Reactions of Ta$^+$, W$^+$, and Pt$^+$ with H$_2$, D$_2$, and HD:
Effect of Lanthanide Contraction and Spin-Orbit Interactions on Reactivity and Thermochemistry

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There have been extensive experimental studies of the reactions of atomic first-row and second-row transition metal cations with dihydrogen and its isotopic analogues in our group. For third-row transition metal cations, however, only La$^+$ and Lu$^+$ systems have been studied experimentally although theoretical calculations are in literature.[1-4] This study is designed to quantify the thermochemistry and mechanisms of reactions of Ta$^+$, W$^+$, and Pt$^+$ with dihydrogen by guided ion beam tandem mass spectrometry.[5] Ta$^+$, W$^+$, and Pt$^+$ are formed largely in their ground electronic states using a DC discharge flow-tube source. For comparison, *ab initio* calculations are used to calculate bond energies for M$^+$–H and potential energy surfaces (PESs) for M$^+$ + H$_2$. Here B3LYP density functional theory with a 6-311+G(3p) basis for H and Hay-Wadt relativistic effective core potentials for these metals is used.

The kinetic-energy dependence of product cross sections is analyzed to determine E_0, the energy threshold for product formation at 0 K using Eq. (1), where σ_0 is an energy-independent scaling factor, E

$$\sigma(E) = \sigma_0 \sum g_i (E + E_{el} + E_i - E_0)^n / E \qquad (1)$$

is the relative kinetic energy of reactants, E_{el} is the electronic energy of metal cation, and n is an adjustable parameter. The sum considers contributions from rovibrational states of hydrogen at 300 K, denoted by i, having energies E_i and populations g_i, where $\sum g_i = 1$. From the thresholds measured, bond dissociation energies (BDEs) for the metal–ligand cations observed in these reactions can be calculated using an equation of $D_0(M^+–H) = D_0(H–H) – E_0$, where $D_0(H–H) = 4.478$ eV and $D_0(D–D) = 4.556$ eV. In all cases, the experimental BDEs refer to the ground spin-orbit state at 0.0 eV: a^5F_1 for Ta$^+$, $a^6D_{1/2}$ for W$^+$, and $a^2D_{5/2}$ for Pt$^+$. However, our calculations do not explicitly include spin-orbit interactions and are referenced to the properly weighted mean of all spin-orbit levels in the ground state term: 0.466 eV for Ta$^+$(a^5F), 0.514 eV for W$^+$(a^6D), and 0.418 eV for Pt$^+$(a^2D). Thus, all calculated bond energies must be corrected for these different asymptotic energies to properly compare with experimental values.

The endothermic cross sections in the H$_2$ and D$_2$ reaction systems are analyzed in detail using Eq. (1). Typical modeling is shown in Fig. 1 and can be seen to reproduce the experimental result very well. The optimum values of the parameters in Eq. (1) are listed for these systems in Table 1. These BDEs derived are consistent with *ab initio* calculations performed here and in the literature (Table 1).

Table 1. Parameters of Eq. (1) Used in Modeling Reactions of M$^+$ + D$_2$ / H$_2$ and Bond Energies

Reaction	σ_0	n	$E_0(MH^+)$ (eV)	$D_0(M^+–H)$ (eV)	$D_0(M^+–H)$ (eV)	$D_0(M^+–H)$ (eV) (Theory)
Ta$^+$ + D$_2$	5.1 ± 0.3	1.2 ± 0.1	2.16 ± 0.06	2.37 ± 0.06	2.09 ($^4\Sigma^-$)	2.34 ($^4\Sigma^-$) [1]
Ta$^+$ + H$_2$	4.7 ± 0.4	1.2 ± 0.1	2.09 ± 0.08	2.39 ± 0.08	2.21 ($^4\Phi$)	2.30 ($^4\Phi$) [1]
W$^+$ + D$_2$	5.8 ± 0.3	1.3 ± 0.1	2.24 ± 0.06	2.28 ± 0.06	2.12 ($^5\Pi$)	2.16 ($^5\Pi$) [1]
W$^+$ + H$_2$	6.5 ± 0.4	1.2 ± 0.1	2.23 ± 0.06	2.25 ± 0.06	2.12 ($^5\Delta$)	2.09 ($^5\Delta$) [1]
Pt$^+$ + D$_2$	7.5 ± 0.4	1.1 ± 0.1	1.71 ± 0.05	2.81 ± 0.05	2.55 ($^1\Sigma^+$)	2.73 ($^1\Sigma^+$) [1]
Pt$^+$ + H$_2$	7.4 ± 0.5	1.1 ± 0.1	1.68 ± 0.06	2.80 ± 0.06	2.65 ($^3\Delta$)	2.69 ($^3\Delta$) [1]

The Ta$^+$, W$^+$, and Pt$^+$ systems have higher reactivities towards dihydrogen as compared to their first-row and second-row congener systems partially because of smaller endothermicities. This is largely a consequence of the lanthanide contraction and relativistic effects that allow efficient $6s$-$5d\sigma$ hybridization. Ta$^+$ and W$^+$ systems exhibit similar reactivity because they have similar thresholds, whereas Pt$^+$ is more reactive partly because of a smaller endothermicity.

