argon during condensation at 5 K gave strong NUN and weak UN absorptions, as the present lower substrate temperature enabled trapping of the diatomic molecule.[14,16] The use of isotopically scrambled dinitrogen again verified the symmetrical structure of the linear NUN molecule. Annealing gave evidence for the formation of dinitrogen complexes with both NUN and UN.

Next, spectra were recorded using nitrogen/hydrogen mixtures in excess argon, and the major products for these reagents were observed, as before (NUN at 1050.9 cm^{-1}; $A = 0.12$; the Ar_nH^+ species at 903 cm^{-1}; and the uranium hydrides at 1483.5, 1423.9, 1371.0, and 1182 cm^{-1}; $A = 0.005−0.015$).[16,36,37] Uranium oxide was detected at 819.8 cm^{-1}.[38]

Important new absorptions at 3349.7, 966.9, 752.4, and 433.0 cm^{-1} are listed in Table 1 along with their isotopic modifications. These new bands are shown in Figure 1 for the freshly deposited samples. The NUN band at 1050.9 cm^{-1} (not shown) was 4 times as strong as the new 966.9 cm^{-1} product absorption. Subsequent annealing to 20−30 K had little effect on these bands, but the system pressure increased as H_2 was released by the argon matrix (H_2 boiling point 20.7 K). Although full arc irradiation increased the 1050.9 cm^{-1} NUN band by 20−30% and destroyed the Ar_nH^+ band, as before,[16,36,37] the new product bands were not affected.

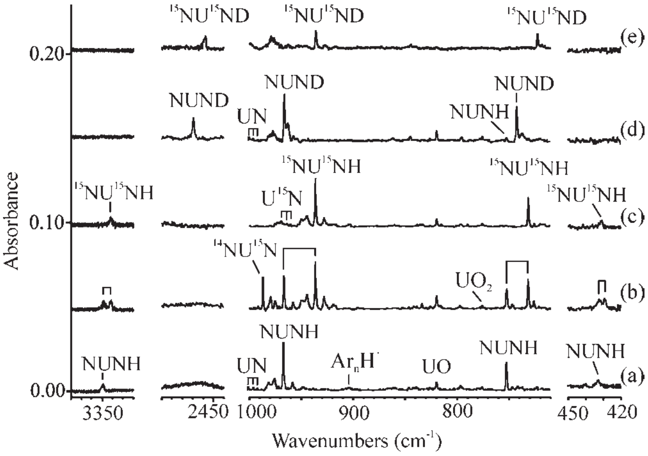


Figure 1. Infrared spectra of the major uranium, nitrogen, and hydrogen reaction products upon codeposition in argon at 5 K. (a) U and N_2/H_2 (0.6% each) codeposited in argon at 5 K for 60 min, (b) U and scrambled $^{14,15}N_2/H_2$ (0.6% each), (c) U and $^{15}N_2/H_2$ (0.3% each), (d) U and $^{14}N_2/D_2$ (0.3% each), and (e) U and $^{15}N_2/D_2$ (0.3% each).

An additional uranium experiment was done with CO added (0.1%) to the argon sample containing N_2 and H_2 (0.6% each), and the above new bands were observed, along with HCO at 1863 cm^{-1} and weak CUO bands at 852 and 804 cm^{-1}.[37] Annealing to 30 K increased the HCO band by 50% but left the CUO bands unchanged.

Nitrogen-15 substitution shifted the above bands to 3342.1, 936.5, 731.3, and 431.0 cm^{-1}, confirming the involvement of nitrogen in the vibrational modes responsible for these new absorptions. Reaction with a $^{14}N_2$, $^{14}N^{15}N$, $^{15}N_2$ sample gave apparent doublets (Figure 1b), indicating the major involvement of a single N atom in each vibrational mode, but the 752.4 and 731.3 cm^{-1} bands shifted inward to 752.1 and 731.5 cm^{-1} with $^{14}N_2$, $^{14}N^{15}N$, $^{15}N_2$ revealing minor coupling with a second nonequivalent N atom (Figure 2b).

