Experimental and Theoretical Evidence for the Formation of Several Uranium Hydride Molecules

Philip F. Souter,[†] Gary P. Kushto,[†] Lester Andrews,*,[†] and Matthew Neurock[‡]

Contribution from the Departments of Chemistry and Chemical Engineering, University of Virginia, Charlottesville, Virginia 22901

Received September 3, 1996[⊗]

Abstract: The primary reaction products of laser-ablated uranium atoms with dihydrogen (UH, UH_2, UH_3, UH_4, U_2H_2, and U_2H_4) have been isolated for the first time in solid argon and identified by the effects of isotopic substitution on their infrared spectra. Calculations, using DFT methods, have been performed to provide theoretical support for the spectral assignments. The molecules $U(\mu\text{-}H_2)U$ and U_2H_4 represent the first examples of an actinide-actinide bond.

Introduction

The reported chemistry of the uranium hydrides is limited to the solid UH_3. Uranium metal will adsorb hydrogen and the thermodynamics of this process have been investigated.[1] Uranium trihydride, UH_3, has been known for many years and is pyrophoric when finely divided. At temperatures of 200−300 °C, the reaction of uranium and dihydrogen gives the more thermodynamically stable β-form of UH_3, but at lower temperatures (*ca.* 0 °C) the α-form predominates; both structures have been studied crystallographically. The trihydride decomposes readily at 300−400 °C and has proven to be an excellent source of either clean, finely divided uranium or very pure hydrogen.[2] To date, however, the only claim of any other species containing just uranium and hydrogen is for the cation UH^+, a product observed during mass spectrometric investigation of the reaction of U^+ with either H_2, H_2O, or H_2S.[3]

There have been several theoretical investigations of the importance of relativistic effects when performing calculations on uranium compounds, including its hydrides,[4−7] and the specific cases of UO_2^{2+} and UN_2 have received detailed attention.[8,9] The dimer U_2 has been calculated and shown to have both a short- and long-distance minimum with bond lengths of 220 and *ca.* 300 pm, respectively.[10] The only previous theoretical investigation of uranium hydrides that may contain a metal−metal bond is of the hypothetical molecule U_2H_{10}, which was shown to have a weak, but significant, U−U interaction.[11] However, no experimental evidence for the isolation of any compound containing an actinide−actinide bond

has been previously presented. A preliminary report on some of this work has appeared in a recent communication.[12]

Pulsed-laser evaporation of metals has been shown to be an effective way to produce metal atoms for reaction with small molecules on condensation in excess argon at low temperatures.[13−18] In particular, laser ablation of a wide variety of metals into hydrogen/argon mixtures has previously yielded a wide variety of novel hydrides.[16,19−21] Here we report the infrared spectra observed for several uranium hydrides, deuterides, and mixed isotopic species generated by the reaction of laser-ablated uranium atoms with H_2, D_2, and HD and isolated in argon matrices.

Experimental Section

The technique used for matrix investigation of the reactions of pulsed laser-ablated metal atoms has been detailed previously.[13−15] FTIR spectra were recorded on a Nicolet 550 at 0.5-cm^{-1} resolution. Typically mixtures of between 0.5% and 4% hydrogen in argon were deposited at a rate of *ca.* 3 mmol/h for 2 h onto a CsI window held at 6−7 K using a Displex (APD Cryogenics), while the uranium metal target (Oak Ridge National Laboratory, 99.9%, natural isotopic abundance) was ablated using 45−60 mJ/pulse of the Nd-YAG 1064-nm fundamental. In some experiments the argon/hydrogen mixture was discharged in a 0.25-in. quartz tube using a relatively low power microwave source (*ca.* 30 W) to provide a source of H atoms. This meant that the discharge was not supported all the way to the end of the tube, which kept the amount of UV-light irradiating the sample to a minimum, thereby reducing the risk of photolytic destruction of potential product molecules. After deposition the samples were annealed to 20 K, photolyzed using a 175-W mercury street lamp (Philips H39KB) with the globe removed, and then further annealed, typically to 30, 35, and 40 K.

Theoretical Section

The Amsterdam Density Functional code (ADF 2.0.1) developed by Baerends and colleagues was used to carry out all the DFT calculations.[22] The DFT calculations employed the Vosko−Wilk−

[†] Department of Chemistry.
[‡] Department of Chemical Engineering.
[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.
(1) See for example: *Gmelin Handbook of Inorganic Chemistry*, 8th ed., System No. 55, U, Suppl. C1; Springer-Verlag: New York, 1977.
(2) Cunningham, B. B. *Prep. Inorg. React.* **1966**, *3*, 105.
(3) Moreland, P. E.; Rokop, D. J.; Stevens, C. M. *Int. J. Mass Spectrom. Ion Phys.* **1970**, *5*, 127.
(4) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.
(5) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719.
(6) Ziegler, T.; Tschinke, V. Density Functional Theory as a Practical Tool in Organometallic Energetics and Dynamics. In *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer Verlag: New York, 1991.
(7) Boerrigte, P. M. *Spectroscopy and bonding of heavy element compounds*. Ph.D. Thesis, Vrije Universiteit, Amsterdam, 1987.
(8) Pyykkö, P.; Li, J.; Runeberg, N. *J. Phys. Chem.* **1994**, *98*, 4809.
(9) Cornehl, H. H.; Heinemann, C.; Marcalo, J.; Pires de Matos, A.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 891.
(10) Pepper, M.; Bursten, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 7804.
(11) Cayton, R. H.; Novo-Gradac, K. J.; Bursten, B. E. *Inorg. Chem.* **1991**, *30*, 2265.

