Atomistic level relativistic quantum modelling of plutonium hydrogen reaction

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Abstract

We have computed the electronic structural and spectroscopic properties for the low-lying electronic states of plutonium hydrides, PuH$_n$ ($n = 2–4$) and their ions which provide significant insight into plutonium hydriding reactions. We have employed a relativistic quantum technique that uses relativistic effective core potentials on Pu. Our computations show that whereas PuH$_2$ and PuH$_3$ form stable $C_{2v}$ and $C_{3v}$ structures which exhibit Pu–H direct chemical bonds, PuH$_4$ becomes a complex of PuH$_2$ with a partially dissociated H$_2$. Our computations show that the H$_2$ dissociation is assisted by PuH$_2$. Electron density contour maps including Laplacians of charge densities support that the Pu site of the hydrided species is depleted substantially in charge thereby causing catalysis of further hydriding. The IR spectra show that the H$_2$ sorbed on PuH$_2$ is partially dissociated. We have also provided comparison of our results with corresponding computations on uranium hydrides.

Keywords: Plutonium hydride; Relativistic quantum modelling; PuH$_2$; PuH$_3$; PuH$_4$

1. Introduction

Actinide hydrogen reactions, particularly those of uranium, plutonium and thorium are quite important in surface and corrosion science of these materials [1] and thus the hydrides of actinides have received considerable attention over many years [1–31]. Some interesting observations pertaining to hydriding is that once hydride is formed further hydrogen reaction seems to take place at a much faster rate. Plutonium seems to exhibit a greater propensity to break the H$_2$ bond compared to uranium [1]. The product of the hydrogen gas reaction with the materials is pyrophoric actinide hydride layers. The hydrides sites exhibit dramatically greater propensity to cause further hydriding [1,9]. Much of the experimental and theoretical works concerning actinide–hydrogen reactions have been focused on uranium [3–19], especially concerning the thermochemistry, diffusion kinetics and mechanisms of U-hydriding.

Spectroscopic studies of actinide hydrides and oxides have been carried out by Andrews and coworkers [2,21–30] who have studied these species using matrix-isolation techniques by reactions of pulsed laser ablated uranium and thorium atoms with gases such as N$_2$, O$_2$, CO$_2$, H$_2$ and so on. The primary reaction products of laser-ablated uranium with H$_2$ gas have been found to be UH$_n$ ($n = 1–4$) and U$_2$H$_n$ ($n = 2–4$) in a solid argon matrix [24,25]. Likewise Andrews and Cho [2] have recently studied the infrared spectrum and structure of CH$_2$=ThH$_2$ species. Souter et al. [26] have demonstrated that the uranium hydrides are more stable compared to uranium and H$_2$ gas. In contrast to uranium hydrogen reaction there is less experimental knowledge of the plutonium hydrogen reaction [1].

Theoretical studies actinide containing species have been on the increase [32–44] as the interplay between the 5f and 6d orbitals seems to be quite interesting for actinide species. The phenomenon of “actinide contraction” can be quite important in the chemistry of plutonium and uranium containing species [43,44]. Moreover, relativistic effects are quite significant for actinides and in fact, the actinide contraction is attributed, in part, to relativity as opposed to incomplete shielding of the 5f shells [43,44]. There have been a number of theoretical studies...
on uranium hydrides to understand the relative role of actinide contraction and relativistic effects in the electronic properties of these species. In the present study, we report the results of relativistic computations on the electronic states of PuH$_n$ ($n = 2–4$) and their ions using the density functional theory (DFT) computations employing relativistic effective core potentials on these species.

2. Computational techniques

All computations of PuH$_n$ species were carried out with relativistic effective core potentials (RECPs) that included all but 6s$^2$6p$^8$4f$^6$7s$^2$ shells of the Pu atom in the core [43,45]. We have employed the (5s5p4d4f/5s5p3d3f) basis sets for Pu and van Duijneveldt’s (5s1p/3s1p) basis set [46] for the hydrogen atoms. We believe that the 5g functions are unimportant for Pu as the 5f orbitals are core-like in their behavior in plutonium hydrides.

