Laying the foundation for a muon-laser spectroscopy

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Abstract

In this report we introduce two novel techniques, laser-muon spin spectroscopy (laser-µSR) where laser excitation follows muon arrival to excite muoniated molecules and laser pump-muon magnetic resonance probe where laser excitation precedes muon arrival to excite molecules reacting with muonium or muoniated free radicals. Both these techniques employ laser excitation to produce a transient while the chemical dynamics of which are probed using muon spin spectroscopy (µSR). By using a tunable laser system it will be possible to measure the electronic and vibrational excitations of a muoniated centre. This will provide an independent tool for radical and site assignments for muon implanted samples. This report presents the proof of principle experiments, using time-resolved Zero-Field µSR (ZF-µSR), to observe the change upon 532 nm laser excitation in the ZF asymmetry of the radical adduct produced by excitation of powdered rose bengal. For the first time these pump-probe experiments extend muonium chemistry to the realm of excited states. The results enable the detection of muoniated molecules by their spin evolution after laser excitation; opening new opportunities to study the chemical dynamics of muoniated intermediates in excited states.

Introduction

Of interest to many applications in transient chemistry, including free radicals are the changes between the ground and excited states. In this report we introduce a new tool, laser-muon spin spectroscopy (laser-µSR) for examining excited state chemistry. Laser-muon spin spectroscopy is based on coupling the powerful techniques of pulsed laser excitation (as pump) and µSR (as probe). This new approach takes advantage of the lasers and the structure of intense pulsed muon beams available at the CCLRC Rutherford Appleton Laboratory (RAL) in the UK. It has applications in radiation chemistry, free radical chemistry, and reaction dynamics, particularly studies of kinetic isotope effects in the excited state at the most sensitive end of the mass scale (i.e., through studies of KIEs of H isotopes). These initial experiments extend µSR, which encompasses muon spin rotation/relaxation and resonance, a suite of magnetic resonance techniques that use positive muons (μ^+) to new domains. Muons which are spin 1/2 particles have a mass approximately 1/9 that of H^+, can be produced 100 % spin polarized and serve as microscopic probes of the electronic and magnetic environments. The 100 % spin polarization of muons and their anisotropic decay, combined with advanced sensitive nuclear physics counting techniques for the detection of decay positrons from muon decays, makes µSR much more sensitive than conventional magnetic resonance techniques[1].

Experimental

These studies were conducted using the DEVA surface muon beam at ISIS and a Nd:YAG laser from the EPSRC Laser Loan Pool. The laser system, which operated at 10 Hz (ca.7 ns pulse, 500 mJ at 532 nm), was triggered to either precede or follow the arrival of each fifth muon pulse (at 50 Hz) with a set time delay. The first four in every five muon pulses provided the information on the ground state. The laser-µSR cells were made in-house. The sizes of the muon and laser input windows on these cells were matched to maximize the overlap between the pump and probe beams.

Spin polarized positive muon beams are produced by nuclear accelerators such as ISIS at MeV kinetic energies (4.1 MeV at surface muon beam lines such as DEVA). After these muons enter and stop in the target, detectors register positrons emitted preferentially along the direction of the muon spin when the stopped muons decay. At DEVA, positron detectors are arranged forward (upstream) and backward, relative to the initial muon spin polarization. For each detector, data is usually collected for 32 µs subsequent to the muon implantation, with the number of positrons detected during each 16 ns time-step recorded and collected in a histogram of counts as a function of time. The probability of detecting the decay positron in a given direction varies, because the muon spin precesses in a magnetic field, either external or internal[1]. Thus µSR, histograms obtained from positron detectors may contain oscillations in the muon decay spectrum, and these oscillations correspond to the time dependence of the muon polarization. Each histogram has the form:

$$N(t) = N_0 e^{-t/\tau_\mu}(1 + A(t)) \tag{1}$$

where N_0 is the overall normalization that depends on a number of factors, such as the solid angle of the positron detectors and the number of stopped muons; τ_μ is the muon lifetime, 2.197 µs, and $A(t)$ is the asymmetry, which represents the µSR signal of interest which is similar to free induction decay in magnetic resonance. A normalised asymmetry, A(t), can be defined in terms of the positron counts from muon decay in the forward $N_F(t)$ and backward $N_B(t)$ positron detectors:

$$A(t) = \frac{N_F(t) - \alpha N_B(t)}{N_F(t) + \alpha N_B(t)} \tag{2}$$

where α takes into account the differences in relative geometry of the stopping muons and detector efficiency.