(12) Souter, P. F.; Kushto, G. P.; Andrews, L. *J. Chem. Soc., Chem. Commun.* **1996**, 2401.
(13) Burkholder, T. R.; Andrews L. *J. Chem. Phys.* **1991**, *95*, 8697.
(14) Hassanzadeh, P.; Andrews L. *J. Phys. Chem.* **1992**, *96*, 9177.
(15) Chertihin, G. V.; Andrews L.; Taylor, P. R. *J. Am. Chem. Soc.* **1994**, *116*, 3513.
(16) Chertihin, G. V.; Andrews L. *J. Am. Chem. Soc.* **1994**, *116*, 8322.
(17) Thompson, C. A.; Andrews L. *J. Am. Chem. Soc.* **1994**, *116*, 10125.
(18) Chertihin, G. V.; Andrews L. *J. Am. Chem. Soc.* **1995**, *117*, 1595.
(19) Tague, T. J., Jr.; Andrews L. *J. Am. Chem. Soc.* **1993**, *115*, 12111.
(20) Tague, T. J., Jr.; Andrews L. *J. Am. Chem. Soc.* **1994**, *116*, 4970.
(21) Chertihin, G. V.; Andrews L. *J. Am. Chem. Soc.* **1995**, *117*, 6402.
(22) ADF 2.0.1, Theoretical Chemistry, Vrije Universiteit, Amsterdam. See also: Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.
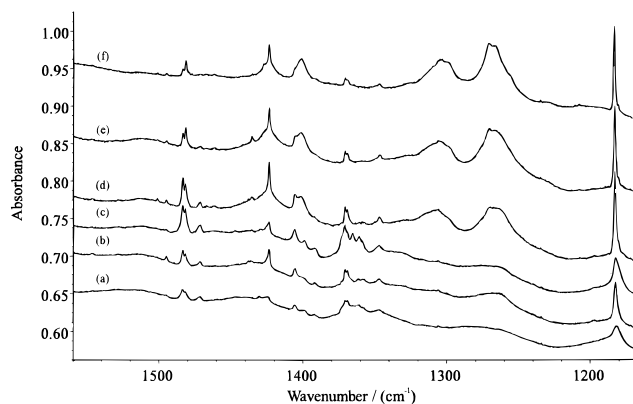
Figure 1. Infrared spectra in the region $1560-1170$ cm^{-1} of the products from the reactions of U atoms with a 2% H_2 in argon mixture during condensation at $6-7$ K: (a) 1-h deposit, (b) annealed to 20 K, (c) photolyzed by a broad-band UV source, (d) annealed to 30 K, (e) annealed to 35 K, and (f) annealed to 40 K.

Figure 2. Infrared spectra in the region $1110-840$ cm^{-1} of the products from the reactions of U atoms with a 2% D_2 in argon mixture during condensation at $6-7$ K: (a) 1-h deposit, (b) annealed to 20 K (c) photolyzed by a broad-band UV source, (d) annealed to 30 K, (e) annealed to 35 K, and (f) annealed to 40 K.

Nusair potential in the context of the local density approximation (LDA), along with the Becke (B) and Perdew (P) gradient corrections to the exchange and correlation energies, respectively. Nonlocal gradient corrections were explicitly accounted for in each SCF cycle. ADF employs a series of Slater basis functions and the adjustable parameter controlling the accuracy of the numerical integration[23] was set at a value of 6.0. A triple-ζ basis set was used for uranium and a triple-ζ basis set with polarization was used for hydrogen. The core electrons in uranium were frozen up to the 5d level to treat relativistic core effects. Quasirelativistic corrections were employed using the Pauli formalism with corrected core potentials. The quasirelativistic frozen core shells were generated using the auxiliary program DIRAC.[22] The resultant approach has been shown to improve results considerably over first-order treatments.[7,24] The current version of ADF does not allow for the storage of a calculated Hessian matrix. It is therefore necessary to reevaluate the force constants for each isotopically labeled species at considerable computational cost, so isotopic calculations were not performed. The accuracy of these DFT calculations is to a large extent dependent upon the basis set but similar quality DFT calculations on systems for which experimental data are readily available typically show errors in bond angles of only a few degrees and errors in the bond lengths of the order of 0.01 Å.[25]

Results and Discussion

Figures 1 and 2 show the spectra of the matrix-isolated products from the reactions of U with H_2 and D_2, respectively, together with their behavior upon annealing and photolysis. Figures 3 and 4 compare the spectra of the matrix-isolated products from the reactions of U with H_2, HD, H_2/D_2, and D_2 and show the difference between experiments with and without the argon/dihydrogen mixture being discharged. The frequencies of the observed bands together with their proposed assignments are presented in Table 1. Below 840 cm^{-1}, weak bands attributable to UO (819.7 cm^{-1}) and UO_2 (777.9, 775.8 cm^{-1}) were observed,[26] but the 1051.0-cm^{-1} band due to UN_2[27] was not observed indicating minimal atmospheric contamination, as further confirmed by the very small intensity of the bands due to CO_2 and H_2O. After photolysis and annealing, a weak band at 877 cm^{-1} was observed to grow in these experiments,