We have employed the density functional (DFT) approach [47–50] that utilized Becke’s three-parameter functional [48] with Vosko et al.’s local correlation part [49] and Lee et al.’s [50] nonlocal part (abbreviated as B3LYP). The geometry searches were carried out at the DFT levels using the redundant internal coordinates. We have calibrated the DFT/B3LYP approach earlier for the equilibrium geometries of actinide species, and we have found that the equilibrium geometries are well represented by the DFT/B3LYP/RECP method. The computations were carried out using the GAUSSIAN ’03 [51] package of codes.

3. Results and discussion

We have computed the equilibrium geometry and the IR spectra of PuH$_n$ species for the values of $n = 2–4$. Fig. 1 shows the optimized equilibrium geometries of PuH$_2$ and PuH$_2^{2+}$. The ground electronic state of PuH$_2$ was found to be a $^7A_2$ electronic state with a bent equilibrium geometry and a bond angle of 104°.

The $^7A_2$ ground state is consistent with two more unpaired electrons in the 5f shell in comparison to the $^5A_2$ ground state of UH$_2$ [52]. The $^5A_2$ state of UH$_2$ exhibits U–H bond distances of 2.126 Å and a U–U–H bond angle of 108° at the DFT level [52]. These results compare quite well with the corresponding results for PuH$_2$ shown in Fig. 1. As can be seen from Fig. 1, the dipositive ion, PuH$_2^{2+}$ exhibits a $^5A_2$ state with considerable elongated Pu–H bond distances of 2.845 Å and thus the Pu–H bonding is weaker in the dication.

The PuH$_3$ species forms a stable pyramidal equilibrium structure with Pu–H bond distances of 2.081 Å and a pyramidal H–Pu–H bond angle of 112°, as seen from Fig. 1. The ground state of PuH$_3$ is a $^6A_2$ state as can be seen from Fig. 1. The UH$_3$ species exhibits an analogous pyramidal structure with U–H bond distances of 2.066 Å and a pyramidal HH–U–H bond angle of 112.3°. However, the ground electronic state of UH$_3$ [52] is a $^4A_2$ state, as expected since U has two less unpaired electrons in the 5f orbital. Thus, the geometries of the two species are analogous in spite of the electronic states and features being different.

Our results on PuH$_4$ are quite interesting in that as seen from Fig. 1, PuH$_4$ forms a distorted structure with two of the hydrogen atoms bonding chemically with Pu. The other two hydrogens are loosely held to Pu but the distances between the hydrogens suggest that the H$_2$ bond is partially dissociated. It is interesting to note that when started with a tetrahedral PuH$_4$ species with all four Pu–H bond distances being equal, the optimized structure has a large imaginary vibrational frequency suggesting that the structure would undergo strong distortion. When distortion was allowed, the method of geometry optimization yields the structure shown in Fig. 1. This structure
should be viewed as a loose complex of PuH₂ with a partially dissociated H₂. This partial dissociation is achieved by electron density exchanges between highly electron-depleted Pu site when PuH₂ is formed and the additional H₂ molecule. This dative interaction causes partial dissociation of H₂. 

Fig. 2 shows our computed IR spectra of PuH₂ and PuH₃ with actual computed vibrational frequencies for all modes in Table 1. The ⁷A₂ state exhibits three vibrational modes, two of which labeled B₂ and A₁ at 1192 and 1208.6 cm⁻¹ are quite close and thus show up as a single peak in Fig. 2. The lower frequency A₁ mode corresponds to the bending motion of the hydrogens and appears as a less intense peak at 487 cm⁻¹. The high frequency modes correspond to asymmetric stretch (B₂) and a symmetric stretch (A₁). The PuH₃ IR spectra exhibit more peaks as expected (Fig. 2). The low frequency mode at 363 cm⁻¹ is quite intense and corresponds to the motions of hydrogens out of the triangular plane in which they are located at equilibrium. This can be envisaged as concerted inversion motions of the three hydrogens. The peaks at 512 and 1457 cm⁻¹ are assigned to E modes while the peak at 1327 cm⁻¹ is the A₁ symmetric stretching mode. The peak at 512 cm⁻¹ corresponds to a doubly degenerate E representation of the bending motions of hydrogens while the corresponding stretching motions of hydrogens at the higher frequency of 1457 cm⁻¹.

