Doing Chemistry with Muons …

Investigating Reaction Kinetics, Rates of H atom abstraction in alkanes

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Outline

- Recap:
  - Muons, chemistry and reactions
  - Studying Muonium (Mu)
  - Kinetic measurements
  - RF measurements
- Alkane abstraction reactions:
  - Formulating a study
- New measurements for propane:
  - Kinetics from source or product states
  - Measuring a slow reaction – RF methods
  - Story so far

Acknowledgements

Experiment Team:

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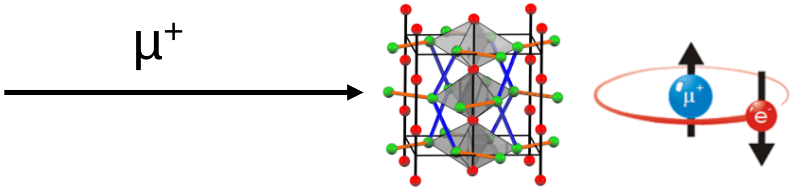
Recap

(from Chemistry and Pulsed Techniques lectures)

Muons, chemistry and reactions

- Muons



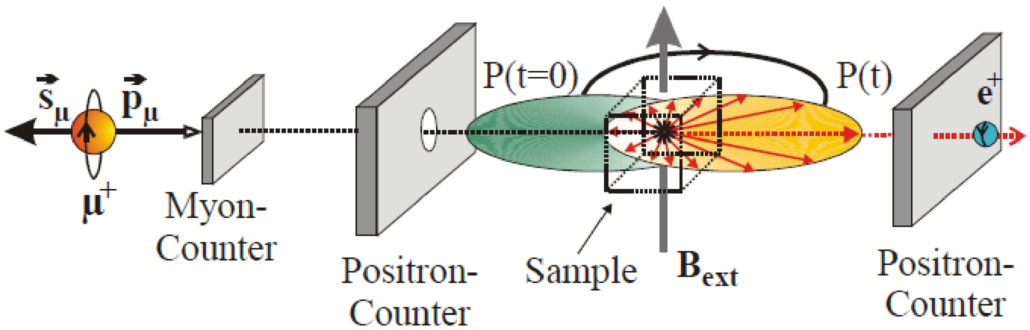
Mu, paramagnetic
(bound muon and electron)

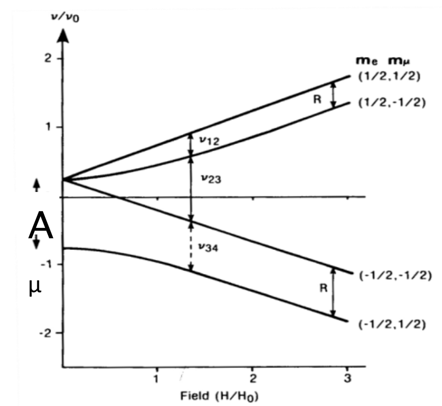
- Chemistry
  - Depending on Mu being chemically equivalent to H-atom
  - Greatly extends isotopic mass comparison
    ($m_{Mu} / m_H \sim 1/9$; $m_{Mu} / m_D \sim 1/18$)

- Reaction
  - *Abstraction*: Mu + RX ⟹ MuX + R·

TF Measurements - Muonium

For a field perpendicular to the muon spin ('TF'):