The calculations show that the reaction of Pt$^+$ + H$_2$ can proceed via a long-lived stable PtH$_2^+$ intermediate (Fig. 2), thereby leading to a statistical behavior with a near 1:1 PtH$^+$/PtD$^+$ ratio observed at lower energies. We performed relaxed PES scans starting with the bound PtH$_2^+$ species and systematically

lengthening one of the Pt–H bonds. These scans lead to ground state products with no barriers in excess of the endothermicity. We also considered a collinear reaction between Pt^+ and H_2. Initial approach of $Pt^+(^2D)$ to H_2 forms a Pt^+–H-H adduct and then lengthening of the H-H bond leads to PtH^+ + H products with no barrier in excess of the endothermicity. This is consistent with the increasing branching ratio with increasing energy, a direct abstract mechanism like that observed in the Ni^+ and Pd^+ systems.

Calculations indicate that high-spin ground states of Ta^+ and W^+ interact with H_2 repulsively (Figs. 3 and 4), consistent with expectations of impulsive mechanism which are based on diabatic reactivity "rules" established for the first-row transition metal cations. However, there is extensive coupling among PESs of differing spin for Ta^+ and W^+ systems because of strong spin-orbit interactions due to the lanthanide contraction and relativistic effects, unlike the first-row transition metal cations. Thus, H–M^+–H intermediates can be formed with a barrier below the endothermicity of M^+–H + H products, thereby providing low energy pathways that involves an insertion mechanism on low-spin surfaces. This is consistent with the near 1:1 MH^+/MD^+ ratio observed in the reactions of HD at lower energies. At higher energies, the branching ratio increases with energy, indicating contributions from direct mechanisms.

The efficient spin-orbit coupling between PESs of different spin for Ta^+ and W^+ systems also leads to enhanced reactivities towards dihydrogen as compared to the first-row and second-row congener systems. However, the surface hopping from the high-spin to the low-spin surfaces for the Ta^+ and W^+ systems also lead to lower reactivities towards dihydrogen as compared to the Pt^+ system in which there is no crossing of PESs with differing spin as shown in Fig. 2.
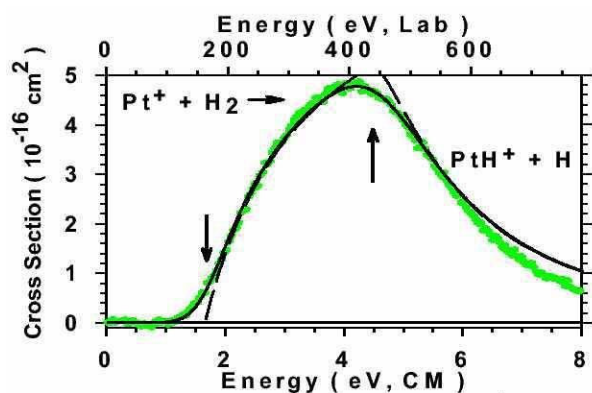

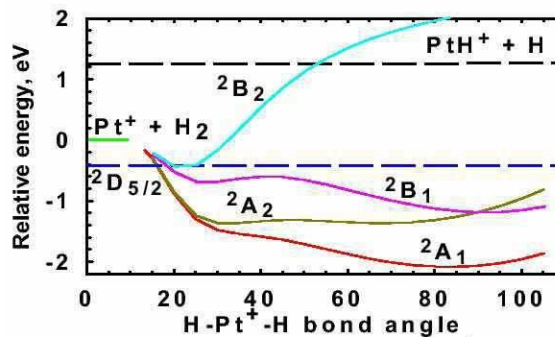Fig. 1. Cross section for reaction of Pt^+ with H_2.

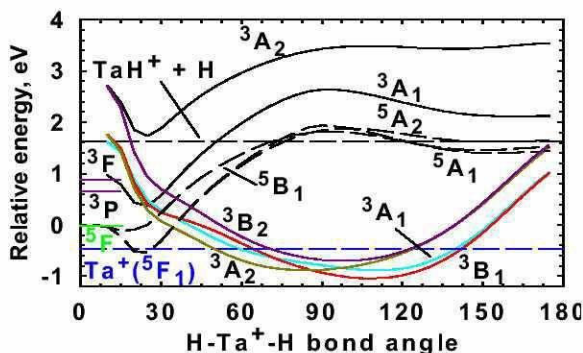Fig. 2. PESs for interaction of Pt^+ with H_2.

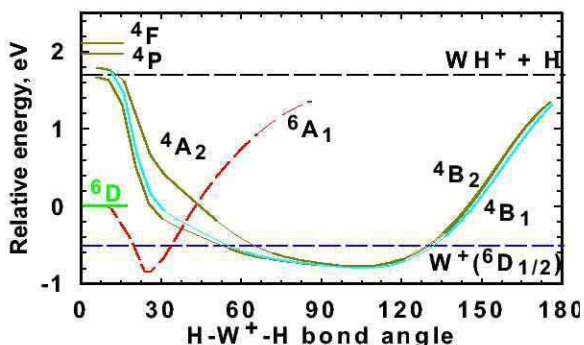Fig. 3. PESs for interaction of Ta^+ with H_2.

Fig. 4. PESs for interaction of W^+ with H_2.

1. Ohanessian, G.; Brusich, M. J.; Goddard III, W. A. *J. Am. Chem. Soc.* **1990**, *112*, 7179-7189.
2. Zhang H.; Balasubramanian, K. *J. Phys. Chem.* **1992**, *96*, 6981-6985.
3. Dai, D. G.; Cheng, W.; Balasubramanian, K. *J. Chem. Phys.* **1991**, *95*, 9094-9105.
4. Balasubramanian, K.; Ma, Z. *J. Phys. Chem.* **1991**, *95*, 9794-9800.
5. Loh, S. K.; Hales, D. A.; Lian, L.; Armentrout, P. B. *J. Chem. Phys.* **1989**, *90*, 5466-5485.