The IR spectra of PuH₄ that we have shown in Fig. 2 is quite interesting and striking in that it exhibits an intense peak near 2272 cm⁻¹ which is purely a H–H stretching mode of the weakly bound H₂. The frequency is about half of the free H₂ vibrational frequency which is experimentally established as 4401 cm⁻¹. The fact that the frequency is reduced to half the free H₂ frequency is fully consistent with the partially dissociated H₂ sorbed on PuH₂. This is suggestive of catalysis by Pu to dissociate other hydrogens once PuH₂ is formed. There is one more shearing mode of the hydrogens weakly bound to PuH₂ at 2896 cm⁻¹. The other peaks below 1361 cm⁻¹ primarily correspond to H–Pu–H modes where the hydrogens are chemically bound to Pu. The weak mode at 1168 cm⁻¹ corresponds to a kind of shear vibration of the hydrogens not bonded chemically to PuH₂. The remaining low frequency modes are some kinds of bending or torsional modes involving all four hydrogens. Thus, the IR spectrum of PuH₄ is really that of H₂ physisorbed on to PuH₂.

The dipole moments of PuHₙ species reveal an interesting trend. As seen from Table 1, among the species that we have studied here, the PuH₂ species exhibits largest dipole moment consistent with the substantial charge transfer from Pu to the hydrogens. Addition of another hydrogen to PuH₂, which results in the formation of PuH₃, reduces the dipole moment from 5.88 to 4.15 D. That is, three hydrogens compete for the charge transfer and since there is considerable charge transfer from Pu to these hydrogens the effective charge transfer to the chemically bonded hydrogens is reduced resulting in a large reduction of the dipole moment.

Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>ν₁ (cm⁻¹), intensity</th>
<th>ν₂ (cm⁻¹), intensity</th>
<th>ν₃ (cm⁻¹), intensity</th>
<th>ν₄ (cm⁻¹), intensity</th>
<th>μₑ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuH₂</td>
<td>⁷A₂</td>
<td>487: A₁, 78</td>
<td>1192: B₂, 746</td>
<td>1208.6: A₁, 359</td>
<td>4.88</td>
<td></td>
</tr>
<tr>
<td>PuH₂⁺</td>
<td>⁵A₂</td>
<td>233: A₁, 4.7</td>
<td>479.8: A₁, 0.12</td>
<td>484.8: B₂, 0.17</td>
<td>5.88</td>
<td></td>
</tr>
<tr>
<td>PuH₃</td>
<td>⁶A₂</td>
<td>362: A₁, 434.7</td>
<td>512: E, 29.8</td>
<td>1327: A₁, 52.5</td>
<td>4.15</td>
<td></td>
</tr>
<tr>
<td>PuH₄</td>
<td>⁵A₁</td>
<td>277: B₂, 1168: B₁, 2272: A₁</td>
<td>478: B₁, 1311: B₂, 2896: A₂</td>
<td>518: A₁, 1362: A₁, 808: A₁</td>
<td>1.022</td>
<td></td>
</tr>
</tbody>
</table>
The Mulliken populations seem to provide further insight into the nature of these species. The PuH$_2$ species exhibits Mulliken populations of Pu (0.679), H$_1$ (−0.339), and H$_2$ (−0.339). The charges of chemically bonded hydrogens are about −0.34 for PuH$_2$ and thus about 0.68 charge is depleted from Pu in the case of PuH$_2$. The PuH$_3$ Mulliken charges are Pu (1.029), H$_1$ (−0.343), H$_2$ (−0.343), and H$_3$ (−0.343). It is interesting that the Mulliken populations of the three hydrogens in PuH$_3$ are quite close to the corresponding hydrogen population in PuH$_2$. Consequently, Pu is depleted by 1.029 electronic charge due to the presence of three hydrogens. Thus, more charge is depleted on Pu in PuH$_3$ compared to PuH$_2$. On this basis then we can predict that an additional H$_2$ approaching PuH$_3$ will be partially dissociated due to exchange of charge densities and thus PuH$_3$ would also assist in further hydriding once it is formed. The PuH$_4$ species exhibit overall Mulliken charges of Pu (0.955), H$_2$ (−0.35), H$_3$ (−0.35), H$_4$ (−0.128), and H$_5$ (−0.128), where H$_2$ and H$_3$ are chemically bonded hydrogens to Pu. We thus observe that the chemically bonded hydrogens, namely H$_1$ and H$_2$ exhibit about the same Mulliken charges as PuH$_2$. An additional 0.128 electronic charge is donated to physisorbed H$_2$ to cause partial dissociation. We note that there is dative exchange of charge densities between Pu and hydrogens. The dipositive ions such as PuH$_2^{2+}$ and PuH$_3^{2+}$ have significant positive charges on both Pu and H and thus charge repulsions between Pu and H cause the Pu–H bond lengths to elongate. For example, the Mulliken populations of PuH$_2^{2+}$ are Pu (1.776), H$_1$ (0.112), and H$_2$ (0.112), thus both hydrogens are positively charged causing repulsion between Pu and H. Thus, Pu–H bond lengths change from 2.145 to 2.855 for PuH$_2$ and PuH$_2^{2+}$, respectively.

