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Computational Modeling of Uranium–Hydrogen Reactions: Trends and Influence of Elements

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Introduction

Actinide chemistry is very interesting because the role of actinide 6d and 5f orbitals in chemical bonding is very intriguing; under certain conditions these orbitals play a significant role in reactivity and bonding, whereas at other times they are not involved at all.1–10 This dramatic variation that depends on the interacting species with the actinide has fueled a number of fundamental studies concerning actinide chemistry. Furthermore, relativity plays a key role in determining the reactivity and bonding of actinide species because inner electrons approach speeds of light due to the large nuclear charge.1–3 Uranium hydriding is one of the important processes that has received considerable attention over many years,11–27 because the hydriding process is not only fundamentally intriguing, but is also a key process in uranium corrosion and thus is of significant applied interest in actinide material chemistry. As seen from the work of Mintz and Bloch,18 exposure of uranium to hydrogen gas results in hydriding of uranium producing pyrophoric uranium hydride layers. Consequently, there is considerable effort to understand the kinetics, thermodynamics, and mechanism of this reaction, which are still not fully explained.

Condon and Larson11 have proposed that the uranium-hydriding (U–H) reaction is controlled by diffusion of hydrogen in the reactant phase before nucleation to form the hydride phase occurs. From the slopes of the Arrhenius plot the activation energy was calculated as 6.35 kcal/mol. Bloch and Mintz14 have proposed the kinetics and mechanism for the U–H reaction over a wide range of pressure and temperature. Powell et al.16 have found reversible hydrogen sorption on the UH3 reaction product from kinetic effects at 21°C, which demonstrates catalysis of the hydriding process in the
presence of UH₃, DeMint and Leckey¹⁷ have shown that Si impurities accelerate U-hydriding rates. Balooch and coworkers¹⁹,²⁰ have determined the gaseous reaction products and the rate of reactions of uranium hydriding using modulated molecular-beam mass spectrometry. Balooch and Siekhaus²⁰ have examined the interaction of hydrogen with uranium in the presence of impurities. Andrews and coworkers²⁸-³⁴ have pioneered the gas-phase chemistry of a number of uranium-containing species using matrix-isolation techniques by reactions of pulsed laser ablated uranium atoms with gases such as N₂, O₂, CO₂, H₂, and so on. In particular, the primary reaction products of laser-ablated uranium with H₂ gas have been found to be UHₙ (n = 1–4) and U₂Hₙ (n = 2, 4) isolated in a solid argon matrix.²²,²³

Actinide-containing species are of considerable theoretical interest because of due to the interesting role of relativistic effects¹⁻³ on the nature of bonding and the phenomenon of “actinide contraction.” The contraction has been shown, in part due to relativity, as opposed to incomplete shielding of the 5f shells. Thus there have been several theoretical studies on uranium hydrides to understand the relative role of actinide contraction and relativistic effects in the electronic properties of these species. Theoretical studies of metal-hydride interactions have been the subject of many studies.³⁵-⁴³ These studies have considered not only transition-metal interaction with H₂ but also rare earths¹ and actinides.⁹,¹⁰,⁴⁰

We focus here on the nature of bonding, especially electronic, charge density, and electronic topography features that seem to offer significant new insight into uranium–hydrogen reactions. Laplacians of charge densities indicate active sites for the hydriding reactions. Moreover computations studies provide new insight into which elemental impurities catalyze hydriding, which elements do not play any role in hydriding, and which even inhibit hydriding reactions.

