Muons in Chemistry: Remarkable H Atom Isotopic Mass Effects

Background Perspective

The study of chemical reaction rates or "chemical kinetics" is fundamental to the study of chemistry itself and is intimately connected as well to life's biochemical and biological processes. Most chemical reactions proceed by a complex mechanism that involves a series of elementary steps and it is often the role of chemical kinetics studies to identify these steps, with one typically expected to be rate determining.

Key to kinetics studies is the utilization of isotopes, which has given rise to the term "kinetic isotope effects" (KIEs). The textbook definition of an 'isotope' is an element with the same nuclear charge but differing numbers of neutrons in its nucleus and hence differing nuclear masses. The nature of the chemical interactions of isotopes is expected to be the same since these are determined by the outer electrons, far removed from the nucleus. That is not to say, however, that chemical reaction rates are insensitive to changes in isotopic mass; quite the contrary, as countless studies of isotopic labeling in reaction kinetics and equilibrium can attest to. The most sensitive effects of this nature are found at the lightest end of the atomic mass scale, for the H atom. A dramatic example can be found in life processes: water is essential to life whereas "heavy water", D_2O, is toxic.

Deuterium was discovered in 1932 by Harold Urey and since the D atom has an extra neutron it has twice the mass of the H atom. Not long after, tritium was discovered (Rutherford, 1934), which has two neutrons and hence three times the H atom mass. However, tritium is radioactive and is dangerous to human health, and hence has seen little practical use in the study of (thermal) chemical reaction rates. The question could then be asked, "how to extend the H atom atomic mass scale beyond even this factor of three?" The answer is provided by muon science.

Muons and the μSR Technique

Muons are elementary particles, like electrons, and also come then in two charge states, μ^+ and μ^-. They are naturally occurring on earth as components of high-energy cosmic rays, which provided the basis for their discovery in 1947. They are produced artificially at nuclear accelerators, like the TRIUMF cyclotron (not much more than a stone's throw from UBC Chemistry), and are unstable particles with a mean life of 2.2 μs. From a chemistry perspective their interest is two-fold: muons are produced 100% spin-polarized (contrast with $\sim 10^{-3}$ % in NMR near ambient temperature), which makes them easy to detect, even at concentrations equivalent to $\sim 10^{-15}$ molar; and the intrinsic muon mass, which is only about 1/9th the proton mass. This report is concerned with the second point, the impact of the muon mass on the chemical sciences.

The 2.2 μs lifetime of the muon is due to a weak interaction decay process in which either a positron (e^+, from μ^+ decay) or an electron (from μ^-) and two neutrinos are emitted. The decay e^+/e^- is emitted *preferentially* along the muon spin, a consequence of parity violation in the nuclear weak interaction (as is the 100% spin polarization of the muon, produced from pion decay). This munificence of Nature also provides the basis of the μSR technique. Since more e^+/e^- are emitted in a preferred direction with respect to the muon spin, this difference in intensity is easily detected, providing a measurement of the interaction of the muon spin with its environment (somewhat akin to measurements of T_1 or T_2 spin relaxation rates

in magnetic resonance), and in particular here of chemical reactivity. In this regard, there are two highly important muon 'isotopes' of the H atom, "muonium" and "muonic helium".

The muonium atom is perhaps the perfect isotopic analogue of H, being composed of a positive muon and an electron (Mu= μ^+e^-), but with a mass of 0.114 amu, endowing it with the character as the *lightest* isotope of the H atom. (Though lacking any neutrons in its "nucleus", the muon mass is still 200 × the electron mass, and hence the mean radius and ionization potential of Mu, which is what ultimately determines its chemistry, are virtually the same as for H.) The first accurate study of Mu chemical reactivity was of the Mu + Br_2 reaction in the gas phase, carried out by a UBC Chemistry group at UC Berkeley in 1973, prior to the commissioning of the first muon beams at TRIUMF some 3 years later.