Results and Discussion

When a positive muon is implanted in a molecule or material it is called a muoniated species. Our initial experiments explored the possibility of studying the electronic excitation of such a muoniated centre in a molecule formed by addition of muons to rose bengal (4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein, $C_{20}H_2Cl_4I_4Na_2O_5$, - RB), a halogenated xanthene dye (Figure 1), which has been used as a photosensitizer in photodynamic therapy (PDT)[2]. The photochemistry of RB has been extensively studied and several photophysical parameters associated with its triplet and singlet states have been determined. It is known that in the presence of H^+ there is a red shift in the RB absorption spectrum[3]. The same effect has also been observed for other halogenated and non-halogenated dyes, which show a red shift of ~50 nm in the protonated form[4]. This could be considered similar to the case where μ^+ is added to RB,

since the chemistry of μ^+ containing molecules is similar to the chemistry of H^+ containing molecules, except for possible quantum effects such as zero point vibrational and tunneling effects. During this experiment (Figure 2) the muon signal amplitude (asymmetry) in powdered rose bengal is monitored with and without 532 nm laser excitation (20 mJ at the sample in 20×20 mm beam) at zero magnetic field (Figure 3). RB has a strong absorption close to 532 nm due to a strong $\pi \rightarrow \pi^*$ transition. The subsequent analysis shows a statistically significant effect (Figures 3 and 4), with very clear differences between the two spectra shown in Figure 3. When a magnetic field is applied along the direction of spin of muons or in Zero Field (ZF) environments, in the absence of a local magnetic field, there is no precession since the applied field (if any) and muon spin polarisation are co-linear. Under these conditions, each muon is in a stationary state. If a local magnetic field is present the time evolution of the muon spin can be measured in ZF. The ZF laser-µSR data such as that presented here can make a unique contribution to the field of transient excited state chemistry; similar measurements such as ESR are generally performed in large applied magnetic and resonating radio frequency fields. With this spectroscopic technique we should be able to tune the laser frequency to induce an electronic transition or a photochemical reaction that would lead to a muon-electron hyperfine interaction. In this way, we will be able to characterize
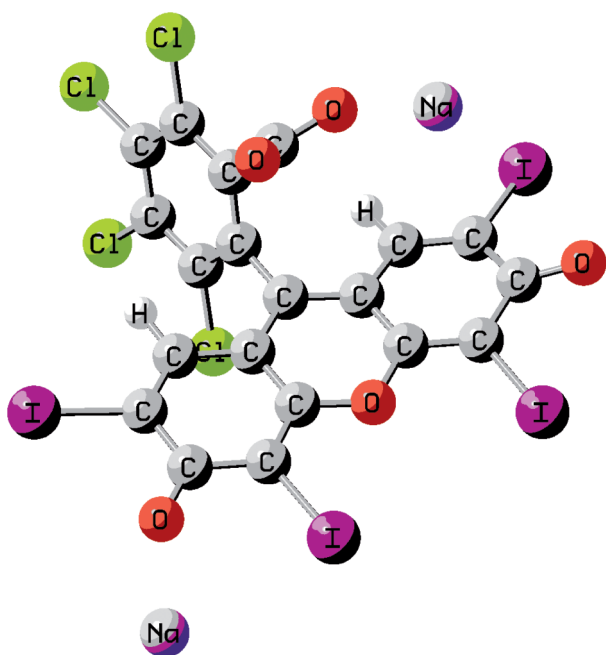