**Potential Energy Surfaces of Reactions: Key to Understanding Hydriding and to Providing Activation Energies**

We have computed the potential energy surfaces for the uranium–hydrogen reactions and the charge topographies as a function of a particular elemental impurity as well as for pure uranium. Figure 1 shows our computed potential energy surfaces as a function of H–U–H bond angle for the insertion of a U site into H₂ for several electronic states obtained using higher and lower levels of theory. As can be seen from Figure 1, the activation energy barrier is quite sensitive to the level of theory employed. A uranium site in the material must surpass a barrier of 20.9 kcal/mol at the lower CASSCF level but at the higher level, the spin-orbit contribution lowers the activation energy barrier for the U-hydriding dramatically. As can be seen from Figure 1, the activation energy barrier for U-hydriding is lowered from 22 kcal/mol to 12 kcal/mol mainly by spin-orbit coupling. The UH₂ species becomes substantially more stable at the MR-RCI level primarily because of the dynamical electron correlation effects and thus the UH₂ product is 35 kcal/mol more stable than U + H₂ at this level, while at the CASSCF level, UH₂ is only 22 kcal/mol more stable than U + H₂. Our computed vibrational frequency for
the symmetric stretching mode of 1468 cm\(^{-1}\) at the MP2 level is in very good agreement with the experimental value of 1423.6 cm\(^{-1}\) obtained by Andrews and coworkers\(^{33}\).

We have also computed the potential energy surface of UH\(_3\), which is a more stable hydride than UH\(_2\). In the solid state, UH\(_3\) is the product of U-hydriding and it forms this product in pyrophoric layers. The asymmetric stretching E vibrational mode of UH\(_3\) has been observed experimentally\(^{33}\) with a frequency of 1346.8 cm\(^{-1}\) compared with our result of 1293 cm\(^{-1}\) and the MP2 result of 1541 cm\(^{-1}\). A striking feature is that the UH\(_3\) species become substantially more ionic for UH\(_2\) and UH\(_3\) compared with UH. At a given level of theory, at the MP2 level for example, the dipole moments of UH, UH\(_2\), and UH\(_3\) are 3.6, 6.9, and 6.3 D, respectively, suggesting that the UH\(_3\) and UH\(_2\) species are fully ionic exhibiting a U\(^+\)-H\(^-\) ionic bond for each U-H interaction. The strong ionic character of UH\(_3\) seems to be responsible

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**Figure 1.** Comparison of CASSCF (without spin-orbit) and MR-RCI (with spin-orbit) bending potential energy curves of UH\(_2\) for the ground state.
Figure 2. Bending potential energy curve of U^{+3} + H₂ to demonstrate the catalytic activity of UH₃. The potential energy surface of the UH₃ product + H₂ shows that the U site in UH₃ spontaneously forms a complex with an additional H₂ without barrier. There is no activation barrier for H₂ dissociation by UH₃.

for the observed catalytic activity\(^{16}\) of UH₃ in enhancing further uranium hydriding once the UH₃ product is formed. We have considered U^{+3} + H₂ interaction with the objective of studying the role of the UH₃ product in further U-hydriding as there seems to be experimental evidence by Powell et al.\(^{16}\) that once the UH₃ product is formed it seems to rapidly catalyze the further hydriding of uranium. Figure 2 shows the potential energy surface for the interaction of the ionic U^{+3} present in UH₃ with an additional H₂. An additional H₂ approaching UH₃ would attack the uranium site and it is modeled by U^{+3} interaction with H₂. As seen from Figure 2, U^{+3} attaches to H₂ spontaneously without an activation barrier through the formation of a complex with H₂. This demonstrates that the U^{+3} site in the product UH₃ binds to H₂ spontaneously forming a complex in which H₂ is separated far enough so as to cause liberation of hydrogen atoms in the presence of the UH₃ product. The primary driving force for this catalytic activity is the high ionicity of the uranium site in UH₃, which leads to the attachment of H₂ without a barrier.