The new bands shifted with deuterium substitution using the D_2 reagent to 2489.2, 966.5, and 742.4 cm^{-1} and below our range of detection. Shifted bands were also observed for uranium

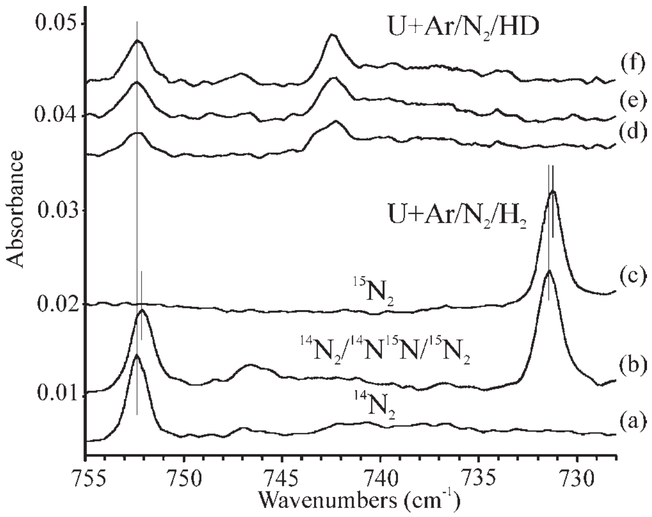


Figure 2. Expanded frequency scale spectra of the NU═NH stretching mode from uranium atom reactions with three nitrogen isotopic modifications and H_2 and with N_2 and HD. (a) U and $^{14}N_2/H_2$ (0.6% each) codeposited in argon at 5 K for 60 min, (b) U and scrambled $^{14,15}N_2/H_2$ (0.6% each), (c) U and $^{15}N_2/H_2$ (0.3% each), (d) U and $^{14}N_2$/HD (0.6% each) codeposited in argon at 5 K for 60 min, (e) spectrum recorded after full arc irradiation for 15 min while the sample was temperature-cycled 5 to 20 to 5 K, (f) spectrum recorded after second full arc irradiation for 15 min while the sample was temperature-cycled 5 to 20 to 5 K.

deuterides and the Ar_nD^+ species.[36,37] The 742.4 cm^{-1} deuterium product band revealed a weak satellite at 752.4 cm^{-1} due to the hydrogen counterpart from background hydrogen contamination in the system (Figure 1d). The 742.4 cm^{-1} band was also detected in nitrogen experiments without added hydrogen, and the band increased 5-fold with hydrogen added to the reagent mixture.

A final experiment was done using HD as the hydrogen-bearing reagent, and the diagnostic region of the spectrum is shown in Figure 2d. The strong bands were observed unresolved at 966.7 cm^{-1}, the average of the above hydrogen and deuterium values, and a sharp doublet at 752.4 and 742.4 cm^{-1}, the same as the above hydrogen and deuterium values. The 752.4−742.4 cm^{-1} doublet absorption verifies the participation of a single H (D) atom in the new product species. Next, annealing and full arc irradiation were performed at the same time, and the spectrum in Figure 2e was recorded after full arc irradiation for 15 min while the sample was cycled 5 to 20 to 5 K and the H_2 pumped away, causing a temporary system pressure increase, revealed a 50% increase in the 752.4−742.4 cm^{-1} doublet absorption along with the associated 966.7 cm^{-1} band. A second identical treatment resulted in no system pressure increase, as presumably no HD remained in the sample, but the 752.4−742.4 cm^{-1} doublet absorption increased another 20%, Figure 2f.

Identification of NUNH and Vibrational Assignments. The new NUNH molecule is identified by the four fingerprint vibrational modes described above. The vibrational assignments are indicated by characteristic frequencies and their isotopic shifts, as illustrated by isotopic frequency ratios, and comparison to values calculated by density functional theory. The 3349.7 cm^{-1} band shifted to 2489.2 cm^{-1} with deuterium substitution (isotopic frequency ratio 1.3450), which is characteristic of a N−H stretching mode as verified by the nitrogen-15 shift to 3342.1 cm^{-1} (ratio 1.00227). These band positions and shifts are in very good agreement with the predictions of two density functional calculations using hybrid and pure density functionals (Table 1). The calculated 3530.8 and 3422.3 cm^{-1} harmonic frequencies are 5.4 and 2.5% higher than the observed value, which is in the range found for the B3LYP and BPW91 functionals.[39,40] This discrepancy is due primarily to anharmonicity in the observed band not accounted for in the harmonic approximation used in the calculations.