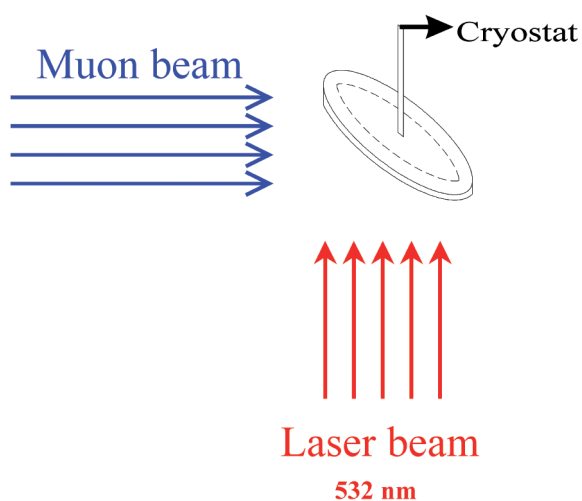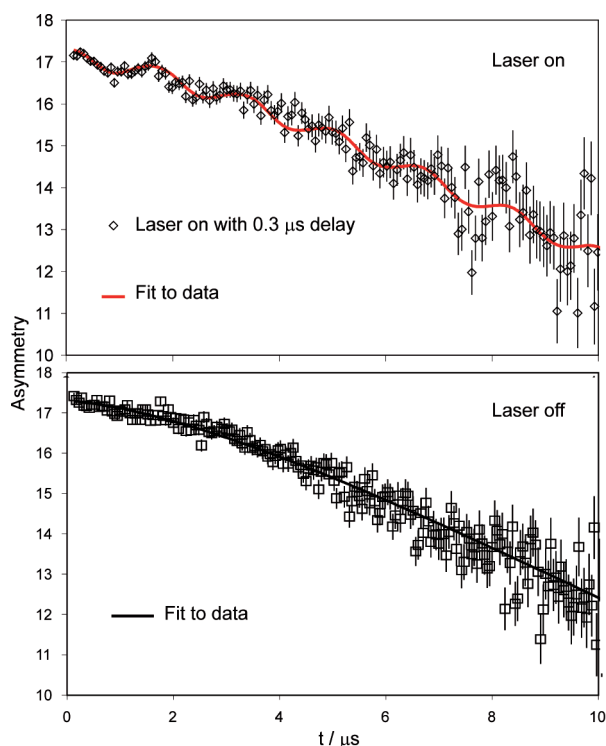**Figure 1. The optimized structure of rose bengal at AM1 level of the theory.**

Figure 2. The schematic of the setup for the experiments on rose bengal powder. The laser and muon window is a thin (0.1 mm) quartz cover slip.

Figure 3. The asymmetry in powdered RB with and without 532 nm laser irradiation (0.3 µs delayed relative to the muon pulse). The curves represent a Lorentzian fit (for the data in the absence of laser excitation) and Lorentzian with oscillatory component (for the data in the presence of laser excitation). The sizes of the error bars are smaller in the laser off experiments due to the longer laser off period compared to laser on (hence the higher statistics of the laser off data).
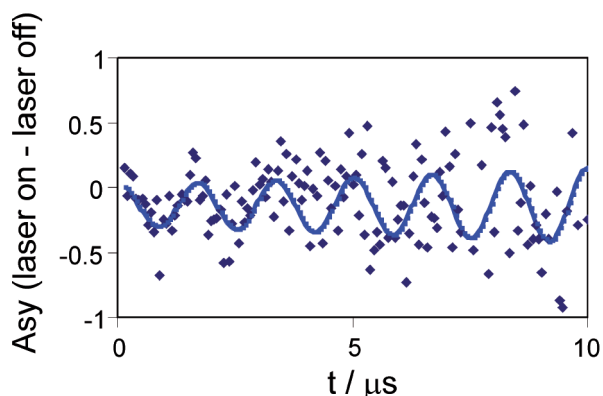
Figure 4. Difference between laser on and off asymmetry at zero magnetic field in powdered RB with 532 nm laser irradiation (0.3 µs delayed relative to the muon pulse).

both the ground state, by following the effect of the laser as a function of frequency, and the excited states, through their hyperfine interactions. Moreover we can characterize the transient species in a time-resolved manner. For example, the asymmetry of RB without and with laser excitation at selected time delays is shown in Figure 5. The observations in Figures 3-5 suggest that laser irradiation will generate local magnetic fields which the muon senses and in which it oscillates after the onset of laser irradiation. The unpaired electrons of free radicals could generate such local magnetic fields through anisotropic hyperfine interactions. However, typical µSR free radical signals decay significantly in a fraction of a microsecond [1]. The fact that we observed the laser induced oscillations

even after 1 µs suggests that the oscillations of the muon spin polarization are due to the excitation of muoniated diamagnetic molecules to the singlet state, followed by intersystem crossing to the triplet state. Muoniated diamagnetic molecules are stable over the muon lifetime, and therefore excitation of these muoniated centres is possible during their lifetime. The laser-induced oscillations are therefore due to muon-electron dipolar hyperfine interactions in the triplet state.

In the results reported above laser radiation is used to excite a transient, produced by muon irradiation, its response to laser excitation is then followed with µSR via its hyperfine interactions in the excited state. With this proof of principal work we have set out to develop a technique to study the chemistry of the transients involved in PDT. This technique also has the potential to be used for the investigation of laser-material interactions.

