Why Muons are Important in the Chemical Sciences: Recent Results on Gold Nanoparticles

- **Extending the H-atom mass scale**

- **A fundamental change in the nature of chemical bonding**

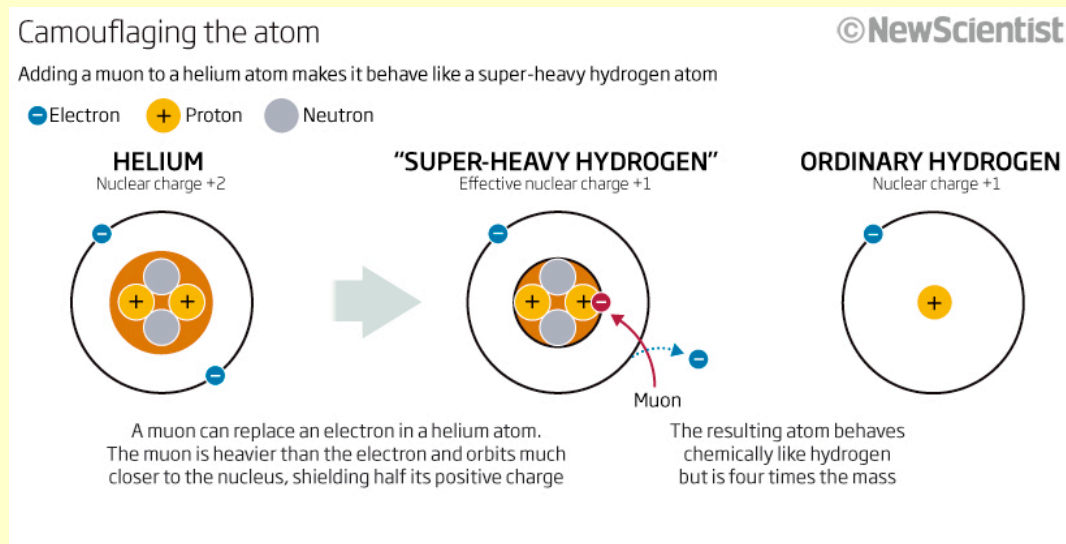- **Quantum mass effects and critical tests of reaction rate theory**

Muons Extending the H-atom Isotopic Mass Scale

Deuterium has been important since its discovery in 1932, but with a mass only twice that of H, its **impact** as a mass probe is limited . **Tritium**, 3 amu, has been important (e.g. in μ^- catalyzed fusion) but is dangerously radioactive.

It is thus only from **muon science** that we can extend the H-atom isotopic mass scale, from its **lightest isotope Muonium (Mu = μ^+e^-)**, with a mass of **0.114 amu** (the muon mass is only $\sim$ 1/9th the proton mass), to its **heaviest Muonic-He** (**Heμ = [^{4}Heμ^-]$^+e^-$**), formed by μ^- capture on He, with a mass **4.11 amu**; providing a **remarkable factor of 36** in isotopic H-atom mass.

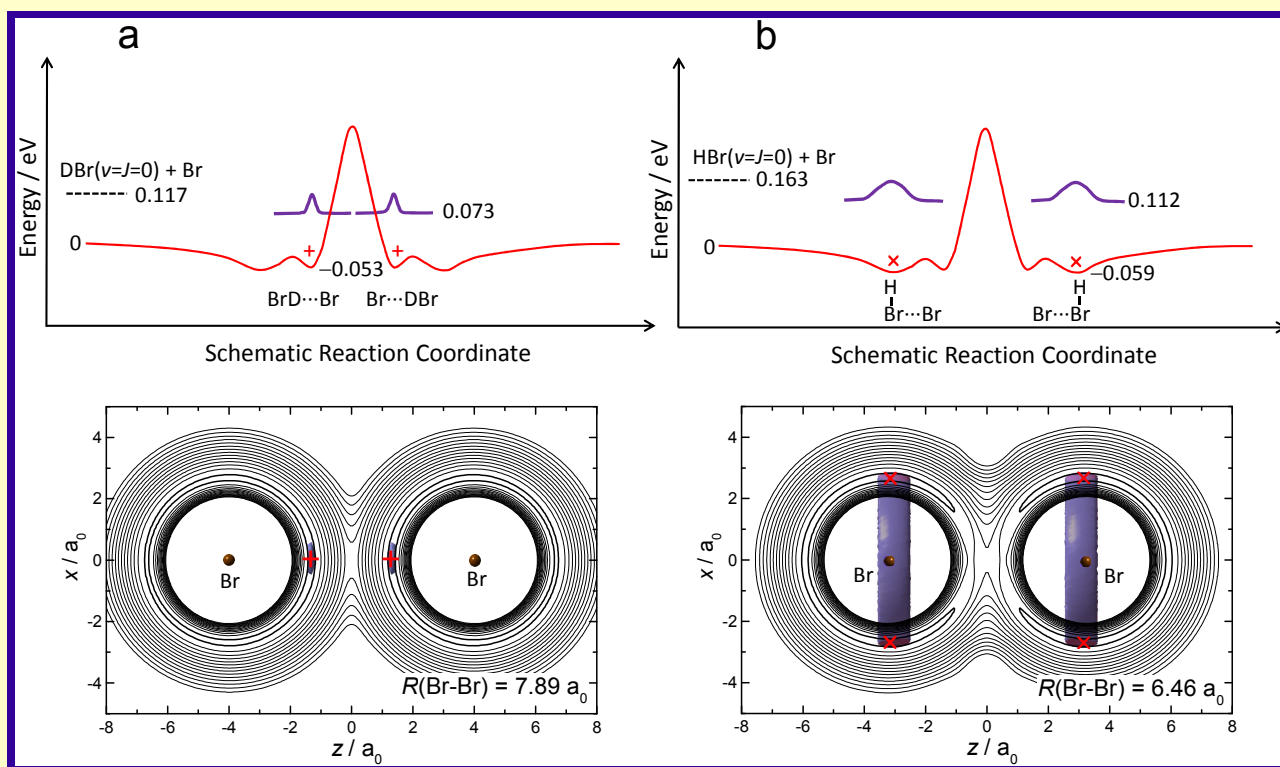| Mu(μ^+e^-)	H(p$^+e^-$)	D(np$^+e^-$)	T(nnp$^+e^-$)	Heμ([$\alpha\mu$]$^+e^-$)	
0.114	1.0	2.0	3.0	**4.11**	amu
13.54	13.60	13.60	13.61	**13.62**	eV
0.531	0.529	0.529	0.529	**0.528**	Å

- Muonium is formed by **cyclic charge exchange** during its slowing-down processes, $\mu^+ +$ 'M' $\rightarrow$ Mu + M$^+$, followed by electron loss, Mu + M $\rightarrow \mu^+$ + e$^-$ + M, a process that can be repeated many times, with the **final result** at near thermal energies being either Mu or μ^+ (as the molecular ion Mμ^+).

- Muonic He (Heμ, or ^{4}H) is formed by μ^- **capture** and in its **1s state** is **400 $\times$ closer** to the nucleus than the outer e$^-$, fully **screening** one proton charge. [Fleming and Mielke et al., Science, JCP, 2011].

Camouflaging the atom © NewScientist
Adding a muon to a helium atom makes it behave like a super-heavy hydrogen atom

● Electron   + Proton   ● Neutron

HELIUM
Nuclear charge +2

"SUPER-HEAVY HYDROGEN"
Effective nuclear charge +1

ORDINARY HYDROGEN
Nuclear charge +1

Muon

A muon can replace an electron in a helium atom. The muon is heavier than the electron and orbits much closer to the nucleus, shielding half its positive charge

The resulting atom behaves chemically like hydrogen but is four times the mass

A Fundamental Change: Vibrational Bonding

- Vibrational bound states in molecules at **potential minima** have been a cornerstone of molecular spectroscopy for decades.