Next, the 966.9 cm^{-1} band shifted to 936.5 cm^{-1} with nitrogen-15 (ratio 1.0325), which is almost the same as the 1.0326 ratio for diatomic UN itself.[14] This agreement clearly identifies a terminal UN vibration. Our DFT calculations predict this mode for NUNH to be 7.1 and 2.7% higher with the same 14/15 isotopic frequency ratio. The lower associated 752.4 cm^{-1} band shifts to 731.3 cm^{-1} with nitrogen-15 (ratio 1.0289), which is less, owing to the involvement of hydrogen in this mode as manifested by the shift to 742.4 cm^{-1} on deuterium substitution. The DFT frequencies in this case are 3.0% higher and 1.0% lower than the argon matrix value, and their 14/15 ratios (1.0309, 1.0310) are slightly higher, again likely due to anharmonicity from the hydrogen participation in this mode. As mentioned above, the reaction with $^{14}N_2$, $^{14}N^{15}N$, $^{15}N_2$ gave slightly shifted doublets (Figure 2), indicating the major involvement of a single N atom and the minor coupling with a second nonequivalent N atom (Figure 2b). Hence, our identification of NUNH is made from the characterization of one N−H and two different U−N stretching modes.

Finally, the linear NUNH molecule has a degenerate U−N−H bending mode, and our DFT calculations predict this strong mode at 425.1 or 463.8 cm^{-1}, which bracket the observed 433.0 cm^{-1} argon matrix value. These calculations predict 2.0 or 2.4 cm^{-1} nitrogen-15 shifts, which substantiates our identification of the linear NUNH molecule from its matrix infrared spectrum.

It is interesting to compare the NUNH frequencies computed by two density functionals with those from the CASPT2 wave function based method. With linear symmetry imposed, the CASPT2 stretching frequencies were 3561, 1036, and 787 cm^{-1}, and with no symmetry these were almost the same at 3548, 1020, and 787 cm^{-1}, and they agree very well with the DFT frequencies (Table 1), particularly the higher B3LYP values. The slightly bent molecule with no symmetry gave UNH deformation frequencies of 519 and 303 cm^{-1}, which bracket the degenerate DFT values.

Reactions Occurring in the Matrix. Our experiments have shown that the reaction of a laser ablated, excited U atom with molecular nitrogen proceeds directly to form NUN, reaction 1.[16] This reaction requires electronically excited uranium because annealing to allow diffusion and potential reaction of trapped reagents does not increase the yield of NUN, but exposure of the cold matrix sample to ultraviolet light from a mercury arc street lamp to excite U increases the NUN signal 3-fold.[16] This finding is in agreement with a more recent CASSCF/CASPT2 investigation of the U + N_2 reaction path, which obtained a 25 kcal/mol barrier for this 59 kcal/mol exothermic reaction.[25c]

$$U^* + N_2 \rightarrow NUN \qquad (1)$$

$$NUN^* + H \rightarrow NUNH \qquad (2)$$

In the present U/N_2/H_2 experiments, the most straightforward reaction to produce NUNH is for vacuum ultraviolet photolysis of H_2 from the laser ablation plume to provide H

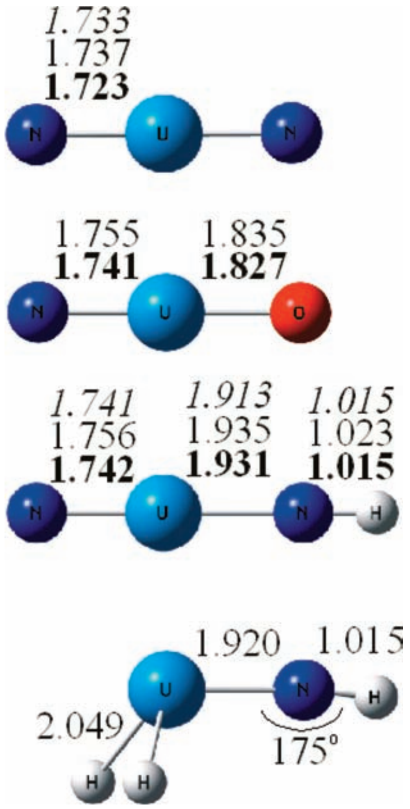


Figure 3. Uranium atom reaction product structures and bond lengths (Å) computed with CASPT2 (italic), BPW91 (normal type), and B3LYP calculations (bold type) for N≡U≡N, N≡U═O, N≡U═N−H, and H_2U═NH, respectively.

atoms for direct reaction with NUN to form NUNH during the laser ablation/irradiation/sample deposition process, reaction 2, which is exothermic by 59 kcal/mol (B3LYP) or 40 kcal/mol (CASPT2). First, from many other investigations[41] and matrix isolation work,[42] the laser ablation plume contains vacuum-UV radiation, which is capable of dissociating molecular hydrogen into H atoms.[43] The observation of Ar_nH^+ and Ar_nD^+ absorptions provides evidence to substantiate the presence of both H and D atoms and high energy radiation.[37,44] The detection of HCO in the CO-doped U/N_2/H_2 experiment and its growth on annealing[37,45] also attest to the formation of H atoms and their reaction in these experiments. Recall, however, that NUNH absorptions *do not* increase on annealing unless annealing and irradiation are performed simultaneously (Figure 2d,e,f). This suggests an energy activation for reaction 2, and PBE/VDZP calculations have found a small 160 cal/mol barrier for reaction 2. Interestingly, this increase of NUNH absorptions under annealing/irradiation conditions where H_2 evaporates from the argon solid, but H atoms remain, based on earlier ESR spectra,[46] provides further evidence for the H atom reaction and casts doubt on any contribution from the 45 kcal/mol endothermic NUN + H_2 → NUNH + H reaction.

