The Muonic He Atom and a Preliminary Study of the $^4\text{He}\mu + \text{H}_2$ Reaction

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Abstract

The muonic atom $^4\text{He}\mu$ has the composition $\alpha^+\mu^- e^-$, and is formed by stopping negative muons in He doped with a small amount of NH$_3$ (or Xe). It may be regarded as a unique heavy H-atom isotope with a mass of 4.1 amu. As such, the study of its chemical reaction rates and comparison with those of the well-known light Mu atom (0.113 amu) allows unprecedented tests of kinetic isotope effects over a range of 37 in mass. As a first example, and one which is of most fundamental interest, we have begun kinetics studies of the $^4\text{He}\mu + \text{H}_2 \rightarrow ^4\text{He}\mu\text{H} + \text{H}$ reaction in the gas phase.

The first measurements, at 295 K, give a rate constant of $k_{^4\text{He}\mu} = 4.1 \pm 0.7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$. In comparison, variational transition state calculations give a value of $2.46 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$, somewhat below the measurement, despite the large error bar, raising the possibility that the calculations, on an essentially exact potential energy surface, have underestimated the amount of quantum tunneling involved, even for this heavy H-atom isotope.

Key words:
He$\mu$ atom, heavy H-atom, hydrogen, reaction rate, kinetic isotope effects, Variational TST

1. Introduction and Motivation

The study of kinetic isotope effects and their impact on reaction rate theory dates back to times not long after the discovery of deuterium by Harold Urey in 1932. Though the H and D atoms differ by only a factor of two in mass, comparing reaction rates on the isotopomers of the H$_3$ potential energy surface (PES) has demonstrated through many years just how important the interface between theory and experiment is. This point was recently brought into focus for the $\text{H} + \text{D}_2$ and $\text{D} + \text{H}_2$ reactions, where calculated rates on the “CCI” surface, including corrections for non-Born–Oppenheimer (BO) effects at the transition state (TS), showed virtually exact agreement between theory and experiment over eight orders of magnitude, prompting the comment that the H$_3$ reaction system was a “solved problem” [1].

Detailed experiments in the gas phase of the lightest H-atom isotope, muonium (0.113 amu) were initiated by the TRIUMF group in the mid 70’s, culminating with the study of the $\text{Mu} + \text{H}_2 \rightarrow \text{MuH} + \text{H}$ reaction [2], the Arrhenius plot for which is shown in Fig. 1, along with the reaction rate theory predictions of the day and a recent, highly accurate, 3D quantum calculation using the CCI surface [1].

There was intense interest 2–3 decades ago in producing polarized muonic He [3–6], for accurate mea-

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Fig. 1. Arrhenius plot for the $\mu + H_2$ and $\mu + D_2$ reactions [2], showing the level of agreement obtained with the 1985 3D quantum calculations of Schatz on the ‘LSTH’ surface and the 1984 variational transition state theory (VTST) calculations of Garrett and Trulhar, both cited in Ref. [2], along with more recent 3D quantum calculations of Mielke et al. on the CCI surface [private communication]. The agreement between experiment and the latter calculations is exemplary. Note how the $\mu + H_2$ reaction is much slower than $D + H_2$ (upper line, from Ref. [1]), a consequence of the huge zero-point-energy shift at the TS due to the $\mu$–H bond being formed.

Measurements of both its Lamb shift [4] and hyperfine coupling constant [5,6] The $^4He\mu$ atom also represents the heaviest H-atom isotope (4.1166 amu) and thereby provides unprecedented opportunities to probe quantum mass effects in reaction rates over a factor of 37 in mass, by comparing with those of Mu. This is the prime motivation of the present research and in particular the first-ever study of the $^4He\mu + H_2 \rightarrow ^4He\mu H + H$ (1) reaction rate, which provides an important new test of reaction rate theory at the heaviest end of the mass scale for the $H_3$ reaction family.

2. Experimental Target and Conditions

The gas target for these experiments is a thick-walled 316-stainless-steel cylinder about 25 cm in length with a Ti front flange and window 2.5 cm in diameter and 3 mm thick. The present experiments were carried out at room temperature with total pressures up to 500 bar, in order to provide a sufficient stopping density for backward $\mu^-$ beams ($\sim 70$ MeV/c) on M9B at TRIUMF, and to ensure that He is the majority constituent, even at high $H_2$ densities: The $H_2$ partial pressure varied in the range $\sim 20$ bar to 120 bar. A small amount of dopant gas, $\sim 1\%$ NH$_3$ in these experiments, was added to the He in order to produce the neutral muonic He atom (see below).