Figure 3. Infrared spectra in the region $1560-1170$ cm^{-1} for samples from the reactions of U atoms with 2% reagent mixtures in argon during condensation at $6-7$ K: (a) H_2, (b) H_2/D_2, (c) HD, and (d) H_2 (discharged) after annealing the deposit to 20 K, broad-band UV photolysis, and further annealing to 30 K.
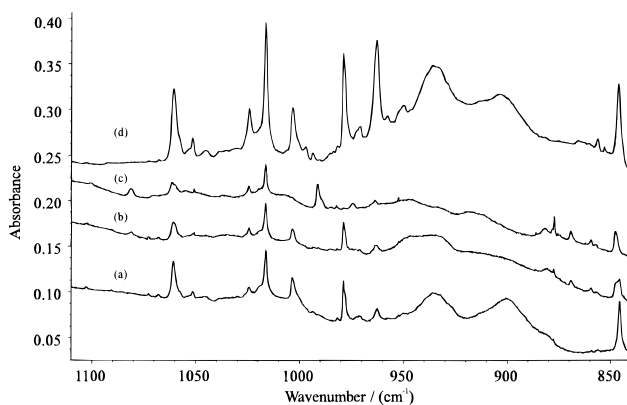
Figure 4. Infrared spectra in the region $1110-840$ cm^{-1} for samples from the reactions of U atoms with 2% reagent mixtures in argon during condensation at $6-7$ K: (a) D_2, (b) H_2/D_2, (c) HD, and (d) D_2 (discharged) after annealing the deposit to 20 K, broad-band UV photolysis, and further annealing to 30 K.

due to the perturbed molecular ion UO_2^+.[26] In the discharge experiments small bands due to the presence of CO_2, CO, CH_4, CD_4, H_2O, HOD, and D_2O were observed in addition to slightly larger quantities of UO and UO_2 than observed without the discharge, presumably as a result of O atoms being stripped from the walls of the quartz tube. The discharge experiments, as expected, increased the yield of products and *significantly* enhanced the relative yields of UH and UH_3. The effects of

(23) teVelde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84 and references cited therein.
(24) Ziegler, T. Calculations of bond energies in heavy element compounds. Ph.D. Thesis, Vrije Universiteit, Amsterdam, 1987. Heinemann, C.; Cornehl, H. H; Schroder, D.; Dolg, M.; Schwarz, S. *Inorg. Chem.* **1996**, *35*, 2463.
(25) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.
(26) Hunt, R. D.; Andrews L. *J. Chem. Phys.* **1993**, *98*, 3690.
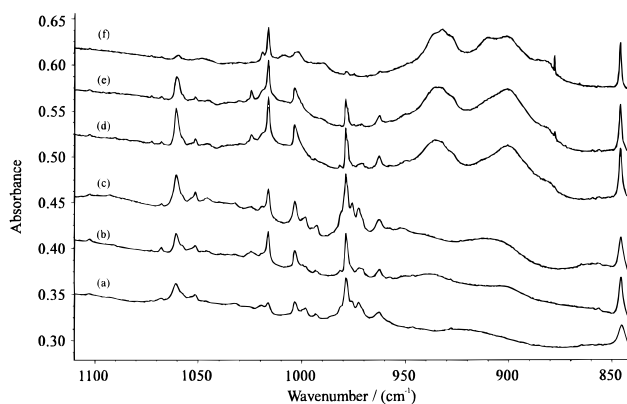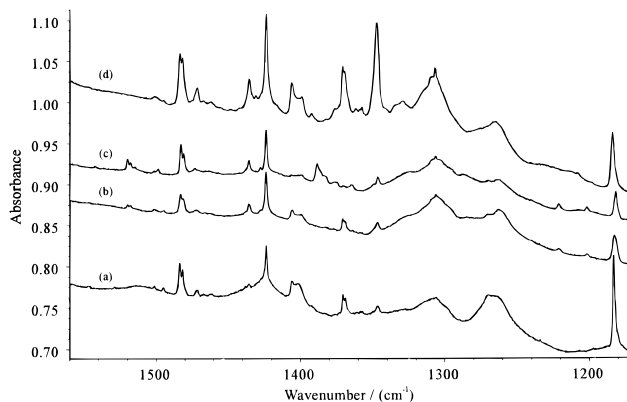(27) Hunt, R. D.; Yustein, J. T.; Andrews L. *J. Chem. Phys.* **1993**, *98*, 6070.

Table 1. Observed Infrared Absorptions (cm^{-1}) of the Dominant Products in the Reaction of Laser-Ablated Uranium Atoms with H_2, D_2, and HD Trapped in an Argon Matrix at 6−7 K

U + H$_2$	U + D$_2$	U + HD	assignment
1423.6	1016.3	1423.6, 1016.3	UH/UD
1435.3	1024.4	1435.3, 1024.4	site/H$_2$ complex of UH/UD
1406.1, 1399.0, 1392.2	1003.5, 998.3, 992.5		ν_1(UH$_2$/UD$_2$)
		1388.3, 1374.6, 1364.4	U−H stretch of HUD
		991.2, 982.1, 974.4	U−D stretch of HUD
1370.7, 1365.3, 1360.6	978.7, 975.7, 972.5		ν_3(UH$_2$/UD$_2$)
1182.4	845.6	~1182, ~845.5	b$_{2u}$ mode of U(μ-H)$_2$U/U(μ-D)$_2$U
		1180.4, 847.6	b$_2$ modes of U(μ-H)(μ-D)U
		1220.6, 869	a$_1$ modes of U(μ-H)(μ-D)U
1346.8	962.5		e mode of UH$_3$/UD$_3$
		1346.1 (963.4)	b$_2$ mode of UH$_2$D(UHD$_2$)
1483.6, 1481.7	~1060.7, 1059.8		as mode of UH$_4$/UD$_4$^{a}
		1519.9, 1517.9	U−H ss mode of UH$_2$D$_2$^{b}
		1482.9, 1481.0	U−H as mode of UH$_2$D$_2$^{a}
		~1081.7, ~1080.6	U−D ss mode of UH$_2$D$_2$^{b}
		~1061.4, ~1060.1	U−D as mode of UH$_2$D$_2$^{a}
~1547	1102.8		ss mode of U$_2$H$_4$/U$_2$D$_4$^{b}
1495.0	1067.9		as mode of U$_2$H$_4$/U$_2$D$_4$^{a}
		1542.7	U−H ss mode of U$_2$H$_2$D$_2$^{b}
		1498.7	U−H as mode of U$_2$H$_2$D$_2$^{s}
		1100.4	U−D ss mode of U$_2$H$_2$D$_2$^{b}
		1070.8	U−D as mode of U$_2$H$_2$D$_2$^{a}