- The possibility of **"Chemical Bonding Without a Potential Minimum"** was predicted long ago [J. Manz et al., CPL 1982] , but heretofore not established.

- **IF** the zero-point energy (ZPE) of the reactant in a chemical reaction is **above** the barrier $V_B^{\ddagger}$ at the saddle point , then vibrational bound states at a **potential maximum** may be stabilized. Since m_{μ}/m_p is $\sim 1/9$, ZPE ($\nu_0 \sim \sqrt{1/\mu_m}$) is **largest** for a Mu bond, giving us the best chance to form vibrational bound states at such a maximum.

- Studies of the Mu + $Br_2 \rightarrow$ MuBr + Br reaction [Fleming and McKenzie et al., *PCCP*, 2012] demonstrated that a free radical intermediate was formed, **but** a van der Waals complex, $\dot{\textbf{Mu}} \cdots \textbf{Br}_2$, **or** vibrationally-bonded $\dot{\textbf{Br}}\textbf{-Mu-Br}$?

- Can **Br-Mu-Br** in fact be bound? High-level quantum chemistry calculations [Takayanagi et. al., *Angew. Chem. Int. Ed.*, 2014] answer **Yes!**

a

Energy / eV

DBr(*v=J*=0) + Br
------- 0.117

0

0.073

−0.053

BrD···Br   Br···DBr

Schematic Reaction Coordinate

R(Br-Br) = 7.89 a_0

x / a_0

z / a_0

Br   Br

b

Energy / eV

HBr(*v=J*=0) + Br
------- 0.163

0

0.112

−0.059

H
|
Br···Br   Br···Br

Schematic Reaction Coordinate

R(Br-Br) = 6.46 a_0

x / a_0

z / a_0

Br   Br

For **all** the **heavy** isotopomers of the Br-L-Br system (H, D, T and ^{4}H), **only** vdW bonding is stable, with PE **minima** on either side of the barrier, for both linear **(a)** and bent **(b)** geometries. Note that the ZPE of DBr/HBr is **below** $V_B^{\ddagger}$ = 0.286 eV.
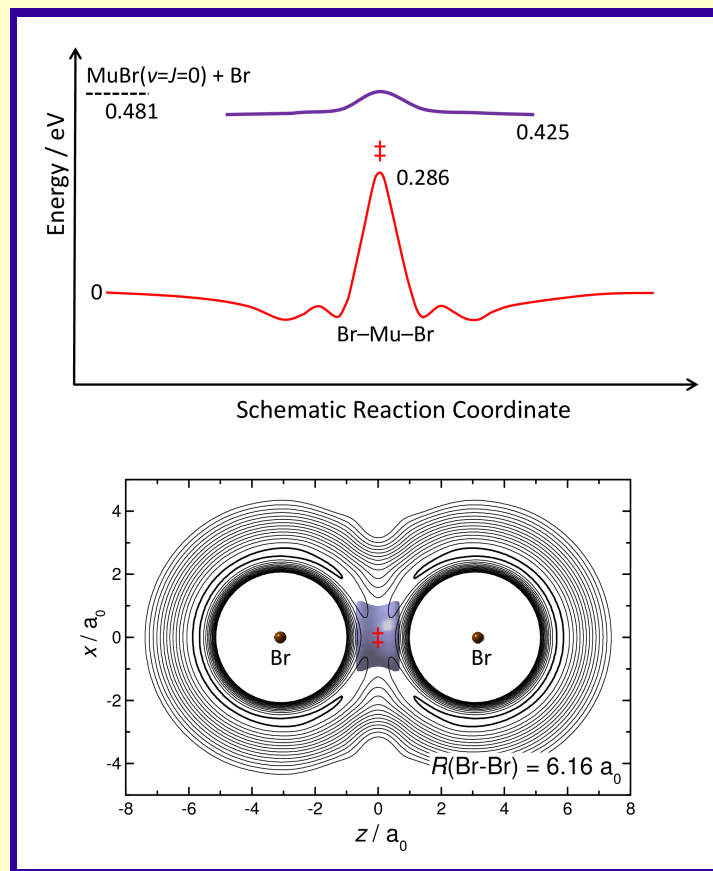
In contrast, for **Br-Mu-Br**, the **increase** in PE (+ 0.286 eV) at the barrier is offset by a larger **gain** in ZPE (-.342 eV), leading to a **vibrationally-bonded** state at the **maximum** of the PES. This is the **first** time that a change in isotopic mass has been shown to cause a **fundamental change** in the nature of chemical bonding.

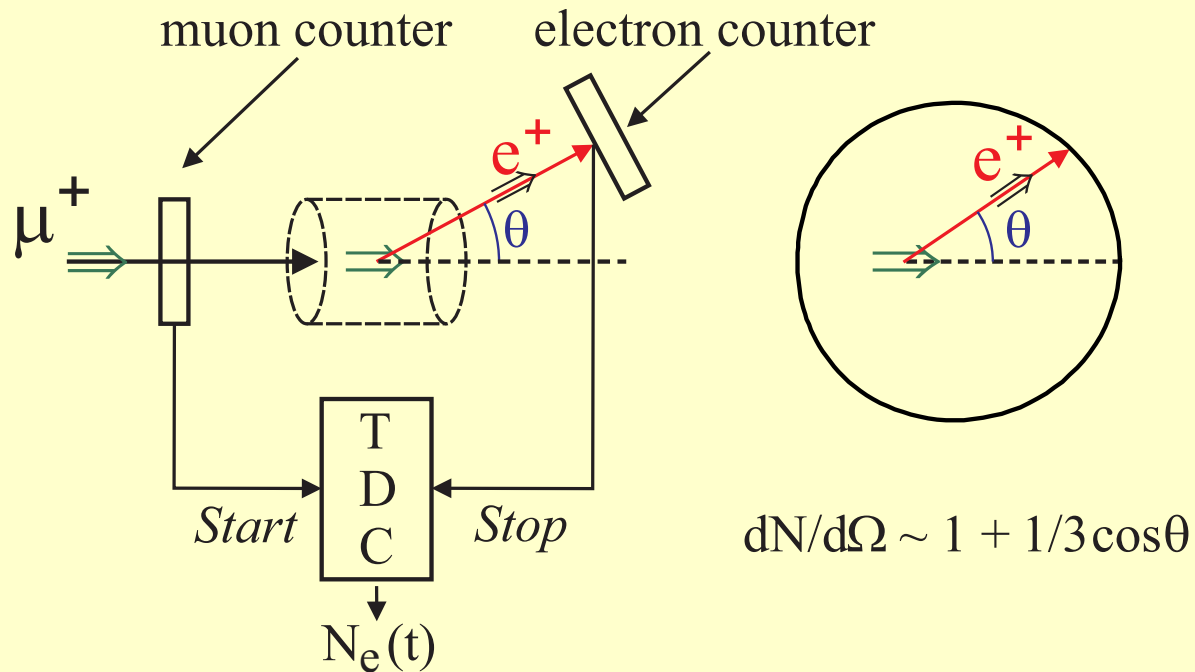# Quantum Mass Effects- Critical Tests of Reaction Rate Theory