The computational models developed reveal that the dissociation of H₂ by uranium is caused by a dative exchange of electronic charge density. This can be demonstrated visually by seeking the plots of the important orbitals involved in the dissociation of H₂ which we have shown in Figure 3. As can be seen from this figure, our computations reveal an electron donor-acceptor model for the U-hydriding, where H₂ exchanges electronic density from its occupied 1σₑ orbital to the uranium (6d σ) orbital, and back donation from the uranium (6d π) orbital back to the H₂ 1σᵣ anti-bonding orbital causes the dissociation of H₂ by uranium. In particular the 5f or 7s orbitals of uranium are not involved in the dissociation of H₂. They do not
Figure 3. Contour plots of the two orbitals of UH₂ in its ground state show that the H₂ (1σg) donation of charge density to U(d σ) and back donation from U(6d π) to H₂ (1σu) to cause dissociation of H₂. Note that the 5f orbitals of uranium are not involved in the breaking of the H₂ bond. Top, molecular orbital plots of U-H₂ interaction show that U(6d σ) interacts with H₂ molecular orbital. Bottom, molecular orbital plots of interaction show that U(6d π) interacts with H₂ antibonding MO.

Participate in the bonding with H₂ because the uranium 5f and 7s orbitals behave like core atomic orbitals. This is caused by relativistic contraction of the 7s orbital. On the other hand, the 6d orbital of uranium expands due to relativity and thus readily overlaps with the H₂ orbitals. It should be noted that the 5f orbital of uranium is not involved in H₂ dissociation specifically for the hydriding, although the 5f orbitals are known to take part in bonding in other actinide complexes of uranium, such as with silicates and carbonates. Thus, we consider this trend to be quite unique to hydriding.
Figure 4. Laplacian of the charge density of UH$_3$, which shows maximal contours at the U site indicating depletion of electronic charge at the U site. Topography of the inverse charge density of UH$_3$ shows that charge depletion on U (high spots) makes the area highly reactive to additional H$_2$.

Figure 4 shows the Laplacian of the total electronic charge density of UH$_3$ near its C$_{3v}$ minimum. The Laplacian contour plots offer useful electronic charge information as it inversely relates to the electronic charge. The region with maxima in the Laplacian is the region depleted of electronic charge and thus an electrophilic region. As seen from Figure 3, there is a large peak at the uranium site, which means significant depletion of electronic density at the uranium site. Consequently, the UH$_3$ product catalyzes the hydriding process by spontaneous formation of a complex of H$_2$ at the U$^{+3}$ site, which opens up the H$_2$ bond sufficiently to cause further U-hydriding to occur spontaneously.

Trends in the Influence of Elemental Impurities in Uranium Hydriding

It is important to understand what roles, if any, the elemental impurities present in the uranium material play on activation energy and hydriding reactions. Thus we have studied a number of elemental impurities such as carbon, silicon, iron, chromium, nickel, rhodium, and tungsten in order to compare and contrast the role of these elements in influencing the hydriding reactions. A common theme that emerged in the study of these elemental impurities is that the Laplacian topography of charge densities offers significant new insight into the active or inactive sites for hydriding. Many of the impurities that are considered here are often present in uranium and thus the computational approaches used here offer a comprehensive model for the hydriding of this material.
Figure 5. Comparisons of Laplacian topographies of elemental C and Al impurities in uranium. Note that neither C nor Al offers a significant peak at the site to act as a catalyst for the hydriding reaction.

Figure 5 compares the Laplacian charge topographies of carbon and aluminum impurities in the vicinity of a uranium site. As can be seen from this figure, whereas a carbon site exhibits a small peak there is no activity at all at the aluminum site. More importantly both carbon and aluminum become insignificant in the presence of a dominating set of peaks near the uranium site. These uranium peaks are, however, somewhat spread out, which clearly suggests that the carbon and aluminum impurities have no role in influencing the hydriding reaction in a positive way so as to act as catalysts. On the other hand, our studies on uranium carbide show that the U–C bond is highly ionic and thus there is considerable accumulation of electron density.
Figure 6. Laplacian topographies of elemental iron and tungsten impurities in uranium. Top, U with Fe impurity inverse charge topography shows U has a larger peak than Fe but Fe has a more significant peak than C. Bottom there dimensional inverse charge topography of U with W impurity shows that the web site is more focused and concentrated for propensity to hydride.

around the carbon site. This would translate into inhibition of hydriding at the carbon site, a phenomenon that has been confirmed experimentally by Mintz and coworkers. These experimental studies show that layers of uranium carbide act as protective layers inhibiting uranium hydriding and corrosion.