There is apparently no significant participation of N_2/H_2 reaction products, as NH and NH_2 are not detected in our samples.[47] Two other products might be considered, quintet U═NH and triplet HN═U═NH, but these are not observed on the basis of frequencies calculated at the DFT level (803 cm^{-1} for the former product and 835 cm^{-1} for the latter). The lack of UNH is probably due to the production of UN signals at less than 1% of NUN absorbance values. Apparently, the reaction of NUN and H_2 does not proceed under the conditions of these experiments, and the available H atoms probably react with excess NUN rather than with NUNH. Furthermore, the low yield of N atoms, based on the very small yield of UN relative to NUN, is too low to expect any significant reaction with the UH product formed in the U and H_2 reaction.[36]

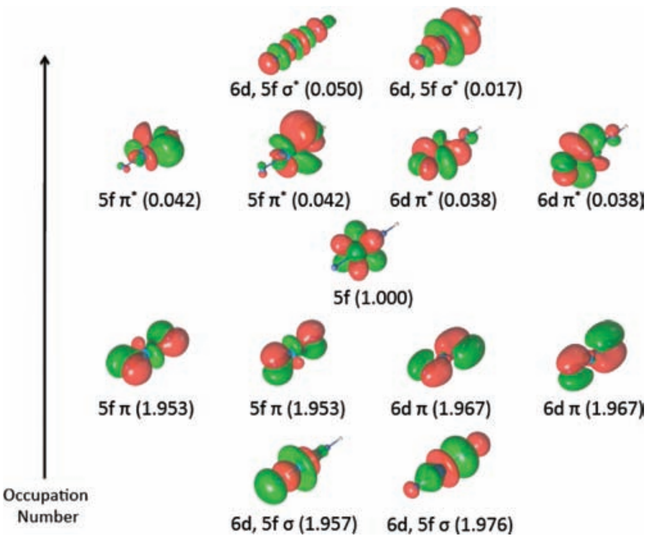


Figure 4. Molecular orbitals for NUNH plotted using an isodensity of 0.04*e* au^{-3}.

Multiple Bonding in NUNH. Computed bond lengths for four molecules containing uranium nitrogen multiple bonds are shown in Figure 3 using three different theoretical methods. The terminal nitride bond in NUNH is slightly longer than that in NUN, and the 966.9 cm^{-1} stretching frequency is 63 cm^{-1} lower than the 1030 cm^{-1} average value for NUN itself.[16] The imido bond in NUNH is also slightly longer than that in the imine, and the 752.4 cm^{-1} U−N stretching frequency is slightly lower than the H_2UNH imine value of 820 cm^{-1}.[19]

The charge distributions in the NUN and NUNH molecules are very similar (CASSCF Mulliken partial charges are $^{-0.25}$N $^{+0.50}$U $^{-0.25}$N and $^{-0.29}$N $^{+0.54}$U $^{-0.32}$N $^{+0.06}$H); however, the internal UN bond for NUNH is only a double bond whereas the terminal uranium nitride bond is triple. The Mulliken bond orders based on CASSCF orbitals are N−2.91−U−2.19−N−1.05−H and N−2.89−U−2.89−N.

The CASPT2 orbitals for NUNH are plotted in Figure 4. These orbitals are very similar to those of NUN, recently reported,[25a] except for the extra electron in the U 5f orbital. It is interesting to note that the σ bonding orbital for the inside U−N bond is extended substantially to include the N−H bond. As a consequence, it makes little contribution to the inside U−N bond, which is a double bond from the contribution of the four π bonding orbitals over both N−U−N bonds. The CASSCF bond order for the inside U−N bond is dominated by the 5fπ and 6dπ bonding orbitals.[48]

The number of chemical bonds is the same in NUN and NUNH, but they are quite different in important ways (see Figure 5). In NUN, the uranium nitrogen bonds are equivalent by symmetry, but in NUNH, on the other hand, the two N−U bonds differ by nearly a bond order because of the presence of the