μSR Basics:
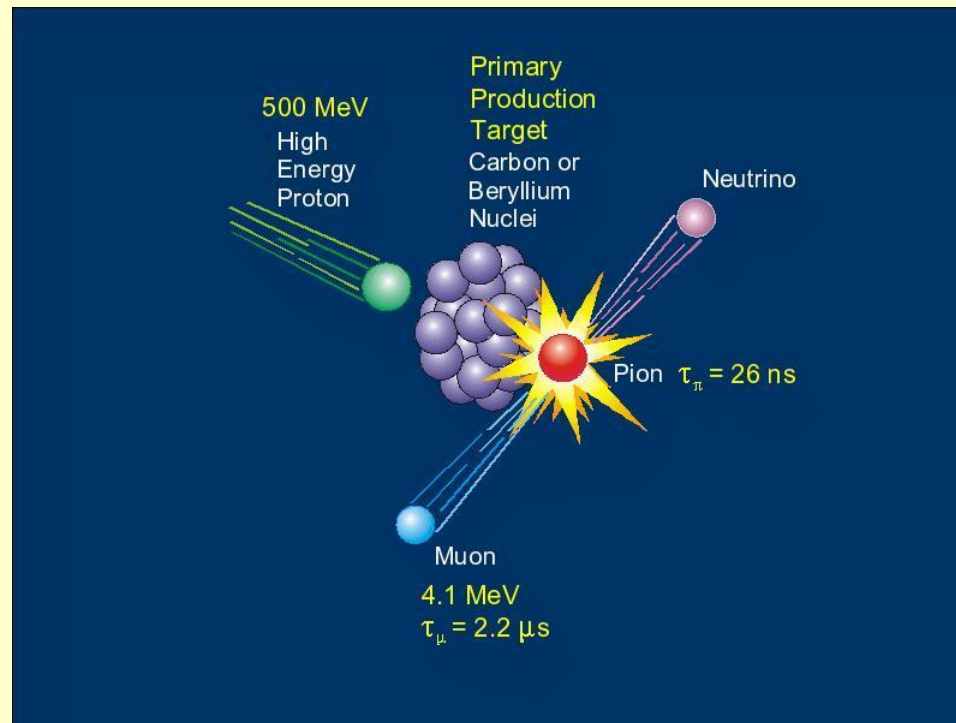
Muons (μ^+, μ^-) have spin 1/2 and, thanks to **parity violation** in the **weak interaction** [Lee and Yang, *PRL, 1957*; Wu, Ambler et al., ^{60}Co β^- decay, and Garwin, Weinrich et al., muon decay *PR, 1957*], are produced **100% spin polarized** with an **asymmetric** decay ($\mu^\pm \rightarrow e^\pm + \nu\overline{\nu}$) pattern in which the **e$^\pm$**, detected in the experiment, is emitted **preferentially** along (opposite to) the muon spin, as illustrated below.
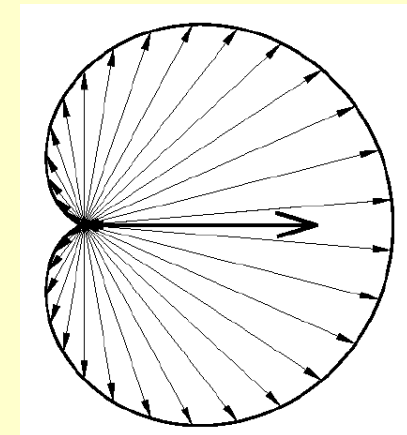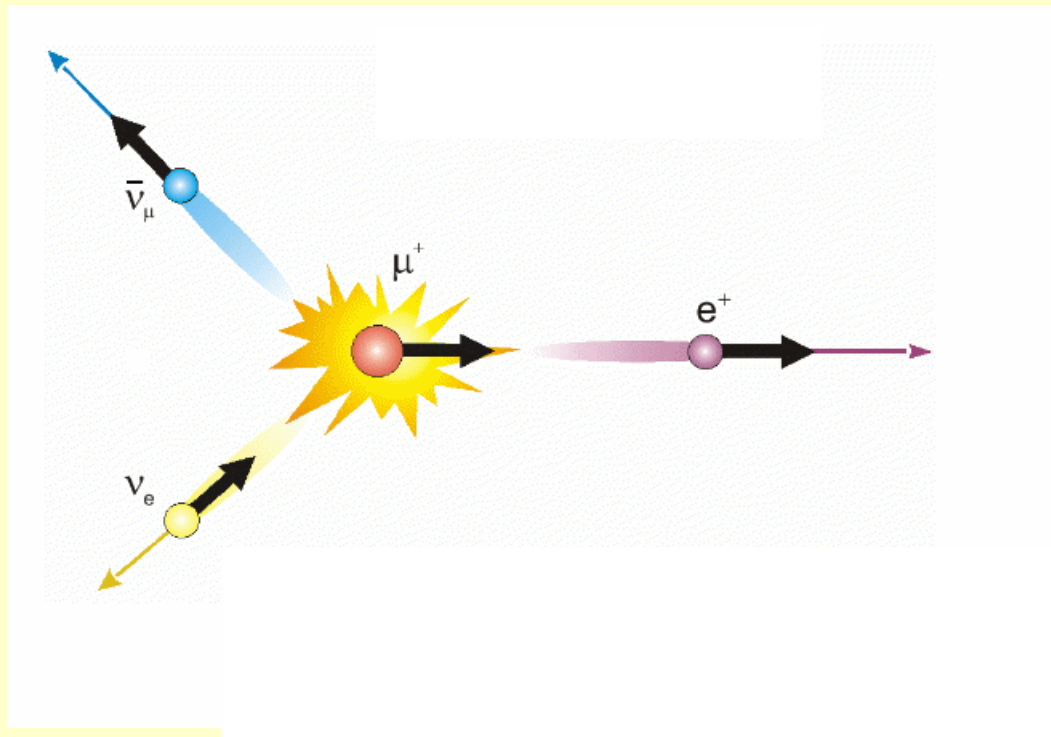
This provides the basis of the μ**SR technique** , illustrated by the schematic experimental setup seen below, where the energy-averaged 'asymmetry' $\langle \mathbf{a}_\mu \rangle$ is $\sim$ 1/3, and gives an **oscillatory** decay pattern in a **Transverse** magnetic field (TF).

muon counter   electron counter

μ^+ e^+ θ

e^+ θ

T D C

Start   *Stop*

$N_e(t)$

$dN/d\Omega \sim 1 + 1/3\cos\theta$

The muon spin will **precess** in a **TF**, giving rise to the 'Asymmetry' function,