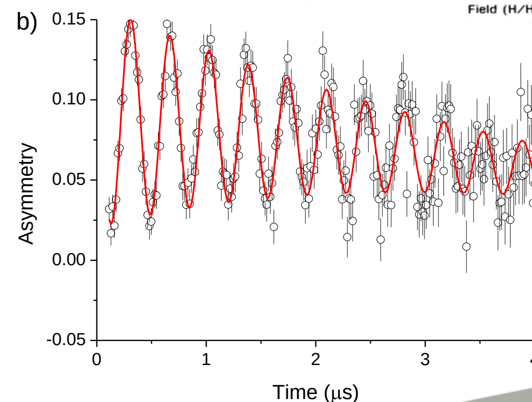




For our Muonium probe in a 2G TF

→ $\nu_{12} \approx \nu_{23}$ ... ν ~ 2.8 MHz

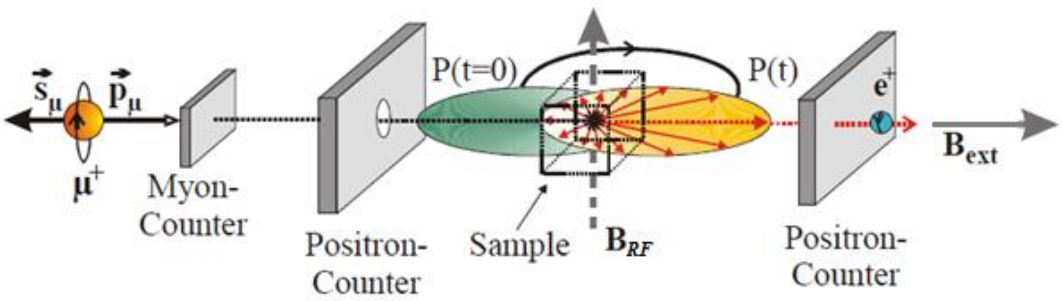
→ Measure decay, λ_{Mu}, for kinetics information



RF Measurements

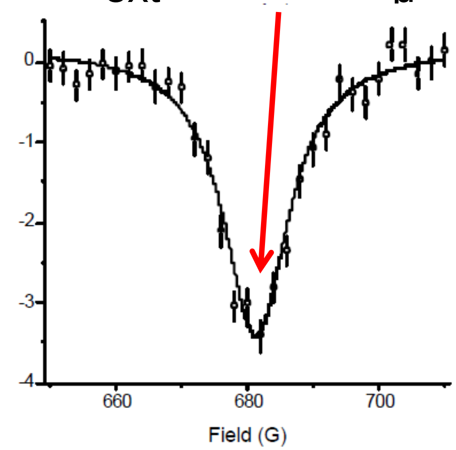
Now we'll use a:

- Static field parallel to the muon spin, B_{ext}
- RF field perpendicular to the muon spin, B_{RF}

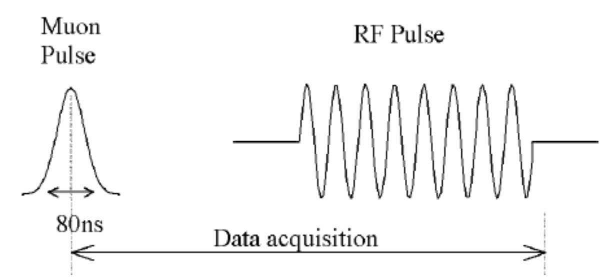


For resonance:

$B_{ext} = \nu_{RF} / \gamma_\mu$



RF Sequence:



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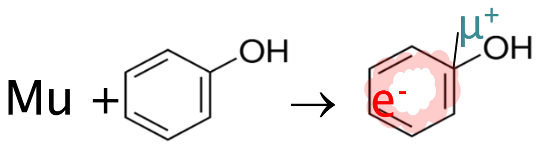
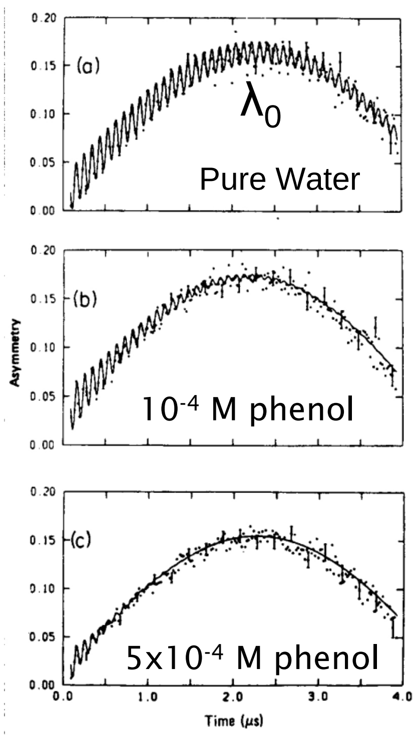
Kinetics Measurements

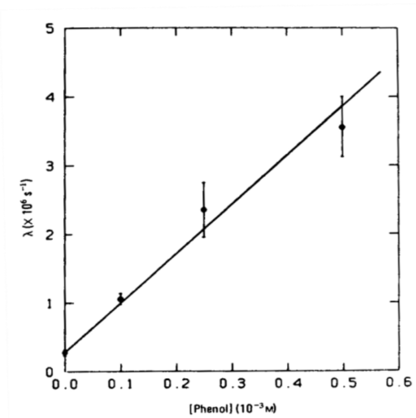
Example: Reaction of Mu with phenol solutions (addition) ...