Much more recently, the chemical reactivity of the *heaviest* isotope of H, muonic He, was initiated at TRIUMF,[1,2] formed in this case by the capture of *negative* muons by ^{4}He, effectively emitting an electron in the process, leaving the neutral atom ($[^4$He$\mu^-]^+e^-$, denoted Heμ or simply ^{4}H), but now with a mass of 4.11 amu. The essential point here is that the μ^-, being 200 times heavier than the electron, orbits 200× closer to the ^{4}He nucleus, effectively fully compensating ("screening") one proton charge. This has been schematically illustrated in the New Scientist (2011) as shown below. (Muonium is just like 'Ordinary Hydrogen' in this picture.) It has also been described in a U-tube video (www.youtube.com/watch?v=7hdVjb2gRgQ).
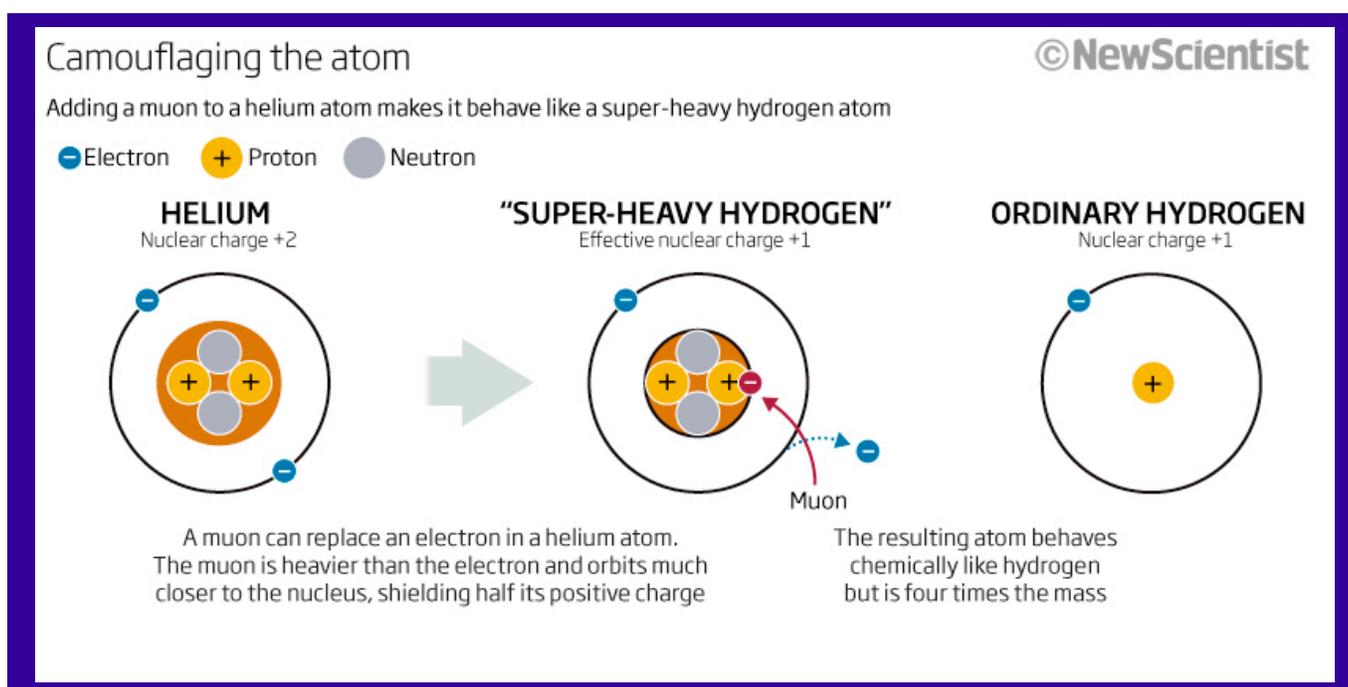

Figure 1: Illustrating the muonic He atom: "Super-Heavy Hydrogen"