In the following we report another novel experiment, pump-probe study, in which the system is excited by laser radiation and the chemical dynamics are probed using µSR. The aim of this second study was to investigate the chemical dynamics of the reaction between Mu and molecules in excited states, in particular electronic excited states, which are just one of the many transient intermediates that play an important role in PDT.

The asymmetry parameter, $A(t)$, in a transverse field experiment includes contributions from paramagnetic Mu, as well as free radical and diamagnetic molecules [1,5]:

$$A(t) = \Sigma_i A_i \exp(-\lambda_i t) \cos(w_i t + \varphi_i) \qquad (3)$$
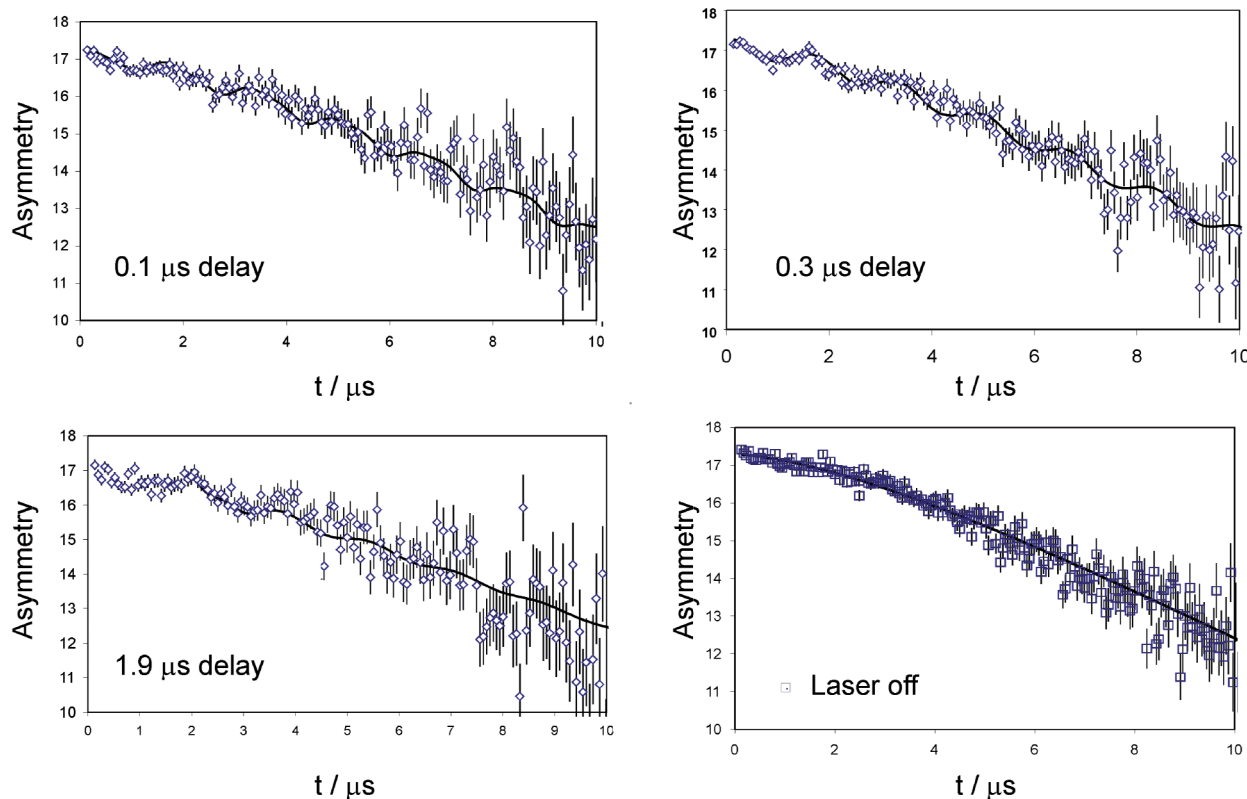
Figure 5. The asymmetry in powdered rose bengal with and without 532 nm laser irradiation (20 mJ/pulse) at different positive time delays relative to the muon pulse.

where t is time, A_i the asymmetry of the fraction i in its given environment, λ_i the relaxation rate of the muon spin in that environment, w_i the corresponding precession frequency, and φ_i the initial phase for this fraction. The parameters of interest, A_i, λ_i, and w_i are extracted from fits of equation 3 to experimental data, and provide information on radiolysis reactions, kinetics, and hyperfine interactions (in Mu or muoniated radicals). At ISIS, the Mu amplitudes are most easily found in a weak field of around 2 G. In these low fields the two muonium "triplet" frequencies are very close and unresolved, so the asymmetry is fitted with a single oscillating term.