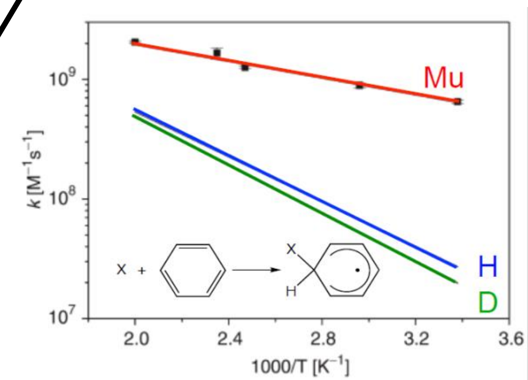
Measure Mu precession…



Plot decay, λ_{Mu}, with conc. …



Follow k_{Mu} with T to determine E_a …



Fit to first order rate equation,

$$\lambda_{Mu} = \lambda_0 + k_{Mu}\,[C_3H_8]$$

to extract k_{Mu}

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Alkane Abstraction Reactions

Abstraction Reactions with Alkanes

Excellent test of reaction rate theory:

- *Study Mu abstraction rates for a homologous series*:

  the lower mass alkanes (CH_4, C_2H_6, C_3H_8, …)

- *Study kinetic isotope effects*:

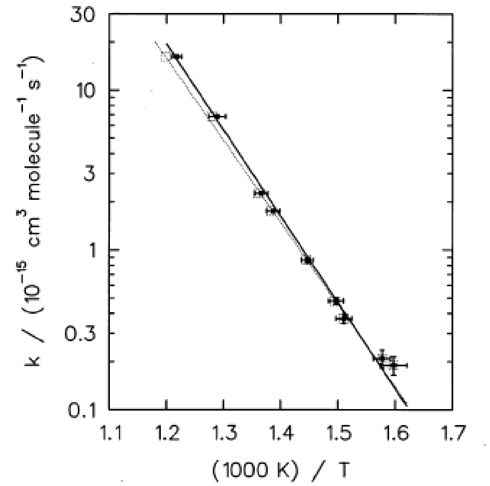
  relate to work reporting abstraction rates for H and D,

  we can extend this to include Mu (m_{Mu} / m_H ~ 1/9)

Homologous Series Comparison

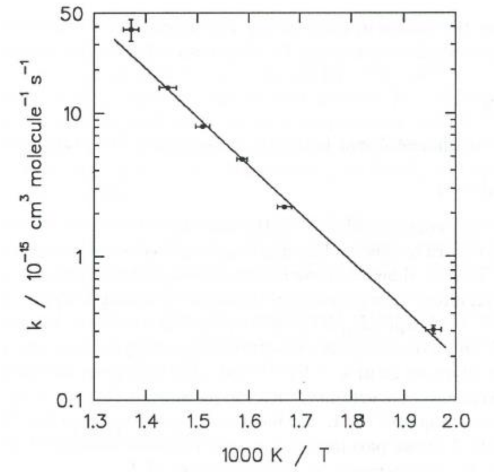
Mu +

CH_4



E_a = 24.6 kcal.mol^{-1}

C_2H_6



E_a = 15.4 kcal.mol^{-1}

Homologous …

same functional groups, similar chemical properties …

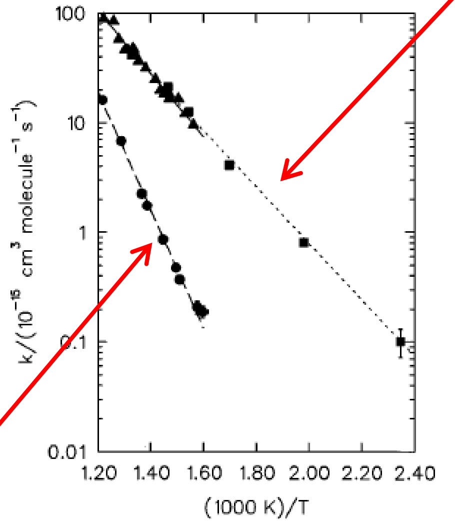
But activation energy for C_2H_6 is <u>lower</u> than for CH_4

