IR spectra of uranium hydride molecules isolated in solid argon

Philip F. Souter, Gary P. Kushto and Lester Andrews*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, USA

The primary reaction products of laser-ablated uranium atoms with dihydrogen (UH, UH_2, U_2H_2, UH_3 and UH_4) are isolated for the first time in an argon matrix and identified by the effects of isotopic substitution on their IR spectra.

Little is known about the chemistry of the uranium hydrides. Uranium metal will adsorb hydrogen and the pyrophoric solid UH_3 has been known for many years,[1] and its solid structure in both α and β forms investigated. UH_3 decomposes readily at 300–400 °C and has mainly been used as a source either of 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] Here we report the matrix IR spectra observed for several uranium hydrides, deuterides and mixed isotopic species.

The technique used for matrix investigation of the reactions of pulsed laser-ablated metal atoms has been detailed previously.[4–6] 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^{-1} for 2 h onto a CsI window held at 6–7 K while the uranium was ablated using 45–60 mJ $pulse^{-1}$ of the YAG 1064 nm fundamental. In some experiments the argon–hydrogen mixture was discharged in a quartz tube using a microwave source at relatively low powers of *ca.* 30 W to provide a source of H atoms. After deposition the samples were annealed to 20 K, photolysed using a 175 W mercury street lamp (Philips H39KB) with the globe removed, and then further annealed, typically to 30, 35 and 40 K.

Figs. 1 and 2 show the spectra of the matrix-isolated products from the reactions of U with H_2, HD, H_2–D_2 and D_2 and the wavenumbers 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,[7] but the 1051.0 cm^{-1} band due to UN_2[8] was not observed indicating minimal atmospheric contamination. The discharge experiments, as expected, increased the yield of products and *significantly* enhanced the relative yields of UH and UH_3. For all quoted hydride wavenumbers in the ensuing discussion, numbers in parentheses refer to the corresponding deuteride counterpart.

UH: the band at 1423.6(1016.3) cm^{-1} is assigned to the diatomic UH(UD) molecule. The H/D isotopic ratio of 1.4008 is below the harmonic diatomic value, 1.4107, as a result of cubic anharmonicity. This product was favoured both at low concentrations of dihydrogen and also in the discharge experiments, especially upon annealing, owing to larger numbers of H atoms present in the matrix. This band was invariant with respect to isotopic substitution and is also observed in the reactions of uranium with either water or methane.[9] 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}.

UH_2: bands at 1406.1(1003.5), 1399.0(998.3), 1392(992.5) and 1370.7(978.7), 1365.3(975.7), 1360.6(972.5) cm^{-1} 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 UH_2 is 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 gave neither HUH nor DUD but new bands at 1388.3(991.2), 1374.6(982.1) and 1364.4(974.4) 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.

U_2H_2: the strong band in the region where bridging U–H(U–D) stretching modes might be expected at 1182.4(845.6) cm^{-1} in the reaction between U and $H_2(D_2)$ is assigned to 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

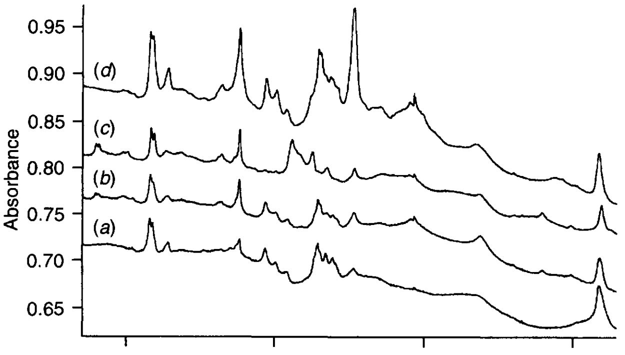

Fig. 1 IR spectra in the region 1530–1170 cm^{-1} for samples from the reactions of U atoms with 2% reagent mixtures in argon during condensation at 6–7 K. (*a*) H_2, (*b*) H_2–D_2, (*c*) HD and (*d*) H_2 (discharged) after annealing to 20 K followed by broad-band UV photolysis.

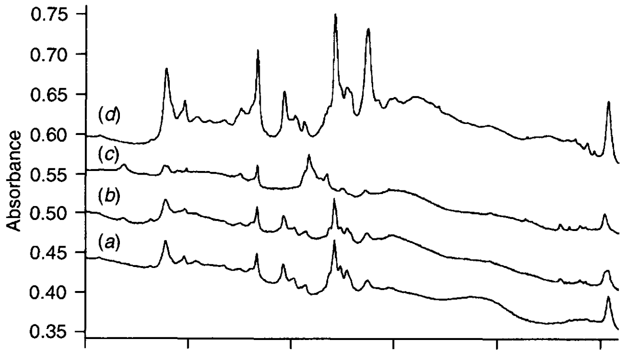

Fig. 2 IR spectra in the region 1100–840 cm^{-1} for samples from the reactions of U atoms with 2% reagent mixtures in argon during condensation at 6–7 K. (*a*) D_2, (*b*) H_2–D_2, (*c*) HD and (*d*) D_2 (discharged) after annealing to 20 K followed by broad-band UV photolysis.