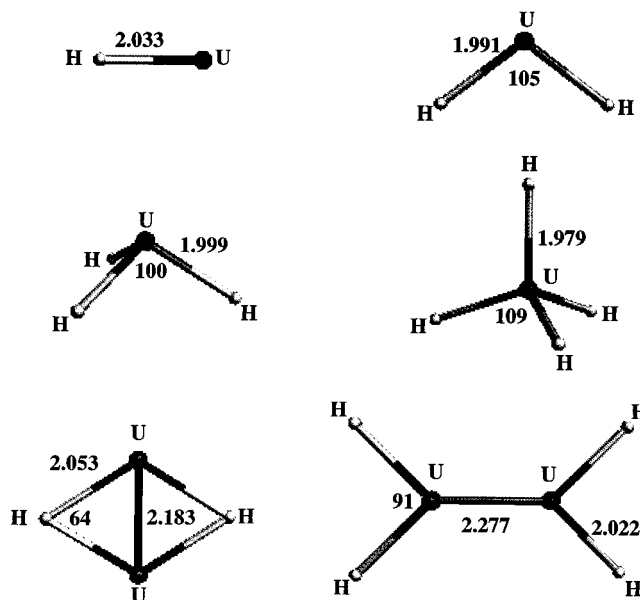^{a} as = antisymmetric stretching. ^{b} ss = symmetric stretching.

Table 2. Results of DFT Calculations on Some Uranium Hydride Molecules

molecule and symmetry	multiplicity of ground state	DFT (LDA + BP)	
		stretching freq	molecular parameters
UH (C$_{\infty v}$)	quartet	ν_1 1353	$r_{(U-H)}$ = 2.03
UH$_2$ (C$_{2v}$)	triplet	ν_1 1431 (a$_1$)	$r_{(U-H)}$ = 1.99
		ν_2 491 (a$_1$)	$\phi_{(HUH)}$ = 105°
		ν_3 1405 (b$_2$)	
UH$_3$ (C$_{3v}$)	quartet	ν_1 1435 (a$_1$)	$r_{(U-H)}$ = 2.00
		ν_2 471 (a$_1$)	$\phi_{(HUH)}$ = 100°
		ν_3 1396 (e)	
		ν_4 528 (e)	
U$_2$H$_2$ (D$_{2h}$)	singlet	ν_1 1251 (a$_{1g}$)	$r_{(U-U)}$ = 2.18
		ν_3 885 (b$_{1g}$)	$r_{(U-H)}$ = 2.05
		ν_4 1234 (b$_{2u}$)	$\phi_{(UHU)}$ = 64°
		ν_6 1025 (b$_{3u}$)	$\phi_{(HUH)}$ = 116°
UH$_4$ (T$_d$)	triplet	ν_1 1562 (a$_1$)	$r_{(U-H)}$ = 1.98
		ν_3 1472 (t$_2$)	$\phi_{(HUH)}$ = 109°
U$_2$H$_4$ (D$_{2h}$)	triplet	ν_1 1475 (a$_{1g}$)	$r_{(U-H)}$ = 2.02
		ν_5 1419 (b$_{1u}$)	$r_{(U-U)}$ = 2.28
		ν_8 1423 (b$_{2u}$)	$\phi_{(HUH)}$ = 93°
		ν_{10} 1397 (b$_{3g}$)	

Figure 5. Calculated optimized structures for the uranium hydrides using DFT methods.

varying the concentration of dihydrogen between 0.5% and 4% were studied. At higher concentrations the relative yields of UH$_3$ and UH$_4$ increased and the bands due to polymeric [UH$_x$]$_n$ grew very markedly upon the higher temperature annealings. Lower concentrations favored the formation of the less hydrogen rich products UH, UH$_2$, and U$_2$H$_2$.

The results of ADF calculations on the various uranium hydride molecules are summarized in Table 2 and Figure 5. For all quoted hydride frequencies in the ensuing discussion, numbers in parentheses refer to the corresponding deuteride counterpart.

UH. The stretching mode of the diatomic UH (UD) molecule is assigned to the absorption at 1423.6 (1016.3) cm^{-1}. The H/D isotopic ratio of 1.4008 is slightly below the harmonic diatomic value, 1.4107, as a result of cubic anharmonicity. This product was favored in both the discharge experiments, especially upon annealing owing to larger numbers of H atoms present in the matrix, and also experiments run using low concentrations of dihydrogen. This band was invariant with respect to isotopic substitution and is also observed in the reactions of uranium with other hydride sources, such as water and methane.[28] The band at 1435.3 (1024.4) cm^{-1} appears to be either a site or a dihydrogen complex of the more prominent feature at 1423.6

(1016.3) cm^{-1}. It too is favored under the same conditions and its intensity also increases upon annealing and decreases slightly upon photolysis, possibly due to the reaction UH + H$_2$ → UH$_3$, as the band assigned to the UH$_3$ molecule is observed to grow on photolysis.

Previous *ab initio* calculations, using a relativistic effective core potential and a double-ζ basis set for uranium, estimated the U−H stretching mode for a sextet ground state to occur at 1321 cm^{-1}.[29] Our DFT calculations predicted that the quartet state was the ground state and that the sextet state lay 1.76 eV higher in energy, with the U−H stretching frequency predicted to occur at 1353 (for the quartet state) and 1321 cm^{-1} (for the sextet state). The calculated stretching frequency for UH is in satisfactory agreement with the observed value and on the basis of the difference in calculated ground state energies UH can be tentatively assigned as having a quartet ground state.