(from Snooks et al, J. Chem. Phys. 102 (1995) 4860)

Isotope Comparison

$^{H}E_a$ = 13.2 kcal.mol^{-1}

CH_4



$^{Mu}E_a$ = 24.6 kcal.mol^{-1}

TABLE III. Comparison of E_a and ΔH^0 for Mu- and H-atom variants of reactions (1)–(5). Temperature ranges for Mu studies: 473–843 K for H_2 and D_2 reactions; 510–730 K for C_2H_6; 626–821 K for CH_4.

Reaction	E_a/(kcal/mol)	Refs.	ΔH^0/(kcal/mol)	Refs.
$H+H_2 \rightarrow H_2+H$	8.5±0.5	11	0.0	3,11
$Mu+H_2 \rightarrow MuH+H$	13.3±0.2	3	7.5	3,11
$H+D_2 \rightarrow HD+D$	9.4±0.3	11	1.0	3,12
$Mu+D_2 \rightarrow MuD+D$	14.7±0.4	3	8.4	3,11,12
$H+C_2H_6 \rightarrow H_2+C_2H_5$	9.8±0.4	38,39	−3.2	40,41
$Mu+C_2H_6 \rightarrow MuH+C_2H_5$	15.4±0.7	10	4.4[a]	10
$H+CH_4 \rightarrow H_2+CH_3$	13.2±0.8	28	−0.2[b]	31,33
$Mu+CH_4 \rightarrow MuH+CH_3$	24.6±0.9	⋯	7.3[a]	⋯

[a]Estimated from ZPE differences, as discussed in the text.
[b]An average of the values calculated in Refs. 31,33,34, as discussed in the text.

C_2H_6: $^{Mu}E_a - {}^{H}E_a$ = 5.6 kcal.mol^{-1}

CH_4: $^{Mu}E_a - {}^{H}E_a$ = 11.4 kcal.mol^{-1}

Difference for C_2H_6 in line with that expected from diff. in ZPE,

But *difference for CH_4 <u>much larger</u> than expected*

(from Snooks et al, J. Chem. Phys. 102 (1995) 4860)

Developing the study

Clear interest in:

- *extending the study to higher mass alkanes*

and

- *continuing isotopic comparison*

Next step:

- To study H abstraction in propane

But this is likely to be a slow reaction…

New Measurements for Propane

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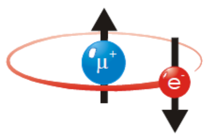
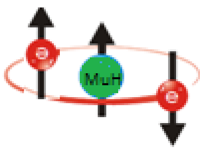
Developing the study

Objective is to measure kinetics for…

$$Mu + C_3H_8 \rightarrow MuH + C_3H_7$$



Para-



Dia-

Change of spin-state
for μ^+ species…
spectroscopically distinct

<u>Either</u>

Measure λ_{Mu} (TF)
but…
slow reaction
$\lambda_{Mu} \approx \lambda_0$
Difficult?!

<u>Or</u>

Try a new technique …

Measure *formation* of MuH
(excite MuH with RF, cf. NMR)

λ_0 not an issue – large field,
better for slow reactions?