The ABCs of Chemical Reaction Rates

Many studies of elementary reaction rates involve atom-diatomic molecule reactions, which can generally be denoted as A + BC → [A–B–C]‡ → AB + C, where [A–B–C]‡ is the "transition state" (TS) between reactants and products. Initially, when 'A' is far from 'BC' ($R_1 = R_{A-BC} \to -\infty$), the interaction potential is just the "Morse potential" of the BC reactant; with a similar result for the AB product after the reaction, where $R_2 = R_{C-BA} \to +\infty$. The "potential energy surface" (PES), $V(R_1, R_2, \gamma)$, is a function of both of these distances and the angle 'γ' between them, though often the minimum is determined by a collinear approach ($\gamma = 0$). The reaction path along the PES from reactants to products for such a case, traversing the [A–B–C]‡ TS in between, is schematically illustrated below.
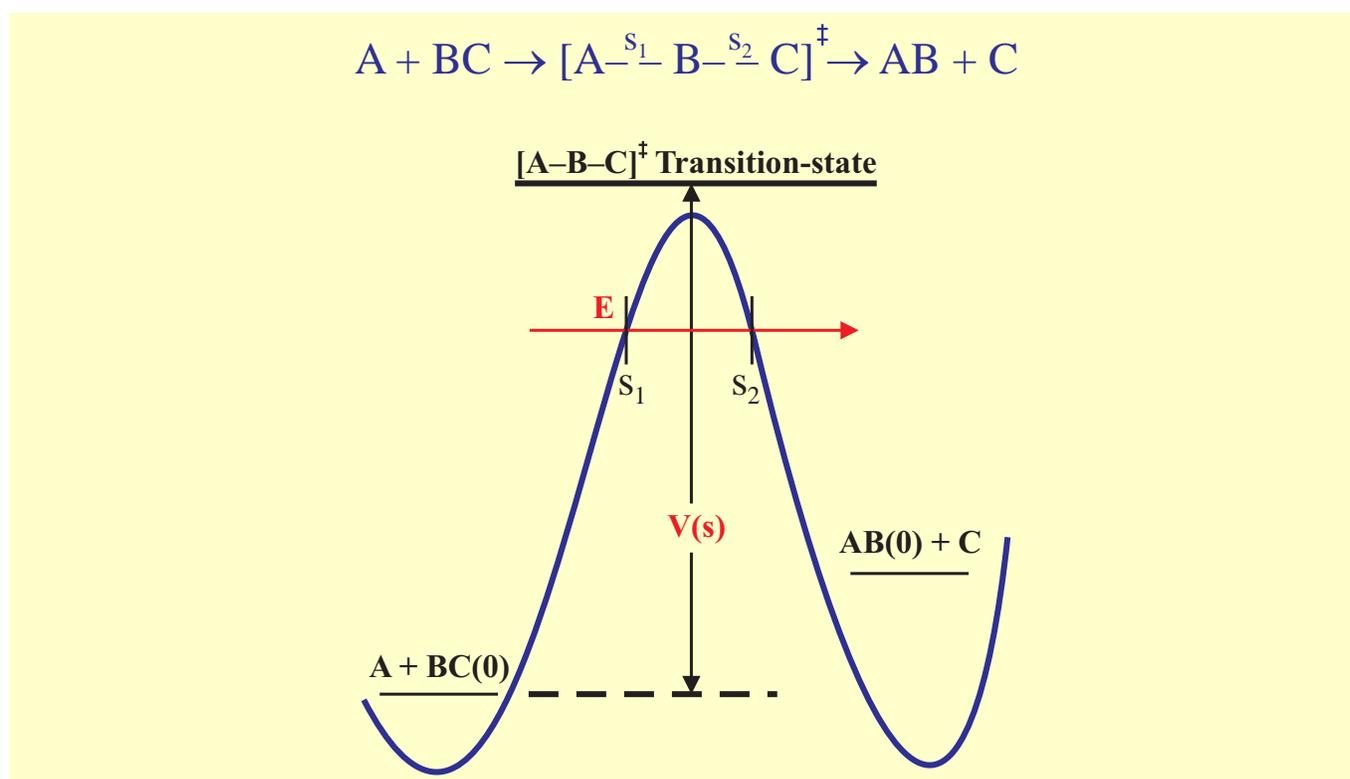

Figure 2: Schematic reaction profile for the A + BC → AB + C reaction

The minima indicated on the blue curve for the reaction path in this figure represent the Morse potentials noted above. The electronic potential energy at the barrier, $V(s)$, depends on the distance 's' = R_2 - R_1 and, for a symmetric reaction like H + H_2 is at a maximum when s =0. The horizontal black lines and labels BC(0) and AB(0) represent the "zero-point energy" (ZPE) of the diatomic reactant and product, respectively. This is a manifestation of the "Uncertainty Principle" in Quantum Mechanics, which states that position and momentum cannot be simultaneously determined with precision; thus even at 0 Kelvin, there must be kinetic energy, called "zero-point energy" (ZPE). This is also true at the TS and gives rise to the definition of $V(s)$ that is indicated in the diagram.

The most important point of note here is that ZPE is $\propto 1/\sqrt{mass}$, meaning that the Mu atom, nine-times lighter than H, can have a huge ZPE effect. For a broad class of chemical reactions this raises the height of the TS barrier, $V(s)$, such that the rate constant k_{Mu} can be $<<$ than k_H, particularly for *endo*ergic reactions ($\Delta H_{Rxn} > 0$), the case depicted by the ZPE levels shown in Fig. 2.

The total energy of the system in the entrance (A + BC) channel, 'E' = $E_{Kin} + V(s)$, is the sum of the kinetic and potential energies and is a conserved quantity for most chemical reactions (at a fixed temperature). Classically, when $E = V(s)$, E_{Kin} must equal zero, at the "classical turning points" s_1 and s_2 shown by the red line in Fig. 2. Reaction rate flux approaching from the left along E would then be reflected back at the point s_1, much like a ball thrown at a brick wall.

However, in QM that is no longer true, again because of the Uncertainty Principle. There is a finite probability that this reaction flux will actually "tunnel" through the barrier, appearing on the other side with exactly the same energy E, albeit with reduced amplitude. Mathematically, the probability of this is $\propto e^{-2\sqrt{mass} \times R}$, where $R = s_2 - s_1$ and is the width of the barrier at energy E. Since the probability of QM tunneling depends exponentially on the (negative) square root of the mass, it will be much more facile for Mu than for H or for any other heavier atoms. This means that k_{Mu} can be $>> k_H$, seen primarily at low temperatures, where classical Arrhenius activation energies ($k \sim e^{-E_a/RT}$) dictate slow rates.