Some of the transition metals, especially those in the third row are known to be good catalysts for hydrogenation reactions. For this reason, we focused our efforts on studying the effect of those third-row transition-metal impurities that are present in uranium. With this objective, we have carried out studies on uranium hydriding in the presence of tungsten, iron, rhodium, and nickel. Figure 6 compares the Laplacian topographies of uranium with iron
and tungsten sites. In contrast to the results for carbon or aluminum shown in Figure 5, certainly iron and tungsten sites are more active. However, the iron site has both peaks and valleys, whereas the tungsten site has a single focused and dense peak. This is in contrast with both uranium and iron sites. It should be noted that the peaks at the uranium site are multiple and somewhat diffuse, whereas the tungsten peak is focused at the site. Thus, the tungsten site seems to exhibit the greatest propensity for uranium hydriding as the tungsten site catalyzes the hydriding reaction. On the other hand, although the iron site exhibits peaks, also comprises a few valleys, suggesting that in this environment it exhibits an ambivalent behavior, that is, both a donor and acceptor of electronic charge. The tungsten site clearly promotes the hydriding reaction. Among other impurities that we have considered thus far, we have found that the rhodium site is also a good hydriding catalyst. These electronic topographies are consistent with the activation energy barriers for these reactions.

**Conclusion**

We have been developing computational models to offer insight into the uranium-hydrogen reactions. We find that the activation energy barrier for the insertion of uranium into H₂ is reduced approximately to half its value by relativity, in particular, spin-orbit coupling. This is made feasible through the spin-orbit coupling of the triplet states with the quintet state in the region of the curve crossing at considerably lower energy than the activation energy barrier for the insertion of the quintet ground state of uranium into H₂ in the absence of spin-orbit coupling.

The computational study reveals that the UH₃ molecule is in a C₃ᵥ minimum and a D₃h saddle point. The inversion potential energy surface of the quartet state of UH₃ reveals that the barrier for the umbrella inversion is much lower than the zero-point vibrational energy of UH₃. Consequently, it was predicted that UH₃ would be a floppy species exhibiting rapid umbrella inversion motion. The bonding in UH₃ was found to be strongly ionic even more than that of UH. Thus the role of the product UH₃ formed in uranium hydriding was modeled by computing the potential energy surface of U⁺₃ with H₂. The potential energy surface shows that in contrast to pure uranium, the U⁺₃ site forms a complex with H₂ in which the H–H separation is far enough to cause adequate dissociation. The hydrogen atoms can diffuse through the lattice through additional attachment to adjacent U⁺₃ sites in UH₃, thus penetrating through the UH₃ layer and causing hydriding of uranium. The UH₃ product catalyzes the hydriding process by formation of a complex with H₂ at the U⁺₃ site, which opens up the H₂ bond sufficiently to cause further U-hydriding. The bond-breaking process in the formation complex assists the formation of hydrogen atoms in the presence of uranium. The hydrogen atoms thus formed cause further U-hydriding, thus explaining the experimental observation of Powell et al.¹⁶

We have developed computational models to study the influence of various elemental impurities in the uranium-hydriding reaction. We find that some elemental impurities such as carbon and aluminum do not have a positive influence in catalyzing the hydriding reaction, whereas other elemental
impurities such as tungsten catalyze the hydriding. There is also experimental evidence\textsuperscript{7} that certain impurities, such as silicon, cause a substantial increase in the rate of uranium hydriding.

We have shown that the Laplacian topographies of charge densities offer significant new insights into the reactive sites and are very successful in predicting relative trends as to which sites are reactive. Our models show that the sites that exhibit dense and focused peaks are particularly active in removing the electron charge density from the hydrogen molecule and thus catalyzing the uranium-hydriding reaction.

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