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Experiment Setup

Experiment requirements make it tough!:

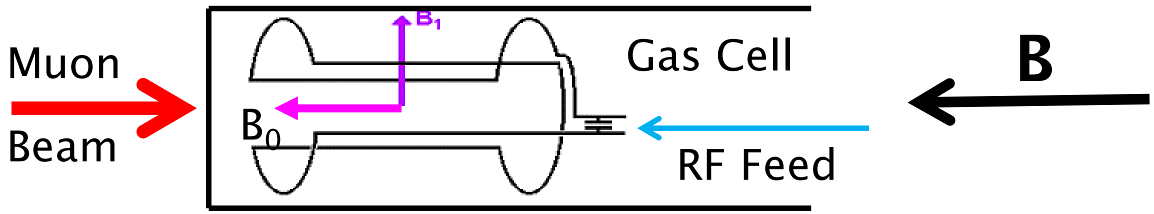
- Working Pressure to 50 bar
- Thin window to admit muons
- Extended path (~cm) to stop muons
- Variable T: ~ -50°C to 250°C
- Resonance cavity

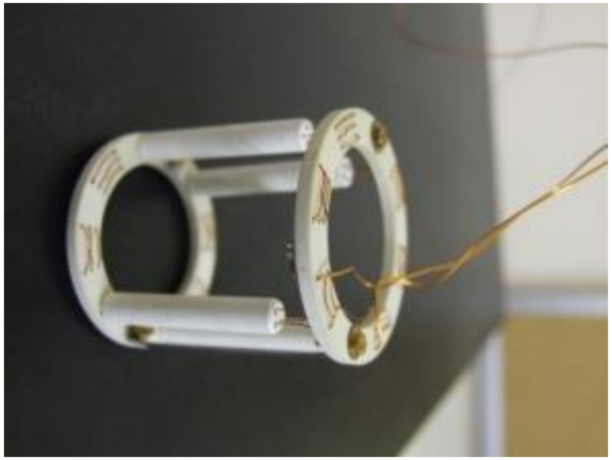
Final design:

- 46cm long x 3.5cm diameter SS cell
- Window 150μm Ti foil
- Circulate oil for T control
- Integral RF coil

Experiment Setup

Geometry

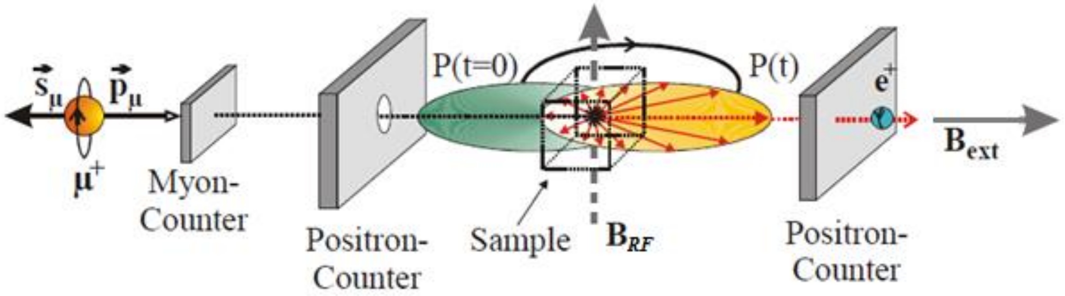


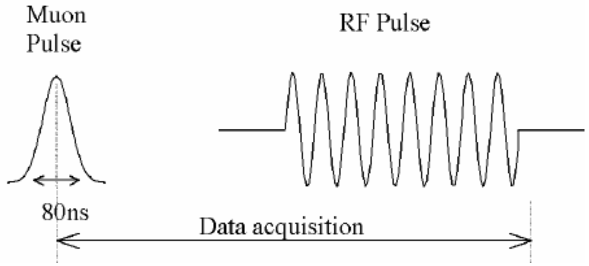


RF Coil: ‘mouse size’ saddle coil

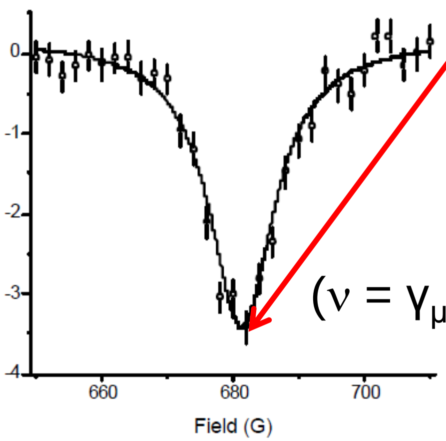
Tuned and matched to 50Ω between ~9-13MHz