$$A(t) = \sum_i a_i e^{-\lambda_i t} \cos(\omega_i t + \phi_i) \, ,$$

where the index *i* labels different magnetic environments, with the **amplitudes**, a_i, and **relaxation rates**, λ_i, of principal interest. An example fit to data for **Mu** reactivity in a weak TF, Mu + 'X' → MuX is shown, exhibiting muon spin **depolarization** due to a change in the muon's environment, with relaxation rate λ_{Mu}. By measuring this for different [X], we can find the **rate constant**, k_{Mu}.
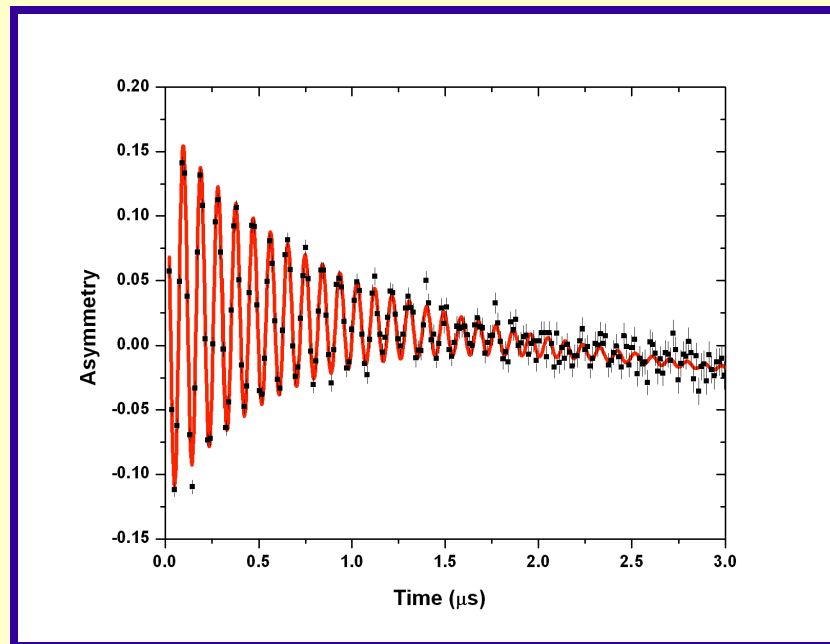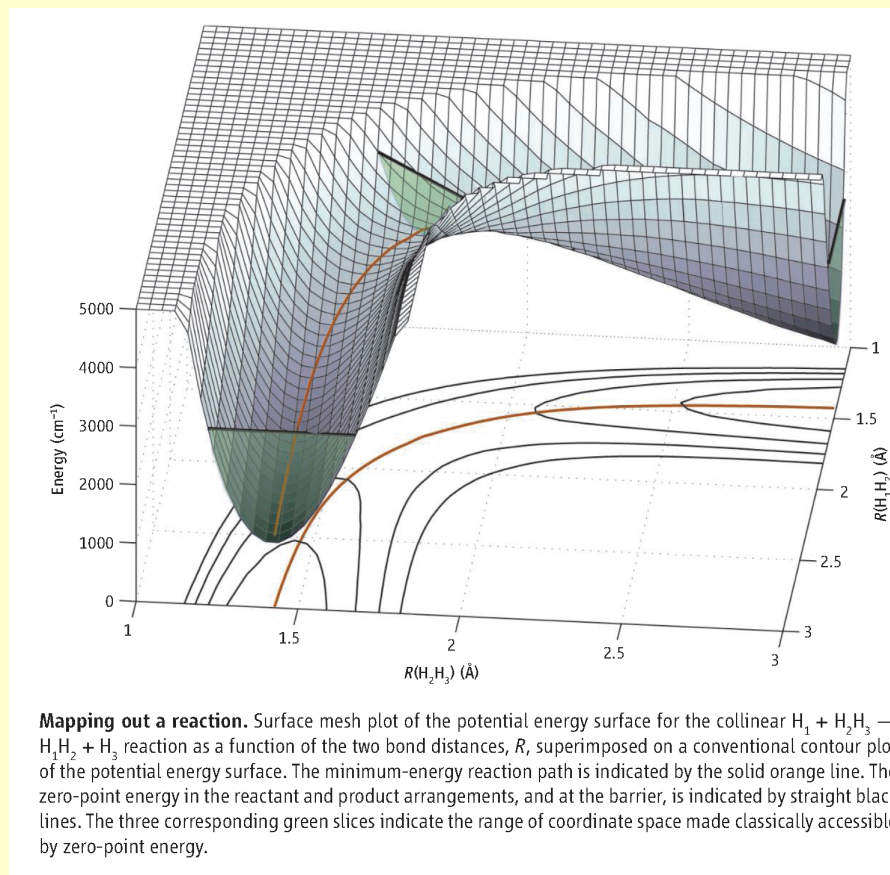
The ABCs of Chemical Reaction Rates:

The simplest reactions are of the form $\mathbf{A} + \mathbf{BC} \rightarrow [\mathbf{A} - \mathbf{B} - \mathbf{C}]^{\ddagger} \rightarrow \mathbf{AB} + \mathbf{C}$, proceeding through the [A-B-C]‡ **'Transition State' (TS)**, the most **fundamental** example being $\mathbf{H_A} + \mathbf{H_B H_C} \rightarrow [\mathbf{H_A} - \mathbf{H_B} - \mathbf{H_c}]^{\ddagger} \rightarrow \mathbf{H_A H_B} + \mathbf{H_C}$, the **"quark"** of the molecular world.

The first requirement to an understanding of chemical reactivity is to determine the **Potential Energy Surface (PES)**, $\mathbf{V}(\mathbf{R_{A-BC}}, \mathbf{R_{C-BA}}, \gamma)$, where $\gamma = 0$ is often the case, including for H_3.

Modern H_3 PESs evolved from the early London potential for H_2 (1929) to the **Born-Oppenheimer** 'Liu-Siegbahn-Truhlar-Horowitz' surface (LSTH, 1979), to its **most accurate** version today, the 'Complete Configuration Interaction' (**CCI, non-BO**) surface of Mielke et al. [*JCP*, 2002 $\cdots$ *Mol. Phys.*, 2015].

Mapping out a reaction. Surface mesh plot of the potential energy surface for the collinear $H_1 + H_2H_3 \rightarrow$ $H_1H_2 + H_3$ reaction as a function of the two bond distances, R, superimposed on a conventional contour plot of the potential energy surface. The minimum-energy reaction path is indicated by the solid orange line. The zero-point energy in the reactant and product arrangements, and at the barrier, is indicated by straight black lines. The three corresponding green slices indicate the range of coordinate space made classically accessible by zero-point energy.

The (BO) 'LSTH' PES for H_3. Morse potentials are seen for H_2 in the 'entrance' and 'exit' valleys, with **ZPE** levels shown by the horizontal lines. With decreasing $H_A-H_BH_C$ separation, the potential increases along the "Minimum Energy Path", (**MEP**, orange line), over the **TS barrier**. [M. Alexander, *Science*, 2011].

The **TS barrier** has two contributions, one from the electronic barrier ($V_B^\ddagger$) along the MEP and one from **ZPE** ($\sum_j E_{j,0}^\ddagger$), defining the **total barrier** for an 'ABC' reaction: $V_{(S)} = V_B^\ddagger + \sum_j E_{j,0}^\ddagger - E_0(BC)$.

$$A + BC \rightarrow [A\overset{S_1}{-}B\overset{S_2}{-}C]^\ddagger \rightarrow AB + C$$
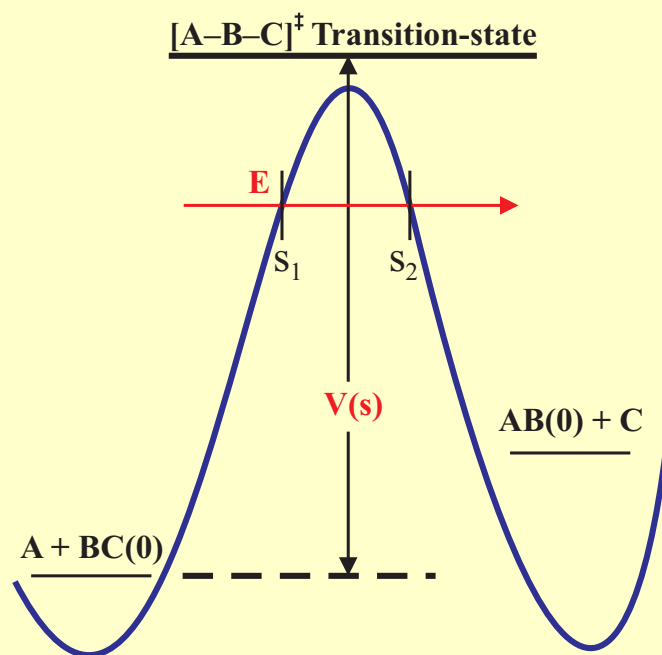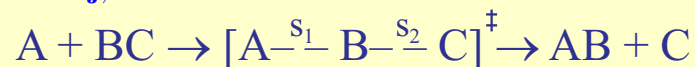
Schematic showing $V_B^\ddagger$ by the solid blue curve, with **ZPE** levels shown by the **black** lines, indicating an **endo**ergic reaction. The **red** arrow indicates a possible 1D tunneling path between the classical turning points S_1 and S_2.