Reactivity of Mu and Heμ with H$_2$: Unique Tests of Quantum Rate Theory

A large number of Mu chemical reaction rates have now been measured, exploiting the unusually light (0.114 amu) mass of the Mu atom, in comparisons with theory. This has now been expanded to include similar comparisons with the reaction rates of the Heμ atom, providing for the possibility of varying the isotopic H atom mass over a *remarkable* factor of 36. In the comparisons with theory that this new development has facilitated, the two quantum mass effects introduced above, ZPE shifts and quantum tunneling, play somewhat competing but often crucially important roles in determining the magnitude of measured rate constants.

The most definitive comparisons are for the reaction rates of Mu and Heμ with H$_2$, which, still today, after an 80-year Odyssey following the Heitler-London-based PES for H$_3$ ($\sim$ 1935), is still the only one known to a level of accuracy high enough to allow definitive comparisons between experiment and rigorous theory. Comparisons of this nature are important for two reasons: first they reaffirm the continuing importance of the synergism between theory and experiment, and second they provide an important "benchmark" for further developments of both experiment and of theory in more complex reaction systems. A realistic sketch of the PE profile of the reaction path for the Mu + H$_2$ system showing the ground (v=0) and first excited (v=1) vibrational states of both the H$_2$ reactant and the MuH product is given below.
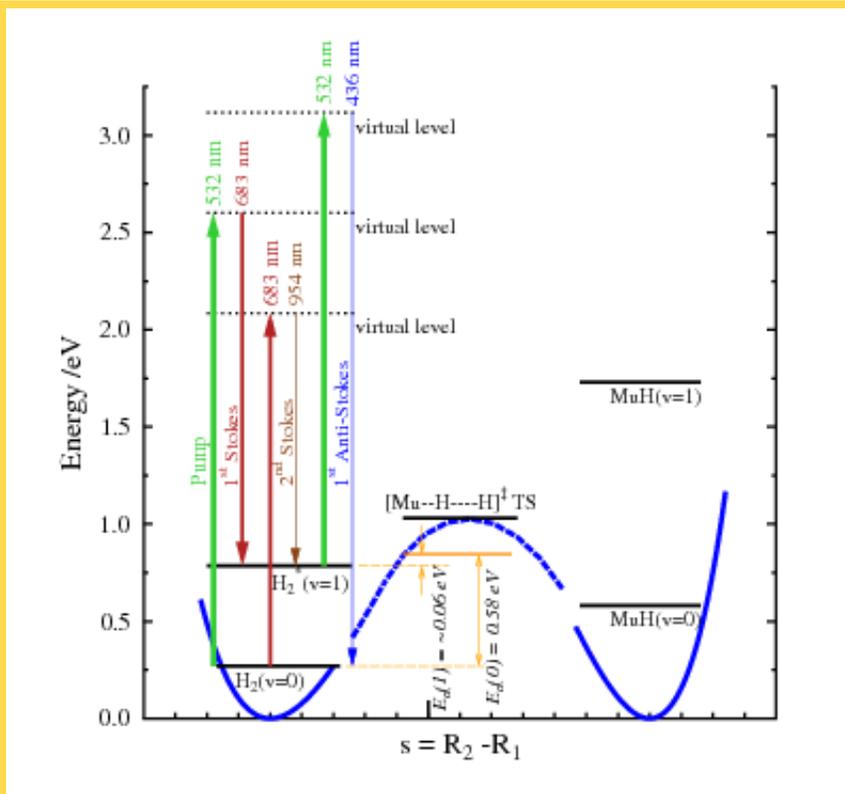
Figure 3: Sketch of the H_3 PE profile showing accurate energies for the Mu + H_2 reaction

The thick broken blue line shows the PE profile through the TS for the Mu +H_2(v=0) reaction, which includes the ZPEs along this reaction path, giving a barrier height of 0.96 eV. The larger tick mark on the abscissa is intended to locate s = 0 for the symmetric H + H_2 reaction, showing that the position of the barrier for Mu +H_2 is "late" due to the endoergicity of the reaction. (The vibrational states of MuH are much higher than those of H_2 due to the inverse mass dependence of ZPE.) In the *absence* of tunneling the experimental activation energy, E_a(T), is often expected to be close to the difference shown by the potential V(s) in the schematic reaction profile of Fig. 2, namely 0.96 - 0.25 = 0.71 eV here for the ("vibrationally adiabatic") v = 0 reaction; the actual measured Arrhenius value is 0.58 eV,[3] shown by the thick horizontal orange line in Fig. 3.

Also shown are several laser-induced photon transitions, which could have been relevant in the first measurement ever of Mu reactivity from a *state-selected* reactant, from the first vibrational state of H_2, the Mu + H_2(v=1) $\rightarrow$ MuH + H reaction.[4,5] In this study a virtual electronic state was pumped by the 2nd harmonic of a pulsed Nd:YAG laser at 532 nm (upward thick green arrow from v=0 in the figure), which emitted a first Stokes line at 683 nm (downward thick red arrow), thereby populating the H_2(v=1) state, as determined by the measured intensity of this line. (The other transitions shown in fact played only minor roles.) The experiment was carried out in a single reaction/laser cell in which the laser profile was perpendicular to the stopping distribution of Mu atoms in H_2 at 50 bar pressure, 300 K. It required a pulsed muon beam at the Rutherford Appleton Laboratory in England, near Oxford.