RF Measurements



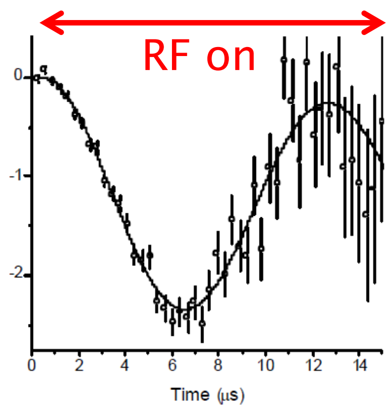


Swept field



$(\nu = \gamma_\mu B_0)$

At Resonance (~681G)



RF Coil tuned 9.2 MHz, (γ_μ = 13.55kHz/G)

RF on for ~32μs following muon implantation

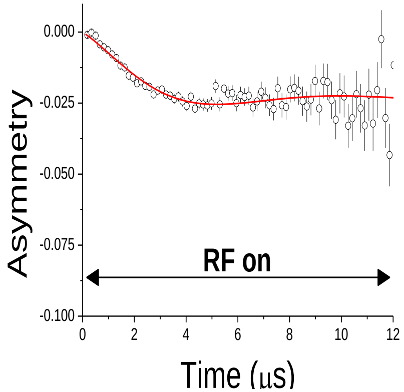
Precession about RF field, $B_1(t)$ ~ 6G

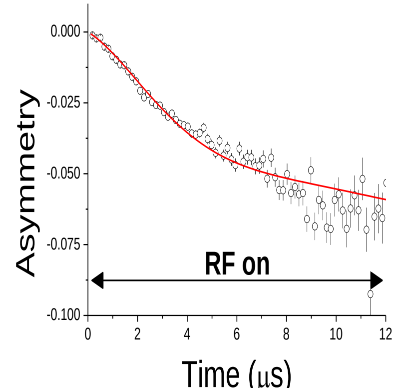
Product (MuH) RF Measurements

$$Mu + C_3H_8 \rightarrow MuH + C_3H_7$$

Propane (+ N_2 buffer to maintain constant stopping distribution)

0.8 bar





4.5 bar

Small signal

⇓

Very slow MuH formation

Signal develops

⇓

Clear MuH formation

Product (MuH) RF Measurements

Expression to signal for state conversion provided by Morozumi *et al* (Phys Lett A 1986 **118** 93):

MuH product - Fit to Data

$$f_{DIA}(t) = A_P \cos(\omega_1 t) + \int_0^t (df_D / dt') \cos(\omega_1 (t - t')) dt'$$

where $(df_D / dt') = \lambda_{Mu} [\mathrm{Mu}]_0 \times \exp(-\lambda_{Mu} t')$

Measure μSR Signal

Extract λ_{Mu}

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Product (MuH) RF Measurements

But lots of parameters to determine ...

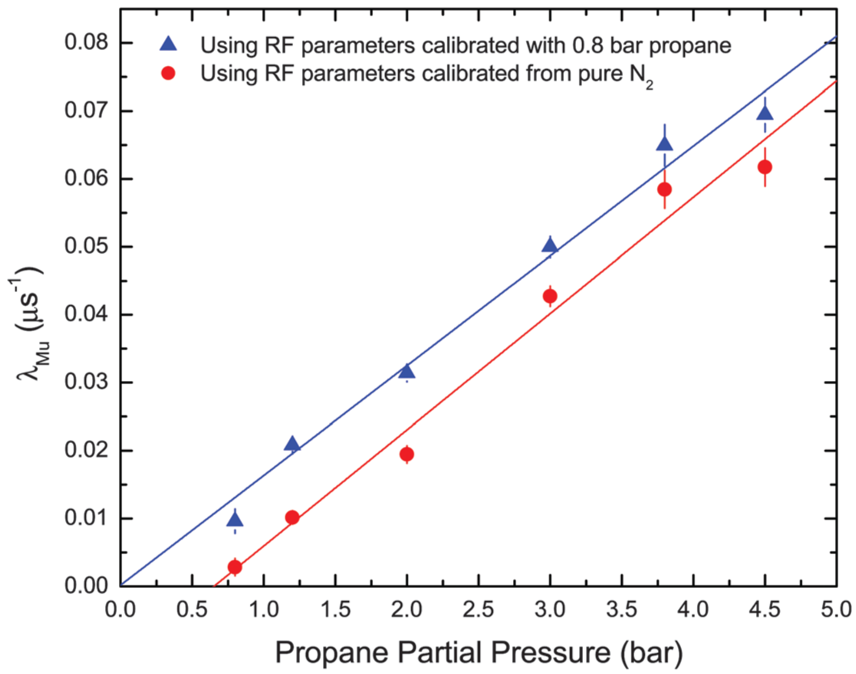
Table 1 Description of the parameters that enter eqn (8) in fitting the RF data for Mu + C_3H_8