This target was placed in the center of the Omni’ spectrometer on the M9B beam line. Two collimators of $\sim 20$ mm diameter were positioned just ahead of the target window. A transverse field (TF) in the range 6.5 to 100 G was provided by vertical Helmholtz coils, and decay electrons were detected by two (left/right) pairs of counters in the plane of precession. Incident gated $\mu^-$ intensity was about 40 k/s with about 1500 total good events per second.

There is a large background with the cyclotron’s pulse frequency plus harmonics, likely originating from $\mu^-$ capture in the collimators giving a plethora of cascade X-rays to trigger the electron counters. This background is removed from the data by subtracting the bins from $t < 0$, offset by multiples of the beam-pulse interval (43.3 ns).

The measured $\mu^-$ asymmetry is very low in muonic He, on the order of 0.01, as opposed to 0.10 for Mu precession, making for typical run periods of 36 hours or more. This in turn impacts on the level of systematic error in these experiments.

The temperature was monitored throughout the experiment, but not actually controlled. Nevertheless, the variation was less than 0.3°C around 21.9°C.

3. Formation of $He\mu$ and its $\mu$SR Observation

Negative muons are captured into high-$l$ atomic orbits at kinetic energies of $\sim 100$ keV [7,8], (roughly where the charge exchange process begins for Mu formation from $\mu^+$ [9]). They then cascade down to the muonic 1s state in a time of $\sim 0.1$ ns for He [3–5]. The accompanying Auger processes eject both atomic electrons, leaving the positive $\alpha\mu = (^4He\mu)^+$ ion, which can be neutralized in a charge-exchange (CE) collision with dopant ‘X’

$$(^4He\mu)^+ + X \rightarrow ^4He\mu + X^+$$

forming the neutral $^4He\mu$ atom, in analogy with Mu formation [9]. Since this CE process is believed to proceed at thermal energies (unlike Mu formation)
it is important to choose a dopant with an ionization potential (IP) less than that of the neutral atom, which for Heμ is essentially the same as other hydrogen isotopes, 13.6 eV. In all previous studies to date, Xe (IP = 12.1 eV) has been used as a dopant but only very weak μ−SR signals at low polarization, ∼2%, were observed. The reasons for this are still not understood.

Typically, and well-established, in the case of $I = 0$ nuclei (like $^4$He) the residual polarization of the $\mu^−$ in the 1s orbital of the muonic ion is $\sim 1/6$ [7,8]; this is then reduced by a factor of two upon formation of the neutral atom by CE, leading to expectations of ∼0.08 for the $\mu^−$SR precession signal of the Heμ atom, but this is much higher than observed. It has long been suspected that the unusually low polarization seen in neutral muonic helium was partly due to the ubiquitous use of Xe as a dopant, since there would be direct competition for $\mu^−$ capture on the Xe, even present in trace amounts (∼1–2%), due to its much higher charge ($Z = 54$), a consequence of the “Fermi-Teller Z law” [8].

This motivated our choice of NH$_3$ as a dopant, since it has both a low IP (10.2 eV) and low-Z constituents. However, the results, though giving a somewhat enhanced amplitude and certainly clearer signals than those reported earlier [3] for the neutral atom, were still disappointingly small. This can be seen in Fig. 2. (Though the fields are slightly different, it is noteworthy that the gyromagnetic ratio for muonic He is slightly larger than for the Mu atom.)

It was also of interest to measure the hyperfine splitting at higher fields and also at higher pressures than had been determined previously up to 18 bar with great precision in resonance experiments [6,10]. However, our measurements at various fields and pressures are much less precise; all combined, their average hyperfine coupling is $\nu_0(\text{Heμ}) = 4465 \pm 9$ MHz. This equals the values at low pressures, but extrapolating the low-pressure trend to 300 bar predicts a value (4468 MHz) that is also well within the error bar of our rough measurement. Nevertheless, this result is the first observation of the hyperfine splitting in muonic He by $\mu^−$SR.