UH$_2$. Bands at 1406.1 (1003.5), 1399.0 (998.3), 1392.2 (992.5) and 1370.7 (978.7), 1365.3 (975.7), 1360.6 (972.5) cm^{-1}

(28) Kushto, G. P.; Hunt, R. D.; Souter, P. F.; Andrews, L. Unpublished results.
(29) Krauss, M.; Stevens, W. J. *J. Comput. Chem.* **1983**, *4*, 127.

correspond to the ν_1 and ν_3 modes, respectively, of a bent UH_2 (UD_2) molecule present in three different matrix sites. The H/D ratios of the two modes of UH_2 (UD_2), averaged for the three sites, are 1.40177 and 1.3996 for the higher and lower energy bands, respectively. The antisymmetric stretching mode of an MH_2 molecule should have a lower H/D ratio than the symmetric stretching mode due to a greater contribution from the metal to the motion, so ν_1 can be confidently assigned to the higher energy bands and ν_3 to the lower energy bands. The UH_2 molecule must be formed by direct insertion of uranium into a dihydrogen molecule as testified by the fact that only HUH and DUD are observed in the reaction between uranium and a H_2/D_2 mix, whereas the reaction with HD produces neither HUH nor DUD, but new bands at 1388.3 (991.2), 1374.6 (982.1), and 1364.4 (974.4) cm^{-1} corresponding to the U−H (U−D) stretching modes of the HUD molecule also present in three different sites. That the U−H (U−D) stretch of the HUD molecule is observed at an energy almost exactly halfway between the ν_1 and ν_3 modes of HUH (DUD) further confirms these assignments. UH_2 is the main product observed in experiments run without discharging the argon/hydrogen mix. Annealing of the matrix causes the yield of UH_2 to decrease, but broad-band UV photolysis markedly increases the intensity of the UH_2 bands, presumably due to photoinduced insertion of U atoms into H_2.[30,31] DFT calculations performed on UH_2 predict ν_1 to occur at 1431 and ν_3 at 1405 cm^{-1}, with intensities of 389 and 381 km/mol, respectively. These values are in good agreement with the experimentally observed numbers and help confirm the identification of the UH_2 molecule. The bending vibration, ν_2, is calculated at 491 cm^{-1} but is either too weak to be observed or occurs out of the spectral range (below 400 cm^{-1}).

UH$_3$. The band at 1346.8 (962.5) cm^{-1} is assigned to the antisymmetric stretch of a pyramidal UH_3 molecule. The band is weak in experiments under normal conditions, but its intensity increases approximately 10-fold in the discharge experiments, where it is one of the major products, giving a strong indication that the absorption is indeed due to a species containing an odd number of hydrogens. The U−H antisymmetric stretch broadens and shifts to *ca.* 1346.5 cm^{-1} in the H_2/D_2 experiments and to 1346.1 cm^{-1} in the HD experiments while the U−D antisymmetric stretch broadens and shifts up to *ca.* 963.0 and 963.4 cm^{-1} in the H_2/D_2 and HD experiments, respectively. These shifts are due to the presence of UH_2D and UHD_2 whose antisymmetric stretches are expected to be very close to the e mode of UH_3, as indeed is observed for similar MH_3 molecules.[32,33] The a_1 modes appear to be either too weak to be observed or obscured by stronger bands in the spectrum. The spectra do not preclude the possibility of UH_3 being planar and indeed this would provide a simple explanation for the failure to observe the symmetric stretching mode as it is forbidden in the infrared; however, DFT calculations, as detailed in Table 2, predict the molecule to be pyramidal, with the hydrogens deviating 26° from a planar D_{3h} structure, and the spectra provide no reason to dispute this finding. DFT calculations predicted the stretching modes of UH_3 at 1435 (a_1) and 1396 (e) cm^{-1} and find reasonable agreement with the observed value for the e mode of 1346.8 cm^{-1}. UH_3 increases in intensity slightly upon photolysis and initial annealing, but at higher temperatures its intensity decreases as a result of polymerization,

as evidenced by growth of very broad features at *ca.* 1305 (935) and 1265 (902) cm^{-1}.

UH$_4$. The bands at 1483.6 and 1481.7 cm^{-1} in the H_2 experiments and *ca.* 1060.7 and 1059.8 cm^{-1} in the D_2 experiments are assigned to the antisymmetric stretching modes of the UH_4 and UD_4 molecules, respectively, present in two different matrix sites. Frequencies for the U−D stretching region are only approximate as the bands due to the two sites are closer in energy and overlap, producing a single broad spectral feature with a more indeterminant maximum. In the reaction with HD, bands occur at 1519.9 (*ca.* 1081.7) and 1517.9 (*ca.* 1080.6) cm^{-1} due to the symmetric U−H (U−D) stretch of the UH_2D_2 molecule and at 1482.9 (*ca.* 1061.4) and 1481.0 (*ca.* 1060.1) cm^{-1} due to the antisymmetric U−H (U−D) stretch of UH_2D_2 present in two different matrix sites. The relative intensities and change in site profile of these two sets of bands mirror each other on both annealing and photolysis, confirming that they are vibrations of the same molecule present in two different matrix sites. The observation of four distinct absorptions due to the four stretching modes of the UH_2D_2 molecule confirms the identification of uranium tetrahydride. Similar evidence has been found for other metal tetrahydride molecules.[21,34] Experiments with HD/H_2 mixtures showed new bands corresponding to the U−H and U−D stretches of UH_3D, while experiments with HD/D_2 mixtures showed new bands corresponding to the U−H and U−D stretches of UHD_3. UH_3D occurs in two different sites and shows a U−D stretch at 1069.8 cm^{-1} (broad), an antisymmetric U−H stretch at 1483.3, 1481.5 cm^{-1}, and a symmetric U−H stretch at 1536.7, 1535.5 cm^{-1}. UHD_3 also occurs in two sites and shows a U−H stretch at 1501.8, 1499.8 cm^{-1}, a symmetric U−D stretch at 1092.8, 1091.5 cm^{-1}, and an antisymmetric U−D stretch at 1059.8, 1060.9 cm^{-1}. UH_2D_2 was present in both these experiments while UH_4 appeared only in the HD/H_2 experiment and UD_4 only in the HD/D_2 experiment. These observations together with the fact that neither UHD_3 nor UH_3D were seen in experiments run with HD or H_2/D_2 show that the formation of UH_4 occurs primarily by stepwise addition of two dihydrogen units, not *via* reactions involving hydrogen atoms. The bands due to these molecules increase markedly in intensity upon both photolysis and initial annealings, but at higher temperatures, they decrease due to polymerization.