Parameter	Description
A_P	The prompt diamagnetic amplitude.
A_D	The diamagnetic amplitude formed by reaction.
$A_{T,Dia}$	The initial diamagnetic amplitude at 20 G, contributions from A_P and A_D.
A_{Mu}	The initial total Mu amplitude. Determined from 2 G TF measurements.
B	The longitudinal field on resonance, 1182 G.
ν_1	The diamagnetic precession frequency on resonance, determined by calibration.
λ_1	The relaxation rate due to B_1 inhomogeneity, also calibrated.
ν_0	The hyperfine coupling constant for the vacuum Mu atom, 4463.3 MHz.
ν_{SF}	The spin flip rate, estimated from T_1 relaxation at the applied field on resonance.
τ	The mean conversion time for the Mu + C_3H_8 reaction, $\tau = 1/\lambda_{Mu}$.

Most can be determined by calibration measurements …
but lots of potential for errors!

Product (MuH) RF Measurements

At 300K, for propane:



Fitting to:
$\lambda_{Mu} = \lambda_0 + k_{Mu}[C_3H_8]$

$\mathbf{k_{Mu} = (6.8 \pm 0.5)x10^{-16}\ cm^3\ s^{-1}}$

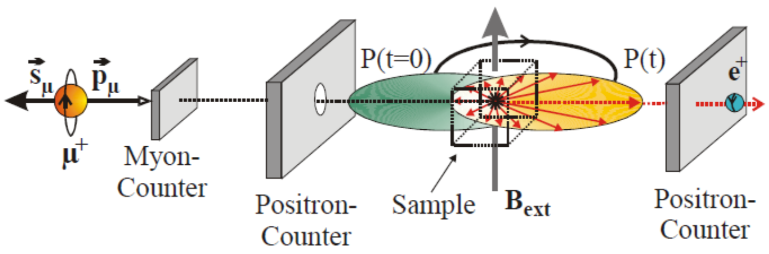
Much faster than expected…
(cf. ~10^{-19} CH_4 / C_2H_6).

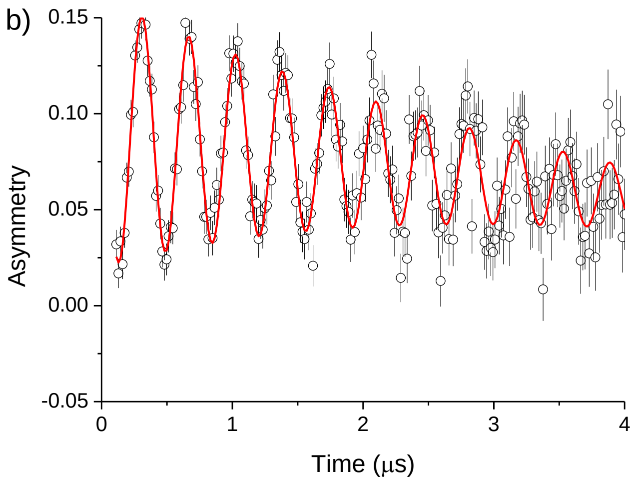
(from Fleming et al, PCCP 17 (2015) 19901) *if it's this fast …*

