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# Fractionation effects in muonium–molecular hydrogen reactions

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The chemistry of the muonium atom ( $\text{Mu} = \mu^+e$ ) is exciting much interest<sup>1</sup> because of its possible application for cool fusion and the extreme isotope shifts encountered when Mu replaces H atoms.

Fractionation of heavy atoms is well known in low temperature reaction environments, such as the interstellar medium, where deuterated species are often superabundant. This fractionation is driven by the vibrational zero-point energy released when an atom is replaced by a heavier isotope. Replacing H with Mu leads to a ninefold mass reduction and one would thus expect extreme fractionation effects. The purpose of this note is to show that these effects should be sufficient to suppress all  $\text{Mu} \leftrightarrow \text{H}$  exchange reactions with the hydrogenic molecular species  $\text{H}_2$ ,  $\text{H}_2^+$ , and  $\text{H}_3^+$  at room temperature.

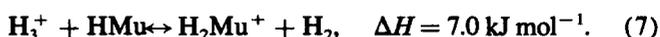
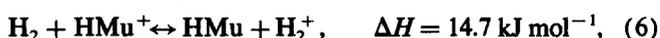
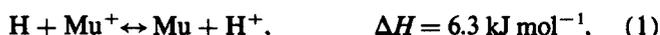
The vibrational calculations used accurate *ab initio* potentials for  $\text{H}_2$ ,<sup>2</sup>  $\text{H}_2^+$ ,<sup>3</sup> and  $\text{H}_3^+$ .<sup>4</sup> The mass of the H atom was taken as 1.007 825 amu and Mu as 0.113 977 9 amu.<sup>5</sup> The diatomic problems were solved by direct numerical integration of the Schrödinger equation using the program due to Le Roy.<sup>6</sup> This gave zero point energies for  $\text{H}_2$ ,  $\text{H}_2^+$ ,  $\text{HMu}$ , and  $\text{HMu}^+$  as 2179.7, 1149.8, 4772.3, and 2516.1  $\text{cm}^{-1}$ , respectively.

Variational nuclear motion calculations for the triatomic systems were performed using scattering coordinates and program TRIATOM<sup>7</sup> which has been used by us<sup>8,9</sup> for several previous studies on  $\text{H}_3^+$ . For the calculations on  $\text{H}_2\text{Mu}^+$  it was necessary to reoptimize the parameters used to generate the Morse oscillator-like functions carrying the motions in the  $r_1$  (H–H) and  $r_2$  (Mu– $\text{H}_2$ ) coordinates. For  $r_1$  the parameters<sup>7</sup> used were  $r_e = 2.0 a_0$ ,  $\omega_e = 0.0112 E_h$ , and  $D_e = 0.06 E_h$ ; for  $r_2$  they were  $r_e = 1.565 a_0$ ,  $\omega_e = 0.030 E_h$ , and  $D_e = 0.033 E_h$ . Otherwise the calculations followed those presented in Ref. 8.

The vibrational zero-point energy of  $\text{H}_3^+$  and  $\text{H}_2\text{Mu}^+$  were found to be 4363.5 and 7603.7  $\text{cm}^{-1}$ , respectively. The value for  $\text{H}_3^+$  has to be increased by the  $J = 1-0$  excitation

energy<sup>9</sup> of 64.1  $\text{cm}^{-1}$  as occupation of the lowest,  $J = 0$ , rotational state is forbidden by nuclear spin statistics.

Finally, the correction to the H atom energy due to the finite nuclear mass of the H and Mu shows that the electron is 525.0  $\text{cm}^{-1}$  less bound in muonium. These data allow the enthalpies of the following ion–neutral and neutral–neutral reactions to be calculated:



All these reactions are sufficiently endothermic to ensure that there is no Mu displacement of H in molecules at 300 K. Similar conclusions must be expected for exchange reactions involving other species containing hydrogens bound to heavier atoms.

One of us (J.T.) wishes to thank Dr. D. J. Arseneau for drawing this project to our attention and for helpful discussions.

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<sup>8</sup>S. Miller and J. Tennyson, *J. Mol. Spectrosc.* **128**, 183 (1987).

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