Table 1 Observed IR absorptions (in 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	*ca.* 1182, *ca.* 845.5	b_{2u} mode of $U(\mu\text{-H})_2U$/ $U(\mu\text{-D})_2U$
—	—	1180.4, 847.6	b_2 modes of $U(\mu\text{-H})(\mu\text{-D})U$
—	—	1220.6, 869.0	a_1 modes of $U(\mu\text{-H})(\mu\text{-D})U$
1346.8	962.5	—	e mode of UH_3/UD_3
—	—	1346.1 (963.4)	b_2 mode of $UH_2D(UHD_2)$
1483.6, 1481.7	*ca.* 1060.7, 1059.8	—	as mode of UH_4/UD_4[a]
—	—	1519.9, 1517.9	U–H ss mode of UH_2D_2[b]
—	—	1482.9, 1481.0	U–H as mode of UH_2D_2[a]
—	—	*ca.* 1081.7, *ca.* 1080.6	U–D ss mode of UH_2D_2[b]
—	—	*ca.* 1061.4, *ca.* 1060.1	U–D as mode of UH_2D_2[a]

[a] as = antisymmetric stretching. [b] ss = symmetric stretching.

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 $U(\mu\text{-D})(\mu\text{-H})U$, with $U(\mu\text{-H})_2U$ and $U(\mu\text{-D})_2U$ 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 $U(\mu\text{-H})_2U$ and $U(\mu\text{-D})_2U$ being the dominant products, but some $U(\mu\text{-D})(\mu\text{-H})U$ also present. The D_{2h} symmetry of U_2H_2 is lowered to C_{2v} for the $U(\mu\text{-D})(\mu\text{-H})U$ entity, and the symmetric stretches are no longer forbidden in the IR. 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 behaviour 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 DFT calculations using the ADF 2.0.1 program,[10] the results of which will be presented in a full paper at a later date. $U(\mu\text{-H})_2U$ 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 length minimum of the U_2 dimer.[11]

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 tenfold in the discharge experiments, where it is one of the major products, giving a strong indication that this absorption is indeed due to a species containing an odd number of hydrogens.

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 stretch 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) cm^{-1} 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.[14,15] 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 1060.9, 1059.8 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.

In conclusion, 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 compound containing an actinide–actinide bond.

The authors thank British Nuclear Fuels plc for financial support in the form of a postdoctoral research associateship (for P. F. S.) and Dr M. Neurock for assistance with the density functional calculations.

References

1 See, for example, *Gmelin Handbook of Inorganic Chemistry*, 8th edn., System No. 55, U, Suppl. C1, Springer-Verlag, Berlin, 1977.
2 B. B. Cunningham, *Prep. Inorg. React.*, 1966, **3**, 105.
3 P. E. Moreland, D. J. Rokop and C. M. Stevens, *Intern. J. Mass Spectrom. Ion Phys.*, 1970, **5**, 127.
4 T. R. Burkholder and L. Andrews, *J. Chem. Phys.*, 1991, **95**, 8697.
5 P. Hassanzadeh and L. Andrews, *J. Phys. Chem.*, 1992, **96**, 9177.
6 G. V. Chertihin and L. Andrews, *J. Am. Chem. Soc.*, 1994, **116**, 8322.
7 R. D. Hunt and L. Andrews, *J. Chem. Phys.*, 1993, **98**, 3690.
8 R. D. Hunt, J. T. Yustein and L. Andrews, *J. Chem. Phys.*, 1993, **98**, 6070.
9 G. P. Kushto, R. D. Hunt, P. F. Souter and L. Andrews, unpublished work.
10 *ADF 2.0.1, Theoretical Chemistry*, Vrije Universiteit, Amsterdam.
11 M. Pepper and B. E. Bursten, *J. Chem. Soc.*, 1990, **112**, 7804.
12 G. V. Chertihin and L. Andrews, *J. Phys. Chem.*, 1993, **97**, 10295.
13 G. V. Chertihin and L. Andrews, *J. Phys. Chem.*, 1995, **99**, 12131.
14 G. V. Chertihin and L. Andrews, *J. Am. Chem. Soc.*, 1995, **117**, 6402.
15 G. V. Chertihin and L. Andrews, *J. Phys. Chem.*, 1995, **99**, 15004.

Received, 12th July 1996; Com. 6/05045J