As in nuclear α-decay, quantum tunneling can be described by a WKB integral

$$P(E) \propto e^{-2\sqrt{\mu_m}/\hbar \times \int_{s1}^{s2} \sqrt{[V(s)-E]}\, ds} \,,$$

from which we are reminded that it depends **dramatically** on mass, as shown below for the $Mu + F_2 \rightarrow MuF + F$ reaction [Takayanagi, *JPChem*, 1997].
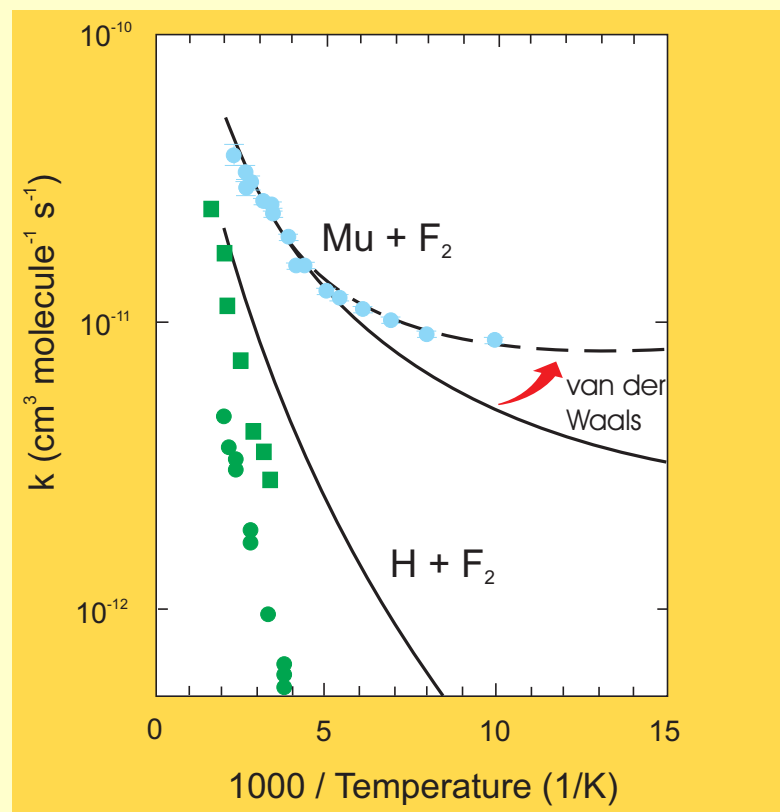
Note that the "activation energy", E_a = -Rdlnk(T)/d(1/T) $\rightarrow$ 0 near 100 K, a **unique** example of **'Wigner threshold tunneling'**, where the de-Broglie wave length Λ_{Mu} is > the barrier width.

Most PES calculations still assume the separation of electronic and nuclear motion, on the basis that the electrons move much faster, the **Born-Oppenheimer** (BO) approximation,

$$\mathbf{H} = \mathbf{T_N} + \mathbf{H^{BO}} \ ,$$

where $\mathbf{T_N}$ is the nuclear KE operator. This **couples** the set of BO eigenstates, so the **fully exact** system can**not** be described by a PES. However, the **diagonal** term $\mathbf{G} = \langle \Psi | \mathbf{T_N} | \Psi \rangle$ does allow us to correct for the nuclear KE in the **GS BO** surface, giving the **"Born-Huang" (BH) surface** ,

$$\mathbf{V^{BH}} = \mathbf{V^{BO}} + \mathbf{G} = \mathbf{V^{BO}} + \mathbf{V^{BODC}}$$

where $\mathbf{V^{BODC}}$ is the "BO Diagonal Correction".

The BO approximation becomes more suspect for **light** atoms and so particularly for Mu, necessitating non-BO corrections for **rigorous** calculations of Mu reactivity. Since BODC is mass-dependent each isotopic combination is described by a **different** PES. The effect on the barrier height is its most obvious outcome and for the **Mu + H$_2$** reaction this is a **4%** effect, which is **significant** in the comparisons between **rigorous** quantum theory and experiment shown below.

The rate constants $k_{He\mu}(T)$ and $k_{Mu}(T)$ are compared for Heμ and Mu reacting with H_2 and with both rigorous **QMT** and **TST** on the **CCI/BH surface**.
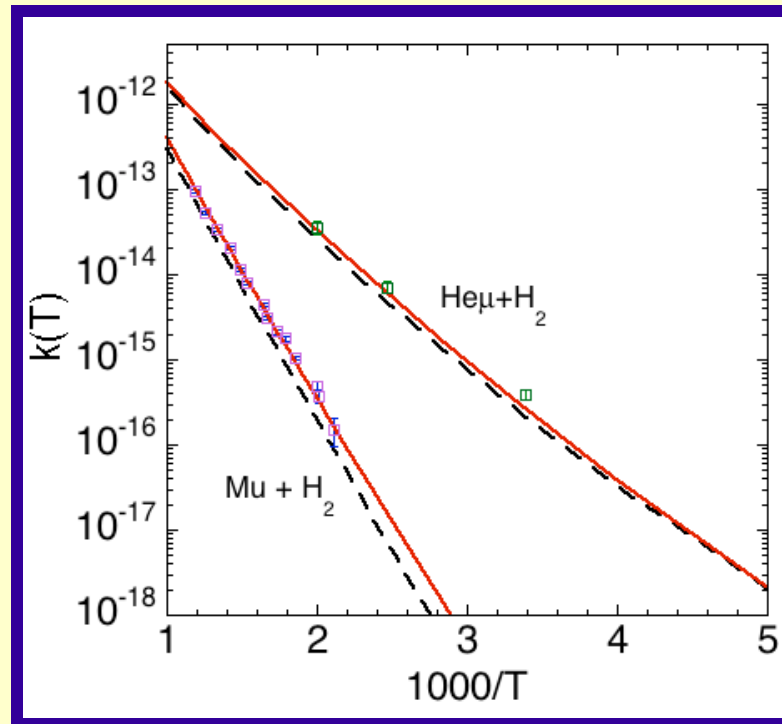
Note that k_{Mu} is $<<$ $k_{He\mu}$, reflecting the **ZPE- enhanced** barrier height (V_S) for the Mu + H_2 reaction. The agreement between QMT and experiment over a **factor of 36 in atomic mass** is **exemplary**! The more approximate TST is also good, though does **not** account as well for Mu tunneling. One can state that reaction dynamics/kinetics for the H_3 system is a **solved problem**, in which **muon science** has certainly played a **key** role.