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The rate constant for the Mu + H_2(v=1) reaction, k_{Mu}(1), was measured at 300 K and is compared in the Arrhenius plot of Fig. 4 with both rigorous quantum theory (blue data point and theory line) and with the experimental and quantum theory results for the thermal (99.9% in the ZPE, v=0 state) Mu + H_2(v=0) (green data points and line) and Heμ + H_2(v=0) (red data points and line). The curvature seen in the blue line is a manifestation of Mu quantum tunneling. Note that, despite its heavier mass, the Heμ reaction is much faster than Mu +H_2, due to the pronounced ZPE shift at the [Mu-H-H]‡ TS, giving a much higher barrier (V(s), Fig. 2), as seen in Fig. 3. Tunneling also plays a significant role in Mu + H_2(0) but only at much lower temperatures.[6]
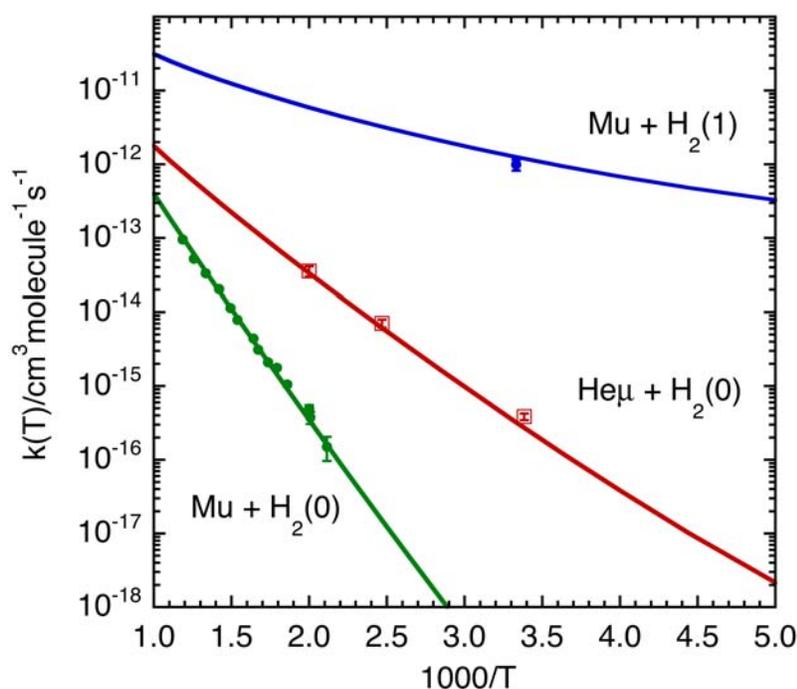

Figure 4: Comparisons between muon experiments and rigorous quantum rate theory results

The level of agreement between rigorous quantum theory and experiment, over a factor of 36 in atomic mass (green and red lines) and 7 orders of magnitude in rate (green and blue lines) is, in a word, *remarkable*! The calculations are based on the 'CCI/BH' (Complete Configuration Interaction/Born Huang) surface of Mielke, Truhlar et al., with corrections for deviations from the Born Oppenheimer approximation, and which is thought to be globally accurate to better than 1%.[2,6] The slope of the blue line in the region of the 300 K point shown is entirely consistent with that expected from the energy difference between the experimental activation energy E_a(0) for the H_2(v=0) reaction and the H_2(v=1) excitation energy of 0.52 eV in Fig. 3, giving E_a(1) $\sim$0.06 eV, shown by the thin horizontal orange line in that figure.

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It can now be stated convincingly that reaction dynamics in the H_3 system is a "solved problem" and there are very few cases in molecular quantum mechanics where that statement can be made. Moreover, in being able to arrive at this assessment, it is important to note that muon science has arguably provided the *most crucial* input, apt testimony to the ongoing importance of the synergism between theory and experiment. This claim will be put further to the test though by coming measurements of the temperature dependence of the Mu + H_2(v=1) reaction rate, to be compared with the theory (blue line) in Fig. 4.