The spin densities of the unaired electrons are distributed among the Pu and hydrogen atoms. The heptet state of PuH$_2$ exhibits distribution of spin densities as Pu (6.163), H$_1$ (−0.082), and H$_2$ (−0.082). This suggests strong spin localization on Pu in the case of PuH$_2$. The quintet state of PuH$_3$ spin density is distributed among the atoms as Pu (5.34), H$_1$ (−0.113), H$_2$ (−0.113), and H$_3$ (−0.113). There is more delocalization of spin densities in the case of PuH$_3$. The quartet spin densities of PuH$_4$ are shared among the atoms as Pu (4.622), H$_2$ (−0.109), H$_3$ (−0.109), H$_4$ (−0.202), and H$_5$ (−0.202), where H$_2$ and H$_3$ are chemically bonded hydrogens to Pu. It is interesting to note that there is greater spin density delocalization on the non-bonded hydrogens which is consistent with partially dissociated nature of H$_2$ physisorbed on PuH$_2$.

It is interesting to compare PuH$_n$ with the corresponding UH$_n$ species. Due to two less electrons in U, the electronic states of UH$_n$ exhibit electronic states [52] with two spin multiplicity lower than the corresponding states of PuH$_n$. The dipole moments of UH$_n$ species are comparable to those of PuH$_n$. For example, the dipole moment of UH$_2$ at the DFT level is 6.2 D compared to 5.88 D for PuH$_2$. Thus, Pu–H bond lengths change from 2.145 to 2.855 for PuH$_2$ and PuH$_2^{2+}$, respectively.

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4. Conclusion

We have computed the electronic states, equilibrium geometries and IR spectra of PuHₙ species for n = 2–4. One of the most fascinating results is that PuH₄ does not exist as a tetrahedral species; instead it distorts into a complex of PuH₂...H₂, where H₂ is partially dissociated and sorbed to PuH₂. Our IR spectra also confirm that H₂ is partially dissociated in this complex. This suggests that once PuH₂ is formed the Pu at the hydrides site becomes an active site for catalysis of further breaking of H₂ molecule in the vicinity. It is thus predicted that the barrier for dissociation of H₂ by PuH₂ would be zero, as H₂ would spontaneously attach to PuH₂ and undergo partial dissociation. This is facilitated by electron donor–acceptor and back transfer process. The results on PuH₃ and PuH₂ show that these species are chemically bonded with a pyramidal PuH₃ exhibiting a characteristic IR spectra attributable to a pyramidal molecule. Moreover, the inversion motion suggests a rather floppy molecule with a surmountable energy barrier that would make this species non-rigid. The PuH₂ molecule is bent with considerable electronic charge transfer from Pu to hydrogens. The extent of charge transfer per hydrogen is about the same in PuH₂ and PuH₃. On the basis of similarity of bonding between PuH₂ and UH₂ we conclude that the 6d orbitals on Pu are involved in bonding with the H 1s orbitals and that the 5f orbitals do not participate in Pu–H interactions or in the dissociation process of H₂.

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References