Further evidence supporting this claim is shown below for the reaction of Mu with a **state-selected reactant**, the Mu + H_2(**v=1**) reaction, where H_2 is 'pumped' to its first vibrational state using a Nd:YAG laser @**532 nm** . This requires a **pulsed** muon beam so was carried out at 'ISIS' in the UK. [Bakule, Fleming & Mielke et al., J. Phys. Chem. Lett., 2012; J. Phys. B. At. Mol. Phys., 2015] . The experimental result (at 300 K) is compared below with the **rigorous QMT** calculations on the CCI/BH surface (**blue line**), along with previous results for the Heμ (**red**) and Mu (**green**) + H_2(v=0) reactions.
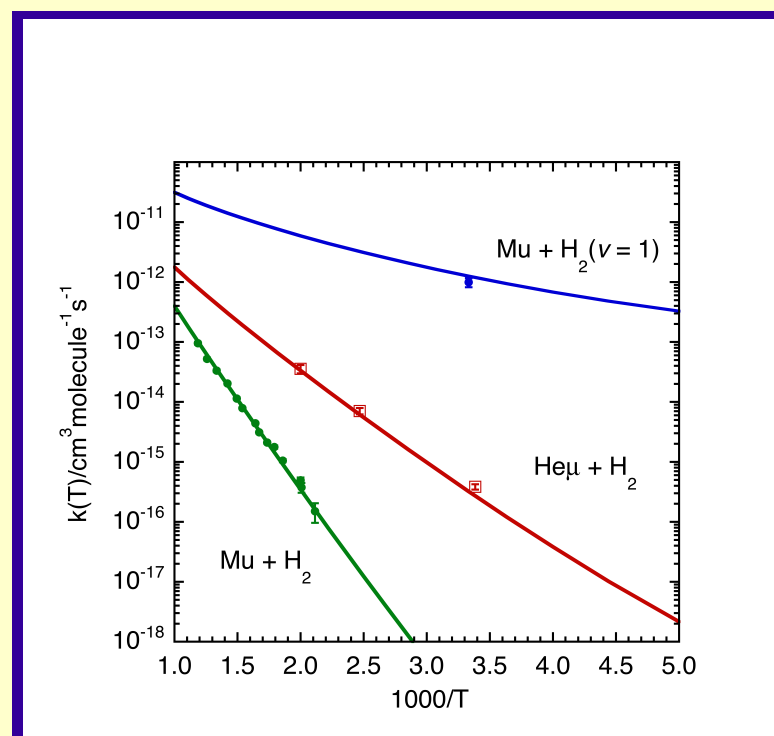
Recent Results On Gold Nanoparticles: Muonium Surface Chemistry

- In general a catalyst, and here a **heterogeneous catalyst**, provides an alternate route to chemical reactivity involving certain **reactive intermediates** at specific surface sites. The **Pt catalytic converters** in our cars are important examples: these bind noxious NO to Pt sites, facilitating its conversion to N_2 and O_2 and CO/Pt to CO_2.

- In the realm of heterogeneous catalysis, **silica-like** environments are important, often involving **H atoms** which can form **free radicals** as reactive intermediates, seen in recent past studies of **muoniated** free radicals formed by **Mu** addition reactions to organic molecules in **zeolites**, alumina-silicate heterogeneous catalysts [Fleming & Chen et al., *J. Phys. Chem. C*, 2013].

- Free radicals formed by H-atom addition are also catalyzed by AuNPs, particularly in **hydrogenation** reactions [Yang et al., *J. Phys. Chem C*, 2011] , exemplified by a recent study of H atoms reacting with solid benzene. The **first** step is H + $C_6H_6 \rightarrow \dot{C}_6H_7$, with subsequent steps leading to fully hydrogenated C_6H_{12} **at 20K**; interestingly, thought to be due to **H-atom tunneling** [Hama et al., *J. Phys. Chem. Letts.*, 2014].

- Recognizing the importance of AuNPs as heterogeneous catalysts prompted our interest in looking at Mu addition to **surface-adsorbed** benzene (Bz) on AuNPs of different sizes, to compare with earlier results in zeolites [Fleming & Roduner et al., *J. Phys. Chem. C*, 2011] and with a recently published paper from TRIUMF on the observation of **chemisorbed Mu** on a 7nm AuNP surface[Dehn, Kiefl and Fleming et al., *J Chem Phys*, (2016)]. There has essentially been **no other data** exploring the interactions of H atoms with AuNPs at the **microscopic level** .

- Benzene has a sequence of three alternating $-C = C-$ bonds, to which Mu can add, forming the **'muoniated'** radical, $Mu\dot{C}_6H_6$, as shown below, interacting with a AuNP (green circle) on a silica lattice.
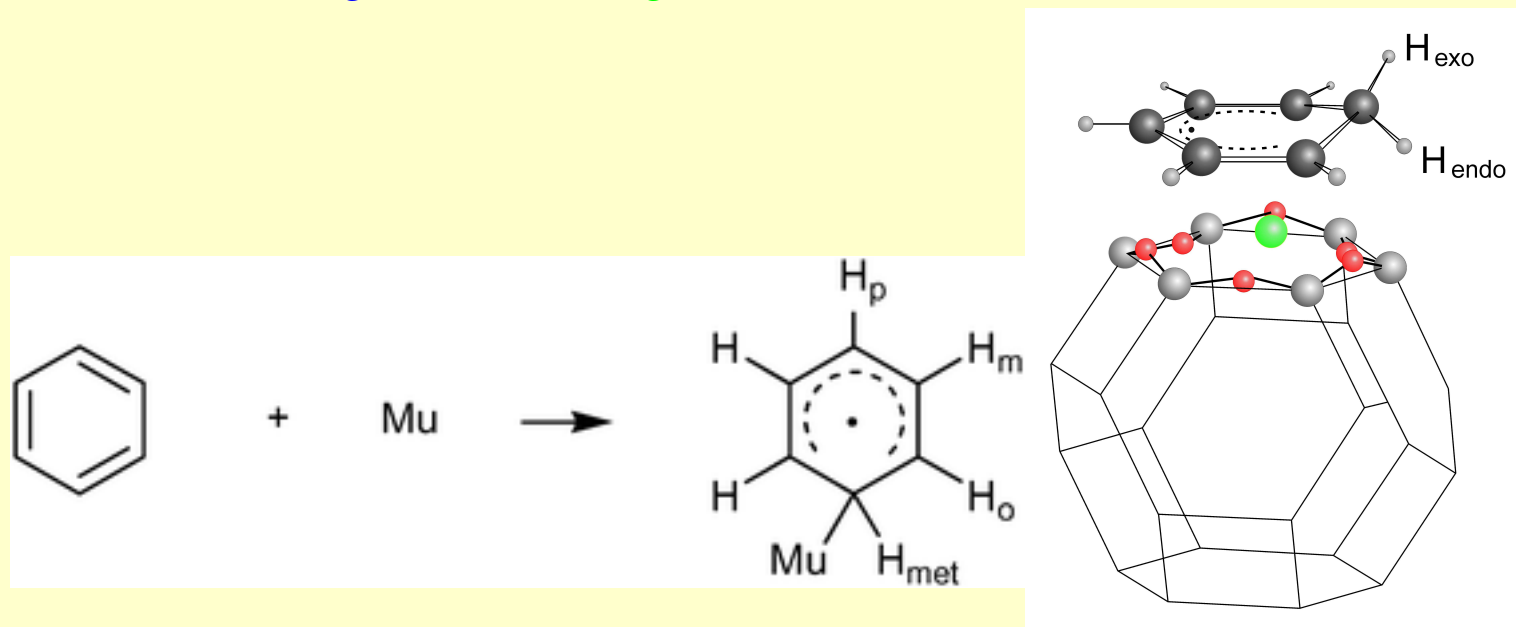
These AuNPs are encapsulated in mesoporous ($\sim$ **10 nm pores**) SBA-15 silica, which serves **two** important purposes.

First it provides a ready **source of muonium**, formed during the slowing-down process in a large silica grain ($\sim 1\ \mu$), and which then thermalizes **within** a mesopore. Secondly, it helps **prevent agglomeration** of the AuNPs which in turn means that these AuNPs are **uncapped**, in contrast to the common practice of using organic thiol compounds (S-bonded) for this.