"Vibrational Bonding" in BrMuBr: a new type of chemical bond

The existence of bond vibrations and ro-vibrational states, eigenstates of the molecular potential, has been a corner stone of molecular spectroscopy since the first studies of the H_2 molecule dating back a century. These are all bound states in molecular potentials $V(R) < 0$ and hence with total energy 'E' = E_{Kin} + V(R) ≤ 0, unless "quasi-bound" by the centrifugal barrier for (v, J) states. In qualitative quantum chemistry calculations carried out on semi-empirical potential surfaces in the 1980s, the possibility of a new type of chemical bond was put forward, one that could actually be stabilized at the *maximum* of the potential, so at the TS or "saddle point" of the reaction and in particular for Heavy-Light-Heavy systems like I-H-I and Br-H-Br. However, despite early promise at the time for the observation of these vibrationally-bound states, from photo-detachment studies of the stable anions [I-H-I]$^-$ and [Br-H-Br]$^-$ at UC Berkeley, it transpired that the widths of the photo-electron spectra measured were far too broad to correspond to the formation of a stable state but instead were indicative of short-lived resonances.

Around this time as well a (1989) kinetics experiment was carried out at TRIUMF, which established that the activation energy for the Mu + Br_2 reaction was *negative*, in contrast to it H atom counterpart, indicative of the formation of an "intermediate complex" in the Mu reaction, possibly due to the formation of the vibrationally-bound Br-Mu-Br state that had been hypothesized in the aforementioned quantum chemistry calculations of a few years earlier. Though tantalizing, this result did not constitute evidence for the observation of vibrationally-bound states though, which remained unconfirmed then for the next two decades.

If such an intermediate complex were formed in the Mu + Br_2 kinetics study, it would have to be a "muoniated" free radical, formed by muonium addition, so the next step was to identify if that was the case. Though a long time coming, in a muon experiment of a different nature, carried out at the Rutherford Appleton Laboratory in 2012, it was established that such a radical does indeed form,[8] but the title of the paper "New results for the formation of a muoniated radical in the Mu + Br_2 system: a van der Waals complex or evidence for vibrational bonding in Br-Mu-Br?" made clear that the jury was still out on whether vibrationally-bound Br-Mu-Br or a conventional van der Waals Mu$\cdots Br_2$ radical was formed and stabilized at the transition state.

This new result provided important motivation for rigorous quantum chemistry calculations that followed soon after, carried out in a collaboration with the quantum chemistry group at Saitama University in Japan,[9] with the title "Fundamental Change in the Nature of Chemical Bonding by Isotopic Substitution", which established that Br-Mu-Br is indeed stabilized at the barrier of the potential in a study of the symmetric Br + LBr → [Br-L-Br] → LBr + Br reaction. Here 'L' represents the five possible light isotopes of the H atom, from its heaviest, muonic He (^{4}H), to its lightest, muonium (Mu). *Only* the Mu atom forms a stable vibrationally-bonded Br-Mu-Br radical at the TS, as may be seen from Fig. 5 below; in contrast,

all the heavier istopomers are only stabilized in van der Waals wells. In a sense, this result also provides the last piece of the puzzle raised by the early kinetics study at TRIUMF and hence an answer as well to the question posed above. It is now highly likely that vibrationally-bound Br-Mu-Br was observed in our recent (2012) muon experiment reported in Ref. 8 as well as in the earlier (1989) Mu +Br$_2$ kinetics one.[7]
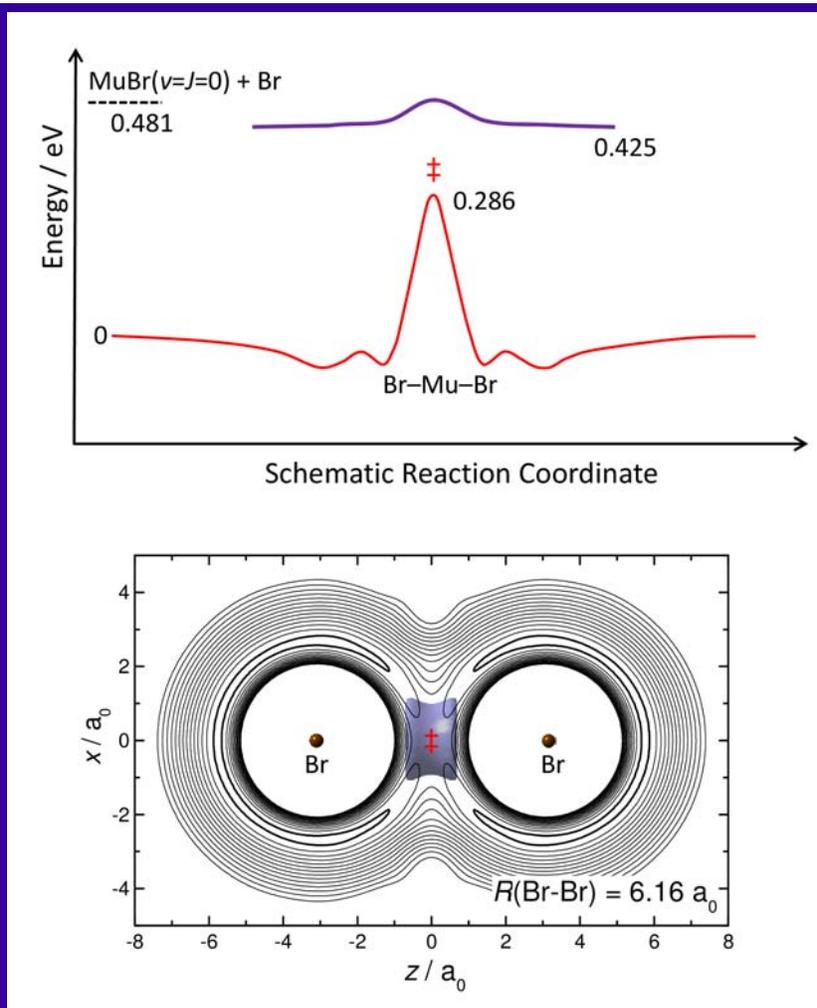