4. Reaction Rate Results

The real focus of the experiment is the measurement of the reaction rate of neutral Heμ, fitting the time-histogram data to

$$N(t) = N_{\text{const}} + N_{\text{Heμ}} e^{t/\tau_{\text{Heμ}}} \left[ 1 + A_{\text{Heμ}} e^{-\lambda t} \cos(\omega_{\text{Heμ}} t + \phi_{\text{Heμ}}) \right] + \sum_i N_i e^{t/\tau_i} \left[ 1 + A_i \cos(\omega_D t + \phi_D) \right]$$

(3)

where the principal quantities of interest in the experiments are the neutral atom asymmetry, $A_{\text{Heμ}}$ and the relaxation rate, $\lambda$, due to the Heμ + H$_2$ reaction. The second term in Eq. (3) involves a sum over different possible diamagnetic environments for $\mu^−$ capture and decay, each with a different lifetime due to nuclear capture [8,11]. Simple pseudo first-order kinetics relates the relaxation rate to the rate constant $k_{\text{Heμ}}$ by

$$\lambda = \lambda_b + k_{\text{Heμ}}[\text{H}_2]$$

(4)

where $\lambda_b$ is a background relaxation rate due to magnetic field inhomogeneity or impurities in the NH$_3$ or He gas.

It can be noted that the (Heμ) signal amplitudes were reduced by at least a factor of two when hydrogen was introduced. This is due to a competitive capture of $\mu^−$ on H where the (Hμ) atom is eventually formed after CE with NH$_3$, and the muonic H-atom is then rapidly depolarized by hyperfine mixing.

The principal result of this experiment is shown in Fig. 3, a plot of the measured relaxation rate $\lambda$ vs.
the淮number density calculated from the \( \text{H}_2 \) pressures. The slope of the fitted line gives the bimolecular rate constant of interest, \( k_{\text{HeHe}} = 4.2 \pm 0.7 \times 10^{-16} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Also shown is the predicted rate constant from a VTST calculation on the CCI surface, discussed below.

**5. Discussion and Comparison with Theory**

The present result is the first-ever measurement of a chemical reaction rate for muonic He. This ‘heavy hydrogen’ rate constant is four orders of magnitude higher than its light Mu counterpart, extrapolating from [2], showing the sensitivity of \( \mu \)SR studies to mass effects in chemical reaction dynamics.

The rate constant was calculated using VTST on the CCI PES [1]. The ground-state vibrational energy levels were computed semiclassically from the CCI potential (using WKB) with all higher energy levels computed using a Morse approximation to the vibrational potential. Remaining uncertainties arise from the anharmonicity of these bound modes, from tunneling approximation, and from the TST method.

In the case of early-barrier reactions, typically exoergic, vibrational ZPE corrections are dominated by the reactant, and hence it is the mass of the incident atom that largely determines quantum mass effects on the reaction dynamics [12]. For late-barrier endoergic reactions, vibrational ZPE shifts at the TS are more like the product molecule. The progression of isotopes from Mu to HeHe takes the H + H\(_2\) reaction from the former to the latter. In the case of Mu + H\(_2\) [12], the shift of the vibrationally adiabatic (VA) barrier makes a huge difference, increasing the activation energy by 4.5 kcal/mol (Fig. 1 [2]).

This is also important for the \( ^4\text{He}^\mu + \text{H}_2 \) reaction, which is slightly exoergic, positioning the VA barrier just slightly ‘early’, and lower than for \( D + \text{H}_2 \) due to the reduced ZPE contribution at the TS (\( x = m^{-1/2} \)). This simple argument would seem to be borne out by the experimental rate constant, which is indeed greater than that for \( D + \text{H}_2 \) at 295 K, by a factor of 1.5, but not by the theoretical calculation of \( 2.46 \times 10^{-16} \) cm\(^3\) s\(^{-1}\), which is somewhat smaller than the \( D + \text{H}_2 \) result, where tunneling would be expected to play a larger role. The fact that the experimental HeHe + \( \text{H}_2 \) reaction rate is also above the theory is interesting, and suggests in turn that there may be more of a tunneling contribution here, even for this heavy H-atom, than might otherwise have been expected. At the same time, it is important to confirm the result with better error bars.

In addition to obtaining more data points at 295 K, in order to refine the comparison between theory and experiment, the next phase of this work is to measure the \( T \)-dependence and hence activation energy of the HeHe + \( \text{H}_2 \) reaction rate.

**6. Dedication**

This paper is dedicated to the memory of Masayoshi Senba, our long-time colleague who made seminal contributions to the field and who passed away last year at far too early an age. The subject of this paper was first raised in discussions with Masa over twenty years ago, so certainly his spirit, at the very least, is present here.

**References**