DFT calculations were performed on the UH_4 molecule and the lowest energy structure had no symmetry, but was approximately tetrahedral. Technical difficulties in the ADF code required its frequency to be determined using a no symmetry model and, as expected for a near-tetrahedral molecule, gave three U−H antisymmetric stretches very close in energy with the U−H symmetric stretch occurring at a much different energy. The very slight deviations from tetrahedral symmetry are within the error margins of the calculation and so it would appear, on the basis of the spectroscopic observations and the calculations, that UH_4 is approximately tetrahedral with the a_1 vibration calculated at 1562 cm^{-1} and the t_2 vibration at *ca.* 1472 cm^{-1}, in good agreement with the observed value for the antisymmetric stretch of UH_4. Upon partial isotopic substitution, the symmetric stretch is no longer forbidden in the infrared. That the a_1 stretching modes of UH_3D, UH_2D_2, and UHD_3 occur higher in energy than the antisymmetric stretching modes finds pleasing agreement with the calculation on UH_4 which predicts its a_1 stretching mode to be higher in energy than its t_2 stretching mode.

U$_2$H$_2$. The strong band present from the reaction between U and H_2 (D_2) at 1182.4 (845.6) cm^{-1} lies in the region where

(30) Carstens, D. H. W.; Brashear, W.; Eslinger, D. R.; Gruen, D. M. *Appl. Spectrosc.* **1972**, *26*, 184.

(31) Steinhaus, D. W.; Radziemski, L. J., Jr.; Cowan, R. D.; Blaise, J.; Guelachvili, G.; Osman, Z. B.; Verges, J. Report No. LA-4501, Los Alamos Scientific Lab, Los Alamos, NM, 1971.

(32) Chertihin, G. V.; Andrews L. *J. Phys. Chem.* **1993**, *97*, 10295.

(33) Chertihin, G. V.; Andrews L. *J. Phys. Chem.* **1995**, *99*, 12131.

(34) Chertihin, G. V.; Andrews L. *J. Phys. Chem.* **1995**, *99*, 15004.

bridging U−H (U−D) stretching modes might be expected to occur and is assigned to the b_{2u} stretching vibration of the rhombic dimer, U_2H_2 (U_2D_2). In the experiments run with HD, bands are observed in the U−H bridging region at 1180.4 cm^{-1} with a shoulder at *ca.* 1182 cm^{-1} and in the U−D bridging region at 847.6 cm^{-1} with a shoulder at *ca.* 845.5 cm^{-1}, implying the formation primarily of U(μ-D)(μ-H)U, with U(μ-H)$_2$U and U(μ-D)$_2$U only present in smaller quantities. In the H_2/D_2 mixed experiments this feature was split into two partially resolved components at 1182.4 (845.6) and 1180.4 (847.6) cm^{-1} with the U(μ-H)$_2$U and U(μ-D)$_2$U being the dominant products, but some U(μ-D)(μ-H)U is also present. The D_{2h} symmetry of U_2H_2 is lowered to C_{2v} for the U(μ-D)(μ-H)U entity, and the symmetric stretches are no longer forbidden in the infrared. In the experiments with H_2/D_2 and HD an extra band is indeed observed at 1220.6 (869.0) cm^{-1} and its relative intensity and behavior upon photolysis and annealing shadows that of the 1180.4 (847.6) cm^{-1} band. The energies of these two modes are well anticipated by ADF calculations, the results of which are detailed in Table 2. Indeed, U(μ-H)$_2$U represents the first discrete isolated molecule that contains an actinide−actinide bond. This U−U bond length is calculated to be significantly shorter than that in metallic uranium and similar to that calculated for the short distance minimum of the U_2 dimer.[10] The mechanism for formation of U_2H_2 cannot only involve the reactions of UH$_2$ and U or U_2 and H_2 as both U(μ-D)(μ-H)U and U(μ-H)$_2$U are observed in the experiments with HD and H_2/D_2 mixtures, so some dimerization of UH must also be occurring. The bands due to these molecules increase slightly upon annealing but are unaffected by photolysis.

The DFT calculations on U(μ-H)$_2$U predict the most intense mode to be the b_{2u} stretching mode at 1234 cm^{-1}, in good agreement with the observed value of 1182.4 cm^{-1}. The observed symmetric and antisymmetric stretching frequencies for U(μ-D)(μ-H)U are extremely close in energy to the calculated a_{1g} and b_{2u} stretching modes of U(μ-H)$_2$U, further confirming the identification of this molecule. Energy calculations on other possible isomers of U_2H_2, *e.g.* HUUH, confirmed the bridged structure to be the lowest in energy.