TF-μSR studies of Mu + Bz on AuNPs
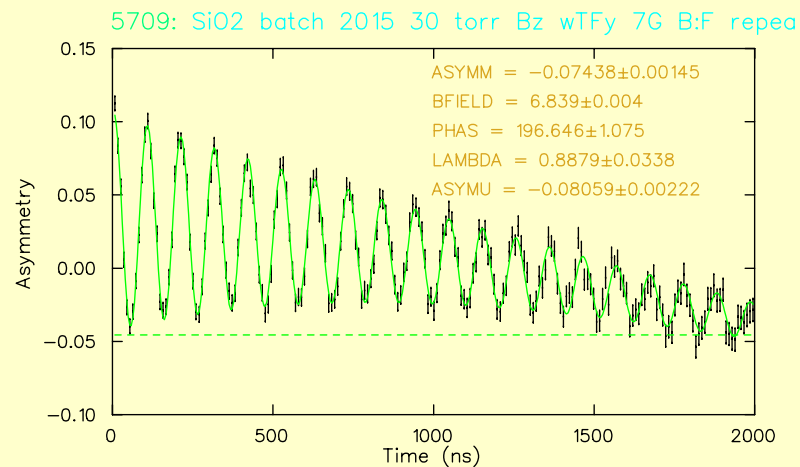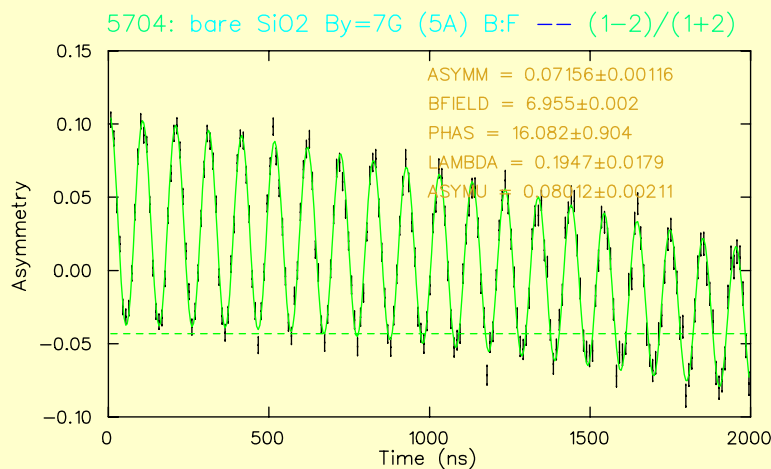
Mu precession for **pure silica** (Left) compared with a loading of **30 torr Bz** (R). The difference in relaxation rates, $\lambda_{\mathbf{Mu}} \sim \mathbf{0.2}\ \mu\mathrm{s}^{-1}$ for the **bare** silica, compared to $\sim \mathbf{0.9}\ \mu\mathrm{s}^{-1}$ for the **30 torr Bz** loading, is noteworthy.

Similar comparisons for a **bare 8 nm** AuNP (Top, L) and loaded with **30 torr Bz (1-2 monolayers)** (Top, R), and for a **38 nm** AuNP, also comparing the **bare** AuNP (Bot, L) with a Bz-loaded sample of **98 torr (3-4 layers)** (Bot, R).
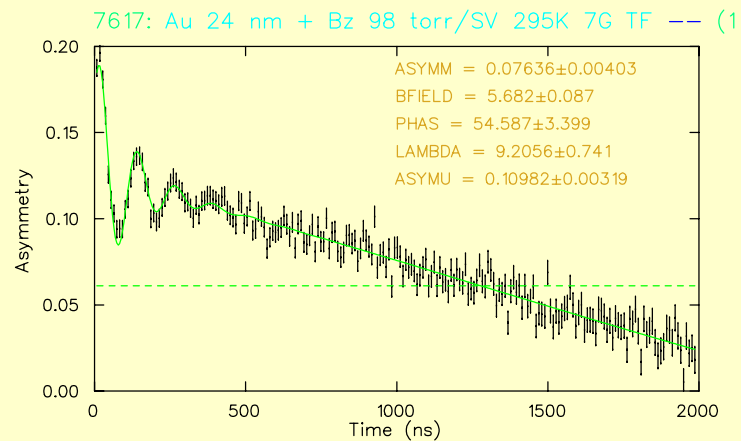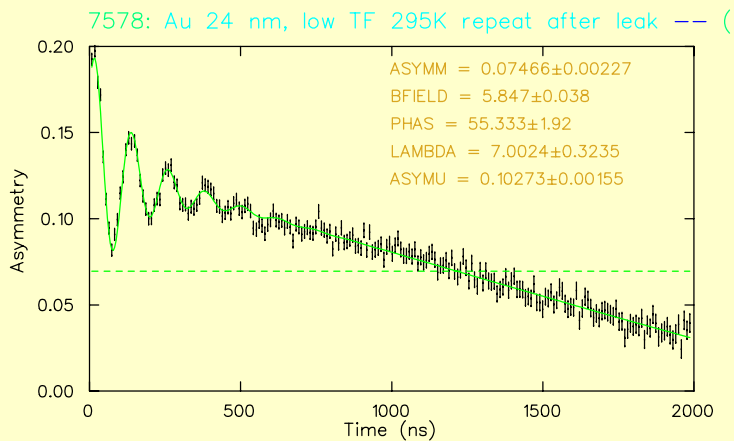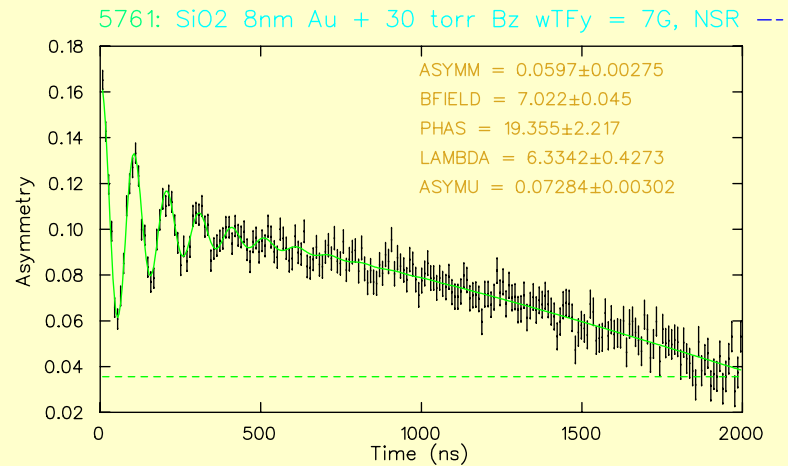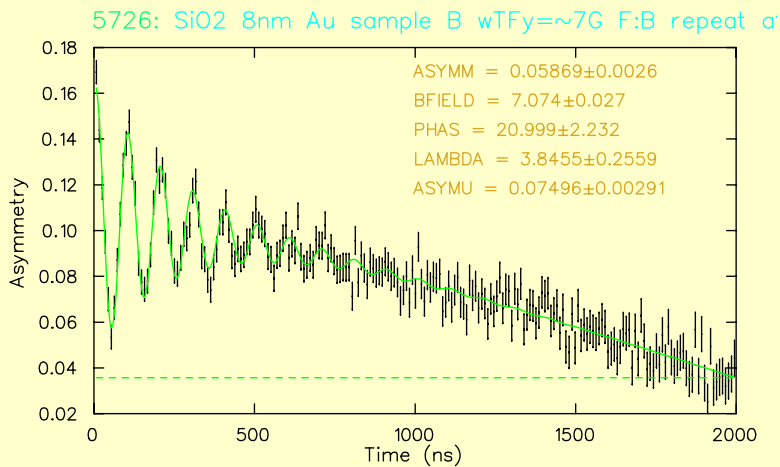
There are **three important points** to be made here:

- The relaxation rates $\lambda_{\mathbf{Mu}}$ are all about **30** × faster on the **bare AuNPs** than on the **bare silica**, strongly indicating an electron-loss reaction of **chemisorbed Mu** with the AuNP surface, $Mu + AuNP \rightarrow MuAu^+ + e^-(AuNP)$, giving a **diamagnetic** $AuMu^+$ product. [M. Dehn et al, *J.Chem. Phys.*, (2016)]

- The relaxation rates $\lambda_{\mathbf{Mu}}$ for the reaction of Mu with **Bz** are also **about 10 times faster** on the **AuNPs** than at comparable loadings in the silica, indicating that the **Bz resides on** the AuNP surface.