Experiments were conducted using aqueous solutions of RB over the concentration range 10^{-5} M to 5×10^{-5} M at 298 K and 1 bar external pressure, and in the presence of a 2 G magnetic field transverse to the muon spin polarization. Timing was arranged so that the beginning of the muon pulse was concurrent with laser excitation. Figure 6 presents an example of the observed asymmetry in a 5×10^{-5} M aqueous solution of RB with and without 532 nm laser excitation (10 mJ at the sample in 2×20 mm beam). The ratio of photons (per pulse) to RB molecules in the path of laser beam is almost 1/1. The curves are fits of equation 3 to the experimental data. The relaxation

rates (λ_i in equation 3) corresponding to the reaction of Mu with RB were always increased after laser irradiation, as can be seen in the example from Figure 6. Thus, the rate constant for Mu reaction (k_2) with RB in its lowest electronic excited state (triplet state) is larger than the reaction with RB in the ground state (k_1). Measurements at different concentrations suggest $k_2/k_1 = 2.0 +/- 0.3$. In the future, by comparing Mu reaction rates with those of atomic hydrogen or deuterium, we can apply laser-muon spin spectroscopy to the study of KIEs as a function of excitation energy for a variety of reactions. All studies of KIEs for Mu reactions have so far involved only molecules in their ground states. Therefore, when it comes to reaction dynamics, the ability to perform studies under laser excitation, as exemplified by our results presented in Figure 6, is important in initiating studies of the most sensitive KIEs (due to large mass ratios H/Mu and D/Mu) in the excited states.

In another pump-probe study we used rose bengal as a photosensitizer (its method of action in PDT) to transform ground state (triplet) O_2 to singlet O_2 and compared the rate of reaction of Mu with triplet O_2 as compared to singlet O_2. Figure 7 presents an example of the observed asymmetry in a 10^{-5} M aqueous solution of O_2 and 10^{-5} M RB with and without (Figure 7b) 532 nm laser excitation. The curves are fits of equation 3 to the experimental data. Again there are very clear differences between the two spectra.
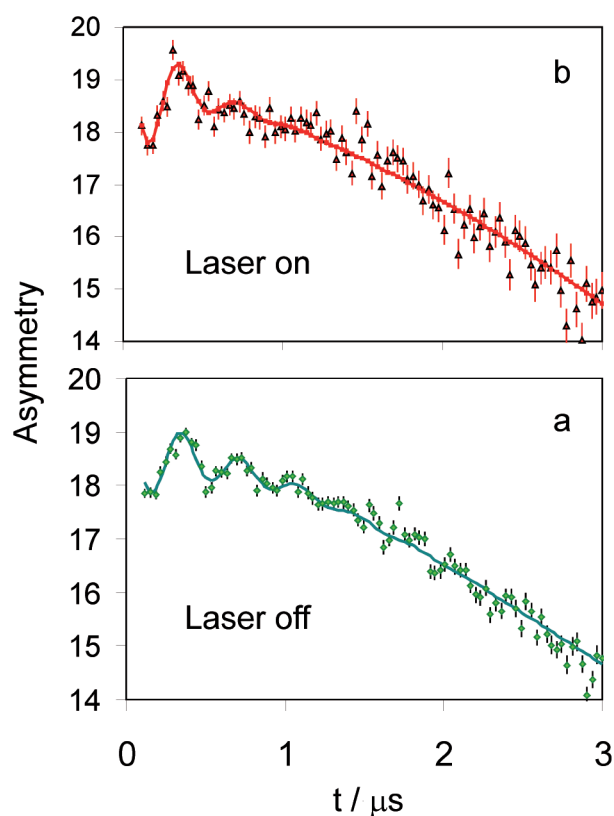