U_2H_4. Weak features were observed in the reaction of U with $H_2(D_2)$ at *ca.* 1547 (1102.8) and 1495.0 (1067.9) cm^{-1}. Bands were observed in the same position in the reaction of U with a H_2/D_2 mixture, but *not* with HD where new bands were observed at 1542.7, 1498.7, 1100.4, and 1070.8 cm^{-1}. These observations imply that the mechanism for the formation of this species must involve stepwise addition of two dihydrogen units as there are no common bands in the H_2/D_2 and HD experiments. That four bands are observed in the HD experiment gives a strong indication that the molecule contains two hydrogens and two deuteriums, but that these bands are not observed in the H_2/D_2 experiment rules out UH$_2$D$_2$ and firmly suggest that the molecule is the dimer of UH$_2$, namely U_2H_4. The observed bands all increase in intensity upon annealing to 20 K, are destroyed by broad-band UV photolysis, but then grow a little upon further annealing probably as a result of dimerization of UH$_2$. The bands due to U_2H_4 were much weaker in the discharge experiments, probably as a result of the greater mobility of hydrogen atoms, present in larger concentrations, favoring reaction of UH$_2$ with H to give UH$_3$.
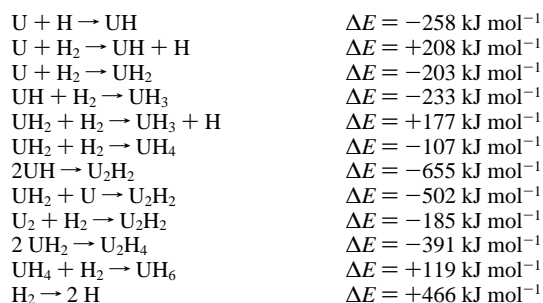
DFT calculations for U_2H_4 were run using models with C_2, D_{2d}, D_2, and D_{2h} symmetries and the model with D_2 symmetry calculated as being lowest in energy, but the calculated geometry was only 0.2° away from planarity and this slight deviation from planarity is within the degree of accuracy of the calculation. The calculated planarity, or near-planarity, of the U_2H_4 molecule

finds pleasing agreement with the observed spectra as only two U−H (U−D) stretches were observed for U_2H_4 (U_2D_4); owing to the center of symmetry, the other two stretches are forbidden in the infrared. The frequencies obtained for the four stretching modes of U_2H_4 are listed in Table 2 and are in moderate agreement with the observed values. The average U−H stretching frequency for U_2H_4 is indeed calculated to be greater than the average U−H stretch in UH$_2$, but not by as much as is observed experimentally. Other possible structures for U_2H_4 of the type HU(μ-H)$_2$UH, such as that observed for Be$_2$H$_4$,[19] can be conclusively ruled out for our observed absorptions. The bands due to such a bridged HU(μ-H)(μ-D)UD molecule would occur at *the same* frequency in both experiments run with H_2/D_2 and experiments run with HD, in marked contrast to the observed behavior of our bands. Additionally there are no bands in the bridging U−H region that are destroyed by photolysis, further confirming that the observed bands belong to a molecule containing no bridging hydrogens. The existence of the isomer of U_2H_4 containing bridging hydrogens, HU(μ-H)$_2$UH, cannot, however, be ruled out as some extra bands are observed in the bridging U−H region which may be due to this molecule, as shall be discussed later.

Polymeric $[UH_x]_n$. Very broad bands at *ca.* 1305 (935) cm^{-1} and *ca.* 1265 (902) cm^{-1} grow in on annealing and correspond to the U−H(U−D) stretching modes of $[UH_x]_n$ ($[UD_x]_n$). They increase in intensity markedly, especially upon annealing at higher temperatures (35 and 40 K), and their intensity is strongest in the experiments with the largest concentration of $H_2(D_2)$ in Ar mixtures, as expected. Similar spectra are seen for other polymeric hydrides, *e.g.* $[GaH_3]_n$.[35]

Other Bands. The feature at 1471.4 (1051.6) cm^{-1} in the reaction of U with $H_2(D_2)$ may well be a third site of UH$_4$. It is strongest in intensity after photolysis and decreases markedly in intensity upon annealing. A weak band appears at 1501.6 (1072.7) cm^{-1} after photolysis, followed by annealing to 30 K, and is isotopically invariant implying that perhaps it is due to a species containing only one H (D), with UH$^+$ (UD$^+$) a possible candidate. This observed frequency is consistent with the value of 1449 cm^{-1} calculated by Krauss and Stevens.[29] The only other band that is unaccounted for occurs at 1200.9 (859.3) cm^{-1} and is present only in the HD and H_2/D_2 experiments and may be due to a bridging U(μ-H)(μ-D) unit of a larger molecule, possibly another isomer of U_2H_4, namely HU(μ-H)$_2$UH. Without the observation of the terminal U−H stretching modes, such an assignment can only be tentative.

Reaction Mechanisms. The proposed mechanisms of formation of the product molecules are illustrated below and information about the energies of reaction, as calculated by DFT methods, is given.