- These TF rates for the reaction of Mu with Bz are found to **scale linearly** with the amount of added Bz, consistent with the mechanism

$$\mathbf{Mu + Bz} \underset{\mathbf{k_d}(\varepsilon^*)}{\overset{\mathbf{k_a}}{\rightleftharpoons}} (MuBz)^* \overset{\mathbf{k_s}}{\underset{s}{\rightarrow}} MuBz,$$
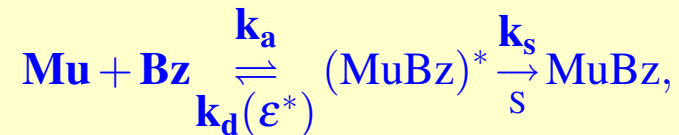
where $\mathbf{k_a}$ and $\mathbf{k_s}$ are rate constants for addition and stabilization of the **transient** complex $MuBz^*$ by collisions with the AuNP surface **'S'**, and $\mathbf{k_d}(\varepsilon^*)$ is the dissociation rate constant at energy ε^*. If the collision rate of $MuBz^*$ with **'S'** is **fast** compared to $1/\mathbf{k_d}(\varepsilon^*)$, the **overall rate** is determined by $\lambda_{\mathbf{Mu}} = \mathbf{k_a} \times \mathbf{N_{Bz}}$ on the surface.

That the formation of the MuBz (Mu$\dot{C}_6H_6$) radical on the surface gives rise to **spin relaxation** is due to the **multiple hyperfine interactions** between many **proton spins** and the muon and electron spins, **depolarizing** the muon.
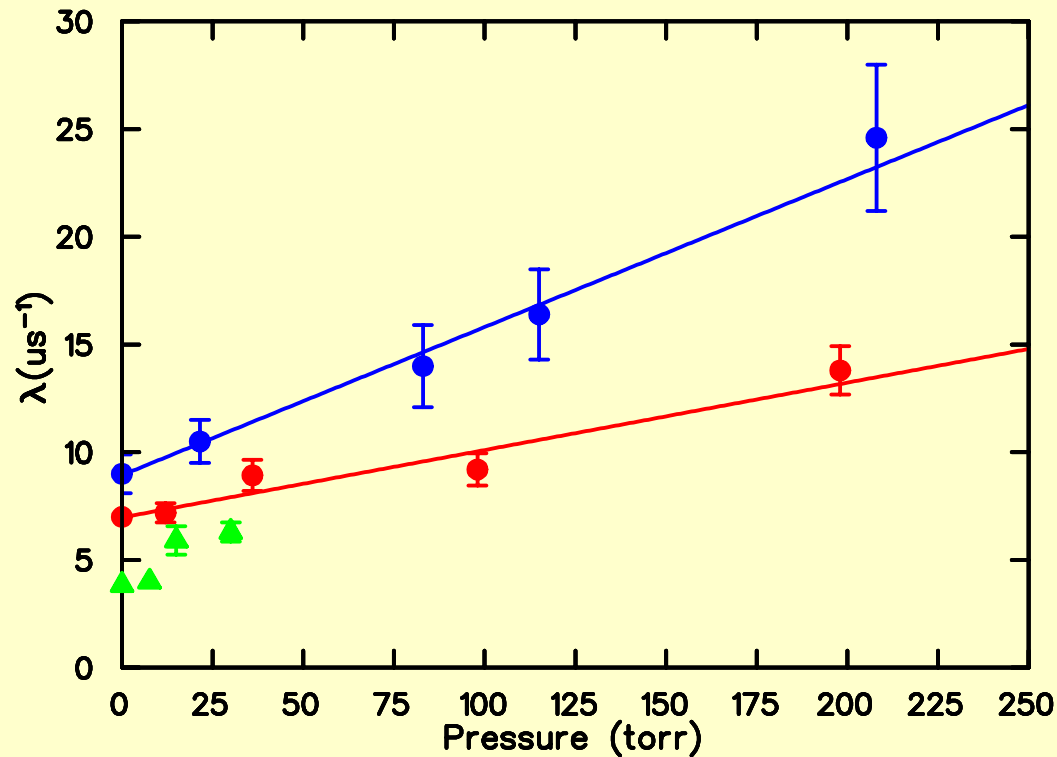
The data points for the 8nm AuNP (**green**) lack a higher pressure point, precluding a meaningful fit, though the **initial slope** does suggest an even **faster** relaxation rate, λ_{Mu}.

The data suggest that most of the added benzene resides **on** the AuNPs, and assuming that it **all** does, then we can find the total **surface concentration** of Bz on these AuNPs and hence the **2D rate constants, k_{Bz},** in units of **$cm^{-2}s^{-1}$** . This is shown in the last column of the table below.

AuNP size (nm)	N_{GNPs}	k_{Bz} (μs^{-1} torr^{-1})	k_{Bz} (cm^2 s^{-1})
8 nm	$\sim 7\times 10^{15}$	$\approx 0.12 \pm 0.03$	$\approx (3.5 \pm 1.0) \times 10^{-9}$
10 nm	$\sim 1\times 10^{16}$	0.068 ± 0.013	$(4.0 \pm 0.8) \times 10^{-9}$
38 nm	$\sim 2 \times 10^{14}$	0.031 ± 0.005	$(5.1 \pm 0.9) \times 10^{-10}$

Important Conclusion:

Given that the **T**ransmission **E**lectron **M**icrographs give an error of $\sim \pm$ 1nm on the AuNP sizes, these 2D rate constants can be seen to **scale inversely** with AuNP size, expected from the literature, but apparently **not** shown before for **any** **H-atom reaction** with a surface-adsorbed reactant on a **metal NP surface**.

Concluding Remarks

- Muons bring **two important aspects** to studies in both condensed matter physics and, as discussed herein, the chemical sciences. The muon provides for a **remarkable factor of 36** in **H atom** mass between Mu and Heμ, which in turn provides for truly **unique tests** of **quantum mass effects** in theory.

- The $\sim$ **100% muon spin polarization** provides the **raison d'etre** of the μSR technique, in which the e^+ (e^-) from μ^+ (μ^-) is emitted **preferentially** along (opposite to) the muon spin direction. This allows us to measure processes with **high sensitivity** which are often difficult to do by other techniques, notably of **transient** free radicals on **metal NPs** in confined environments like mesoporous silica, where **EPR studies** are essentially **non**-existent. **Kudos** to the muon!

- However, the technique is **not** a panacea; indeed, given $\tau_\mu = 2.2$ μs, μSR will **never** be able to compete with the detailed spectroscopy that is possible with **stable** spin probes. On the other hand, future experiments in **muon spin spectroscopy** remain promising and continue unabated, since the **first result** in July 1975 on the old M20 channel. **Kudos** to TRIUMF and the CMMS!

I'd like to close by showing an old picture of that now defunct early **M20 channel**, at the time **we** were installing it, taken in **1974**.