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Fractionation effects in muonium–molecular hydrogen reactions

Jonathan Tennyson and Steven Miller
Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, United Kingdom

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The chemistry of the muonium atom ($\mathrm{Mu} = \mu^+e$) is exciting much interest[1] 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 enviornments, 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 supress all Mu↔H exchange reactions with the hydrogenic molecular species H_2, H_2^+, and H_3^+ at room temperature.

The vibrational calculations used accurate *ab initio* potentials for H_2,[2] H_2^+,[3] and H_3^+.[4] The mass of the H atom was taken as 1.007 825 amu and Mu as 0.113 977 9 amu.[5] The diatomic problems were solved by direct numerical integration of the Schrödinger equation using the program due to Le Roy.[6] This gave zero point energies for H_2, H_2^+, HMu, and HMu^+ as 2179.7, 1149.8, 4772.3, and 2516.1 cm^{-1}, respectively.

Variational nuclear motion calculations for the triatomic systems were performed using scattering coordinates and program TRIATOM[7] which has been used by us[8,9] for several previous studies on H_3^+. For the calculations on $\mathrm{H_2Mu}^+$ 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 ($\mathrm{Mu{-}H_2}$) coordinates. For r_1 the parameters[7] 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 H_3^+ and $\mathrm{H_2Mu}^+$ were found to be 4363.5 and 7603.7 cm^{-1}, respectively. The value for H_3^+ has to be increased by the $J = 1$–0 excitation energy[9] of 64.1 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 cm^{-1} less bound in muonium. These data allow the enthalpies of the following ion–neutral and neutral–neutral reactions to be calculated:

$$\mathrm{H + Mu^+ \leftrightarrow Mu + H^+}, \qquad \Delta H = 6.3\ \mathrm{kJ\,mol^{-1}}, \tag{1}$$

$$\mathrm{H_2 + Mu^+ \leftrightarrow HMu + H^+}, \qquad \Delta H = 31.1\ \mathrm{kJ\,mol^{-1}}, \tag{2}$$

$$\mathrm{H_2 + Mu \leftrightarrow HMu + H}, \qquad \Delta H = 24.8\ \mathrm{kJ\,mol^{-1}}, \tag{3}$$

$$\mathrm{H_2^+ + Mu \leftrightarrow HMu^+ + H}, \qquad \Delta H = 10.1\ \mathrm{kJ\,mol^{-1}}, \tag{4}$$

$$\mathrm{H_3^+ + Mu \leftrightarrow H_2Mu^+ + H}, \qquad \Delta H = 31.8\ \mathrm{kJ\,mol^{-1}}, \tag{5}$$

$$\mathrm{H_2 + HMu^+ \leftrightarrow HMu + H_2^+}, \qquad \Delta H = 14.7\ \mathrm{kJ\,mol^{-1}}, \tag{6}$$

$$\mathrm{H_3^+ + HMu \leftrightarrow H_2Mu^+ + H_2}, \qquad \Delta H = 7.0\ \mathrm{kJ\,mol^{-1}}. \tag{7}$$

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.

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