U + H → UH	$\Delta E = -258$ kJ mol^{-1}
U + H$_2$ → UH + H	$\Delta E = +208$ kJ mol^{-1}
U + H$_2$ → UH$_2$	$\Delta E = -203$ kJ mol^{-1}
UH + H$_2$ → UH$_3$	$\Delta E = -233$ kJ mol^{-1}
UH$_2$ + H$_2$ → UH$_3$ + H	$\Delta E = +177$ kJ mol^{-1}
UH$_2$ + H$_2$ → UH$_4$	$\Delta E = -107$ kJ mol^{-1}
2UH → U$_2$H$_2$	$\Delta E = -655$ kJ mol^{-1}
UH$_2$ + U → U$_2$H$_2$	$\Delta E = -502$ kJ mol^{-1}
U$_2$ + H$_2$ → U$_2$H$_2$	$\Delta E = -185$ kJ mol^{-1}
2 UH$_2$ → U$_2$H$_4$	$\Delta E = -391$ kJ mol^{-1}
UH$_4$ + H$_2$ → UH$_6$	$\Delta E = +119$ kJ mol^{-1}
H$_2$ → 2 H	$\Delta E = +466$ kJ mol^{-1}

As can be seen, the excess energy that ablated uranium atoms possess is necessary to induce reaction with dihydrogen to form

(35) Downs, A. J.; Goode, M. J.; Pulham, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 1936.

Table 3. A Comparison of Some Infrared M−H Stretching Frequencies

metal, M	freq/cm^{-1} for MH$_2$[a]	freq/cm^{-1} for MH$_4$[a]	ref
Mo	1727.4 (ν_1), 1752.7 (ν_3)	1849.2[b]	39
Nd	1193.8 (ν_1), 1148.6 (ν_3)		40
W	? (in range 1930−1820)	? (in range 1930−1820)	37
U	1406.1 (ν_1), 1370.7 (ν_3)[c]	1483.6[c]	this work
Hf	1518.6 (ν_3)	1623.6	34
Th	1480.1 (ν_1), 1455.6 (ν_3)	1444.7[c]	41

[a] In an Ar matrix. [b] In a Kr matrix. [c] Present in different sites (only the highest energy absorption is listed).

UH molecules and H atoms. These data also indicate that the formation of UH$_3$ must proceed *via* addition of H$_2$ to UH, not *via* abstraction of a hydrogen atom from H$_2$ by UH$_2$. The isotopic data have already confirmed that UH$_2$ and UH$_4$ are formed by addition of dihydrogen units, not *via* reactions involving H atoms or H abstraction, an observation supported by the energy calculations. The experimental data indicate that U$_2$H$_2$ is formed both by dimerization of UH and by reaction of either U$_2$ with H$_2$ or UH$_2$ with U and the energy calculations do indeed show that all these reactions are exothermic. The exothermicity of the dimerization of UH$_2$ is also confirmed by thc calculated energies. The absence from the spectra of a candidate for UH$_6$ is endorsed by the calculated endothermicity of the addition of H$_2$ to UH$_4$. The calculated U−H bond energies are similar to those calculated[6] and observed for UCl$_3$H.[36]

Conclusions

The molecules UH, UH$_2$, UH$_3$, UH$_4$, U$_2$H$_2$, and U$_2$H$_4$ have been isolated for the first time in solid argon and the latter two represent the first two examples of compounds containing actinide−actinide bonds. Although vibrational frequencies are not directly related to bond energies, for heavy atoms the correlation between the two parameters is reasonably good as the reduced mass, μ, which is so heavily dependent upon the light atom, in this case hydrogen, hardly varies with the heavy metal present. Table 3 compares the observed frequencies for the uranium hydrides UH$_2$ and UH$_4$ with other hydrides of the types MH$_2$ and MH$_4$, where M is Mo, Nd, W, Th, and Zr. The reaction of dihydrogen/argon mixtures with tungsten gives relatively few products possibly due to their sensitivity to

ultraviolet light which is, by necessity, emitted from the plume generated when ablating tungsten;[37] known tungsten hydrides such as (η^5C$_5$H$_5$)$_2$WH$_2$ are indeed photosensitive.[38] The weak hydride bands that are observed in these experiments lie in the range 1930−1820 cm^{-1}.

The data presented in Table 3 indicate that tungsten forms stronger bonds with hydrogen than does uranium which in turn forms stronger bonds than neodynium; hafnium is also observed to form stronger bonds with hydrogen than thorium.[34,41] That uranium forms a stronger bond with hydrogen than neodymium is in part due to relativistic effects,[4,42] as indeed is the fact that tungsten forms stronger bonds with hydrogen than molybdenum.[42] Element 106 was predicted by Pyykkö and Desclaux to continue the observed trend from Cr to Mo to W and have a higher bond strength due to a combination of the actinoid contraction and relativistic effects.[42] The greater strength of the W−H bond *vs* the U−H bond can be attributed to the better overlap by the 5d orbitals on tungsten than the 6d and 5f orbitals on uranium with the 1s orbitals of hydrogen. It is interesting to note that the bonds in ThH$_2$ are stronger than those in UH$_2$, whereas for the tetrahydrides the pattern is reversed; this is probably due to the increased 5f orbital participation in UH$_4$ *vs* ThH$_4$. Support for this assertion comes from calculations performed by Pyykkö and Desclaux on ThH$_4$ where they removed the 7p orbitals, thereby artificially increasing the 5f contribution to the bonding, and found a substantially lower value for R$_e$ indicating a strengthening of the Th−H bonds.[42]

In summary, the reaction of laser-ablated uranium atoms with hydrogen gives rise to a wide variety of previously unobserved uranium hydride molecular species, including the first observed discrete isolated compounds containing an actinide−actinide bond.

(36) Bruno, J. W.; Stecher, H. A.; Mors, L. R.; Sonnenberg, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275.

(37) Souter, P. F.; Andrews, L. Unpublished results.

(38) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27.

(39) Xiao, Z. L.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.* **1992**, *96*, 636.

(40) Willson, S. P.; Andrews, L.; Neurock, M. Unpublished results.

(41) Souter, P. F.; Kushto, G. P.; Andrews, L.; Neurock, M. *J. Phys. Chem.* **1997**, *101*, 1287.

(42) Pyykkö, P.; Desclaux, J. P. *Chem. Phys.* **1978**, *34*, 261.