Figure 5: Energy profile and probability density distributions for BrMuBr, from Ref. 9

The two minima on the left/right of the maximum in Fig. 5 locate the binding of linear (closest to) and non-linear van der Waals complexes for the heavy istopomers of Br-L-Br. The ‡ locates the position of the saddle point at the potential maximum of 0.286 eV, where the vibrationally-bonded Br-Mu-Br state is located. The 3D probability density distribution is shown in the bottom panel, located midway between the two heavy Br atoms, also shown by the 1D density distribution (purple line) in the top panel at a total energy of 0.425 eV. Note that this is *below* the lowest (v=J=0) state of MuBr, due to the large shift in ZPE caused by the Mu atom.

That is the essential point here, arising from the very light Mu atom mass (0.114 amu), reflecting the proportionality on $1/\sqrt{mass}$ noted above. Thus, once formed, vibrationally-bonded Br-Mu-Br is "trapped" at the TS with the Mu atom oscillating back and forth between the heavy Br atoms, with a lifetime of 2.2 μs due to the decay of the muon, many orders of magnitude *longer* than that of a typical vibrational period. In contrast, the reduced ZPEs of all the heavier isotopomers renders them unstable at the barrier position; instead, these are only stabilized as conventional van der Waals molecules at potential minima on either side of the barrier. Vibrationally- bonded Br-Mu-Br is in fact a uniquely quantum mechanical result; if ZPE did not exist this bond simply could not exist! It is noteworthy that the mass dependence of vibrationally-bound states is just opposite to that of conventional vibrational bonding, i.e. it is the *lightest mass* that is the most bound.
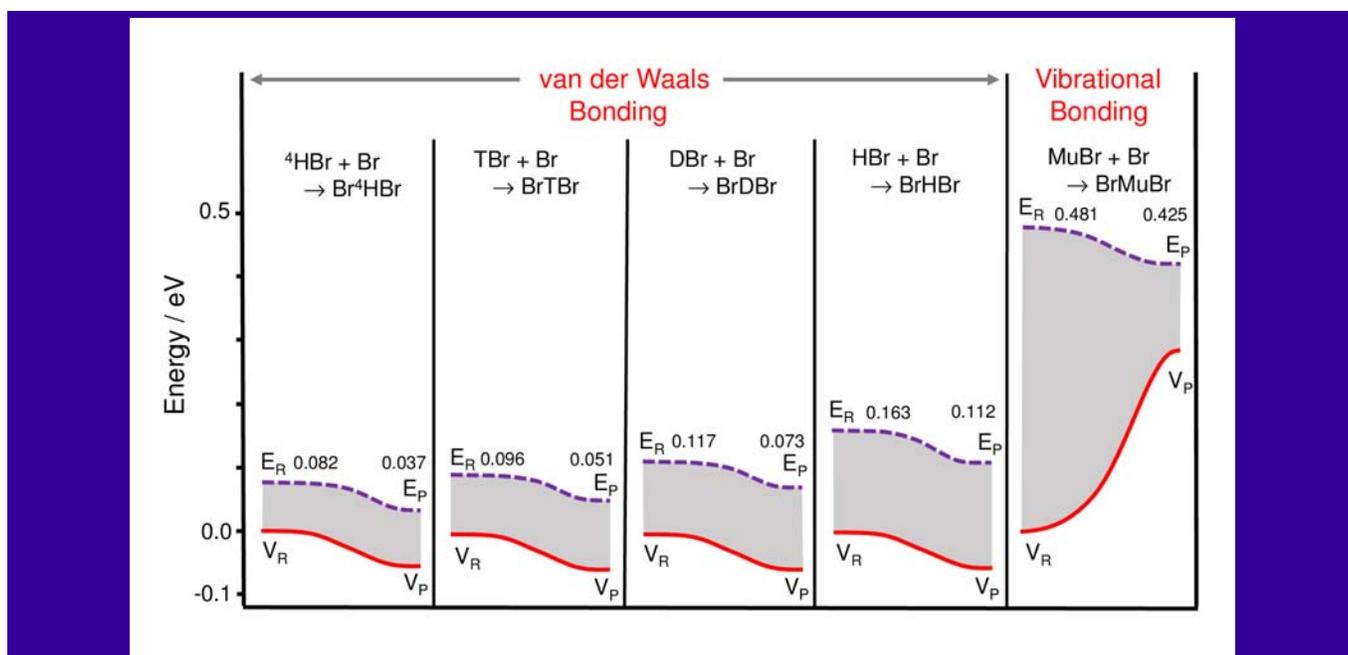

Figure 6: Energetics for the isotopomers of the 'BrLBr' system along the reaction coordinate.