Direct measurement of the disappearance of Mu should be possible for this system

A simpler TF-μSR experiment might be feasible …

Back for TF-μSR …

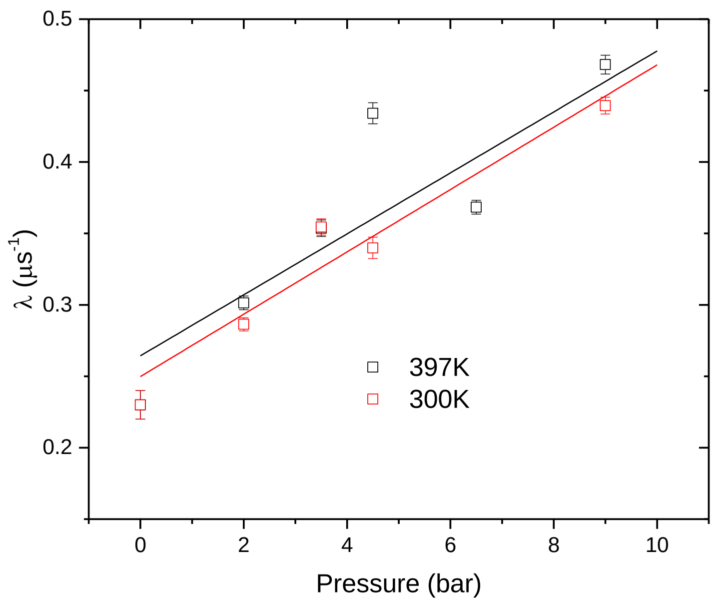




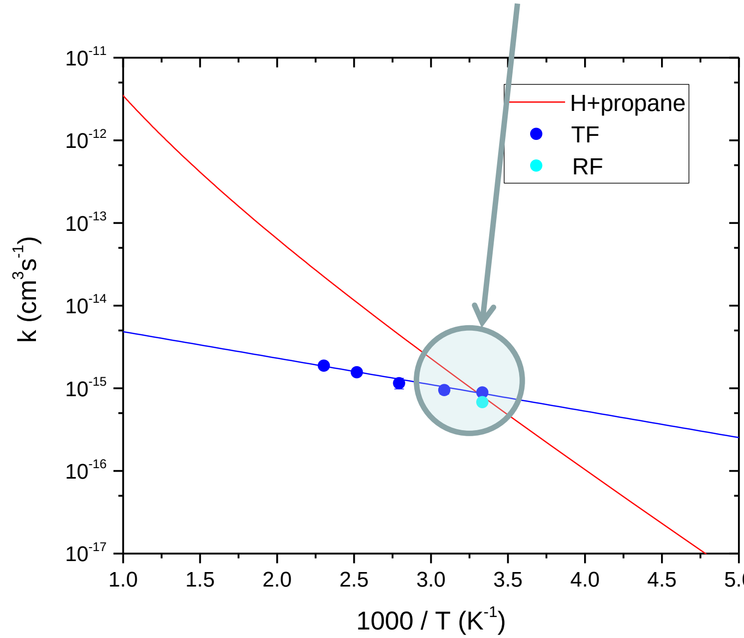
Measure decay, λ_{Mu}, for kinetics information

TF-µSR Measurements

For example, for propane at 300K and 397K:



TF and RF results in good agreement @ 300K



$E_a = 1.63 \pm 0.15$ Kcal/mol

(Fleming et al, to be published)

Summarising what we did …

- Started out by following formation of MuH product using RF techniques
- Obtained a value for k_{Mu} at 300K
- Noticed it was much faster than anticipated
- Continued study by following disappearance of Mu, measuring λ_{Mu} using TF-µSR
- Determined k_{Mu} over a range of temperatures and hence E_a
- What do the results tell us (so far)?

Conclusions

Rate constant at 300K (RF data) surprisingly fast:
k_{Mu} = (6.8 ± 0.5) x 10^{-16} $cm^3 s^{-1}$ (cf. ~10^{-19} CH_4 / C_2H_6).

TF-μSR results confirm this … therefore, a small activation energy is expected. Confirmed by TF measurements:
E_a = 1.63 ± 0.15 kcal/mol (cf. 1/10 value for C_2H_6).

Classical TST theory suggests k_{Mu}/k_H ~ 1/1000,
but experiments suggest k_{Mu}/k_H ~ 1/3.

Results suggest a large and unexpected contribution from quantum tunnelling in the Mu + C_3H_8 reaction.

At this point, help needed from computational chemists!