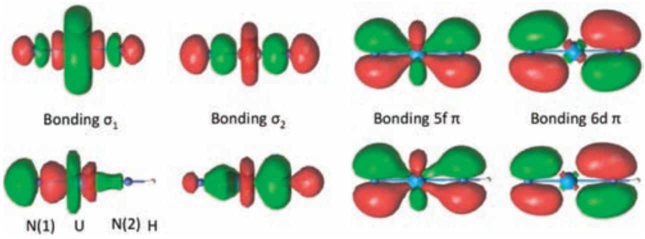
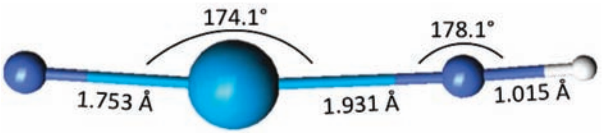


Figure 5. Comparison of σ and π bonding orbitals for NUN (top) and NUNH (bottom).

H atom on one side. The π orbitals are only slightly modified because of the presence of the hydrogen atom, while the σ bonds are significantly different. The σ_1 orbital (lower left in Figure 5) is mainly localized on the terminal N(1)−U bond and only very little on the internal U−N(2)H bond. In contrast, the σ_2 orbital is more delocalized like those in NUN.

The hydrogen atom has a slight positive partial charge of 0.06 from Mulliken population analysis at the CASSCF and also CASPT2 level calculations.

CASPT2 frequencies were initially calculated for the structure optimized with linear symmetry. The resulting structure had an imaginary frequency and is therefore not a minimum. Consequently, a full CASPT2 geometry optimization and subsequent frequency calculations were performed without enforcing symmetry constraints. These calculations gave an optimized structure that was slightly bent and had all real frequencies, which is embedded below. The linear structure is 0.2 kcal/mol higher in energy than the bent structure, but this difference in energy is very small and well within the error associated with CASPT2 calculations. Furthermore, the qualitative appearance of the orbitals does not change when symmetry is removed and the orbital occupation numbers and bond orders remain the same. Therefore, the structure is pliable as opposed to "bent". Given that the minimum energy structure at the CASPT2 level is slightly bent, two frequencies are associated with the UNH bending motion, whereas the symmetric structure has only one degenerate vibrational frequency (Table 1). In solid argon, a single bending mode absorption is observed at 433.0 cm^{-1}.



Comparisons with Bulk Uranium Nitride Complexes. The simple uranium nitrides formed in solid argon without stabilizing ligands provide model compounds for bulk uranium nitride complexes. The uranium dinitride NUN molecule formed by direct insertion of excited U atoms into dinitrogen[16] has a computed triple bond length of 1.73 Å (Figure 3). This may be compared to the U=N bond length of 1.848 Å measured for $U{=}(N\text{-}t\text{-}Bu)_2I_2(THF)_2$.[4] The $U{=}N_{imido}$ bond length calculated here (1.93 Å) is in the range of that for bulk uranium imido complexes such as $Me_3SiNU(N[SiMe_3]_2)_3$ (1.910 Å),[49] $Me_3SiNU(N\ t\text{-}BuAr)_3$ (1.937 Å),[6a] and uranium imido halide complexes (1.97 Å).[7]

Finally, we would like to make the point that if molecules such as NUN and NUNH can be formed under the radiation conditions associated with the laser ablation process and isolated in solid argon, then these stable molecules should be isolable with stabilizing ligands at higher temperatures. Such is certainly the case for NUN.[4,5]

■ CONCLUSIONS

The stable N≡U≡N molecule appears to react with hydrogen atoms under ultraviolet irradiation to form N≡U=N−H, the uranium(V) nitride imide molecule. The relative electronic energy (products minus reactants) of the reaction NUN + H → NUNH is −40 kcal/mol at the CASPT2 level of theory. This unusual U(V) molecule is identified by four fingerprint vibrational modes (N−H, U≡N, and U=NH stretching and U=N−H bending), and it contains a nitride triply bonded to uranium and a parent imine doubly bonded to uranium. The linear structure shows that the nitrogen "lone pair" is involved in π bonding orbitals. Terminal uranium nitrides are very reactive,[10] and argon matrix experiments have isolated five unsupported terminal uranium nitride molecules, UN, NUN, NUO, NUF_3, and NUNH, for infrared spectroscopic characterization.

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■ ACKNOWLEDGMENT

We gratefully acknowledge financial support from DOE Grants Nos. DE-SC0001034 and DE-SC002183, and NCSA computing Grant No. CHE07-0004N. We thank J. T. Yates, Jr. for the $^{15}N_2$ sample.

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