Figure 6. (a) The asymmetry in 5×10^{-5} M RB aqueous solution at 2 G; relaxing signal is due to Mu addition to the aromatic ring of RB in the ground state (in the absence of laser irradiation). (b) The asymmetry in 5×10^{-5} M RB aqueous solution at 2 G when irradiated with 532 nm laser radiation with the beginning of the muon pulse concurrent with laser excitation; the curves are fits of equation 3 to the data. The sizes of error bars are smaller in laser off experiments due to longer laser off period as compared to laser on (hence the higher statistics of the laser off data).
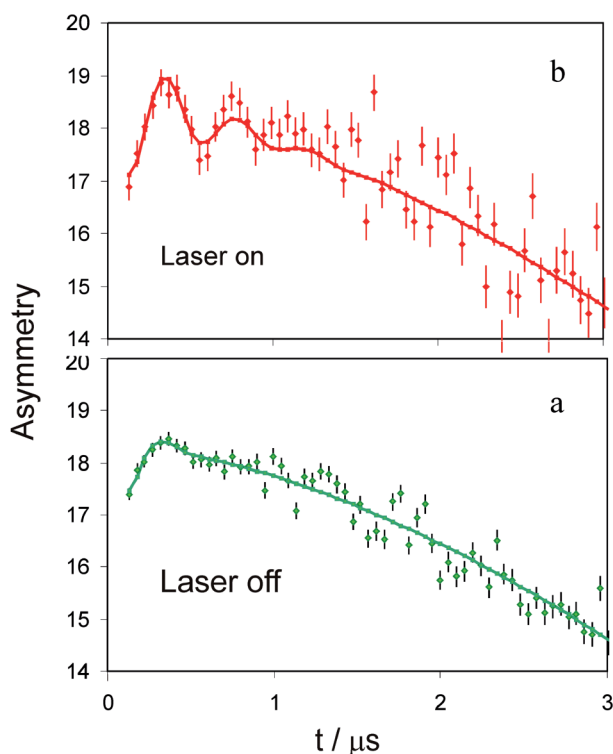

Figure 7. (a) The asymmetry in 10^{-5} M O_2 and RB aqueous solution at 2 G; relaxing signal is due to Mu electron spin exchange with oxygen electron (in the absence of laser irradiation). (b) The asymmetry in 10^{-5} M O_2 and RB aqueous solution at 2 G when irradiated with 532 nm laser radiation with the beginning of the muon pulse concurrent with the laser excitation; the curves are fits of equation 3 to the data. The reaction is addition of Mu to singlet O_2.

Conclusion

In summary we have developed two novel techniques, laser-muon spin spectroscopy and laser pump-muon magnetic resonance probe, which combine the facilities available within the Central Laser Facility and the µSR techniques available within the ISIS facility at RAL. These techniques, which, for the first time, extend muon chemistry into the realm of excited states, have a wide variety of potential applications in the fields of radiation chemistry, chemical dynamics and free radical chemistry. The techniques will allow the study of the dynamics of different intermediates generated during muon thermalization. This would be a unique contribution to the field of non-homogeneous chemical dynamics and reactions under far from equilibrium conditions. Eventually, these studies would allow us to fully characterize the end of track chemistry involved in radiolysis processes.

Our next generation of experiments will study Mu reactivity, similar to the studies of the reactions of Mu with O_2. One experiment of this nature would be to pump a molecule to a vibrational excited state with a tuneable laser, for example H_2O ($v = 4$)*. We would then compare the Mu relaxation rate of the Mu + H_2O ($v = 4$)* reaction with that of ground state H_2O. The latter reaction is extremely slow even at temperatures as high as 400°C and pressures as high as 400 bar[6]. Since Mu + H_2O is quite endoergic, large zero point energy shifts are expected at the transition state. These will be offset by vibrational excitation , yielding orders of magnitude enhancement in rate, a well-known effect in kinetics studies. Such studies of KIEs as a function of excitation energy have never been performed before, since all Mu reactions that have been studied so far involve molecules in their ground states. Our results presented in Figures 6 and 7 are important in opening the door to studies of the most sensitive KIEs in the excited states. Also interesting, but *very difficult* with present muon intensities, is the use of laser-induced fluorescence spectroscopy to measure final state distributions where recent developments in pulsed laser systems in the NIR region might allow for the observation of states such as MuO* (formed, for example, in the Mu + H_2O* reaction in the gas phase).

In the realm of free radical chemistry in excited states, our studies of triplet states could be extended to studies of muoniated free radicals (both organic and inorganic) in different high spin excited states. A combination of these studies with reaction dynamics studies in triplet states as well as mechanisms of reactions under laser excitations will be valuable for further PDT developments. Another application would be studies of laser-induced magnetization, which is similar to laser-induced ZF-µSR oscillations of the present experiments. However, in this case interactions would result from changes in magnetic interactions between molecules rather than local excitations. Also, from the fundamental perspective, our current studies open the door for future studies of hyperfine interactions in selected excited states, in particular selected vibrational and electronic excited states.

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