A summary of the energetics of the Br-L-Br system for all its isotopomers, contrasting the conventional van der Waals bonding of the heavy istopomers from Br-^{4}H-Br to Br-H-Br (4 panels on the left) with that for Vibrational Bonding in Br-Mu-Br, formed from the lightest H atom (Mu, right panel), is shown in Fig. 6. The values for the potential energy, V_R and V_P, and the total ground state energies, E_R and E_P, for the reactants LBr + Br and Products Br-L-Br are given. Note that only Br-Mu-Br shows a dramatic *increase* in potential energy, needed to overcome the potential barrier, but which is over-compensated by a marked decrease in zero-point energy at the saddle point, due to the very light muon mass, providing a *net gain* in energy for this bound-state system that is stabilized at the *maximum* of the potential surface. This result is the very antithesis of "conventional wisdom", which holds that isotopic substitution can*not* change the fundamental nature of a chemical bond, and as such is truly a uniquely important outcome from muon sicence.

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Concluding remarks:

The muon science program at TRIUMF had its genesis in the early days of the operation of that facility in the mid-1970s and has generated several "firsts" since. In the realm of quantum mass effects in the chemical sciences and particularly in the study of reaction rates, the muon has *no* peers, providing for uniquely important tests of both quantum tunneling and zero-point energy over a heretofore *unprecedented* range of a factor of 36 in atomic mass. The recent discovery of vibrationally-bonded Br-Mu-Br is also a uniquely important quantum result on the world stage.

References

[1] "Kinetic Isotope Effects for the Reactions of Muonic Helium and Muonium with H2." D.G. Fleming, D.J. Arseneau, O.Sukhorukov, J.H. Brewer, S.L. Mielke, G.C. Schatz, B.C. Garrett, K.A. Peterson and D.G. Truhlar; *Science*, **331**, 448-450 (2011).

[2] "Kinetics of the reaction of the heaviest H-atom with H2, the ^{4}Heμ + H2 $\rightarrow$ ^{4}HeμH + H reaction: experiments, accurate quantal calculations, and variational TST, including kinetic isotope effects for a factor of 36 in isotopic mass." D.G. Fleming, D.J. Arseneau et. al., *J. Chem. Phys.*, **135**, 18430-17 (2011).

[3] "Experimental tests of reaction rate theory: Mu + H2 and Mu + D2." I.D. Reid, D.M. Garner, L.Y. Lee, M. Senba, D.J. Arseneau and D.G. Fleming; *J. Chem. Phys.* **86**, 5578-5583 (1987).

[4] "State-Selected Reaction of Muonium with Vibrationally Excited H2." P. Bakule, D.G. Fleming, O. Sukhorukov, K. Ishida, F. Pratt, T. Momose et. al., *Phys. Chem. Letts.*, **3**, 2755-2760 (2012)

[5] "An experimental study of the first accurate measurement of Mu reactivity from a state-selected reactant in the gas phase: the Mu + $H_2\{1\}$ reaction rate at 300K." P. Bakule, O. Sukhorukov, K. Ishida, F. Pratt, D.G. Fleming et. al., T. Momose, Y. Matsuda and E. Torikai; *J. Phys. B. (At. Mol. Opt. Phys.)*, **48**, 045204-22 (2015)

[6] "Zero point energy, tunneling and vibrational adiabaticity in the Mu + H2 reaction." S.L. Mielke, B.C. Garrett, D.G. Fleming and D.G. Truhlar; *Mol. Phys.*, **113**, 160-175 (2015).

[7] "Reaction kinetics of muonium with the halogens in the gas phase: Mu + X2 (F2, Cl2, Br2)". A.C. Gonzalez, I.D. Reid, D.M. Garner, D.G. Fleming et. al., *J. Chem. Phys.*, **91**, 6164-6176 (1989).

[8] "New results for the formation of a muoniated radical in the Mu + Br2 system: a van der Waals complex or evidence for vibrational bonding in Br-Mu-Br?" D.G. Fleming, S.P. Cottrell, I. McKenzie and R.M. Macrae; *Phys. Chem. Chem. Phys.*, **14**, 10953-10966 (2012).

[9] "Fundamental Change in the Nature of Chemical Bonding by Isotopic Substitution." D.G. Fleming, J. Manz, K. Sato and T. Takayanagi; *Angew. Chem. Int. Ed.*, **53**, 13706-13709 (2014).