CR8407179

2

THE FORMATION AND REACTIVITY OF THE μ^+ MOLECULAR ION NeMu$^+$

Donald G. Fleming, Randall J. Mikula*, Masayoshi Senba,
David M. Garner and Donald J. Arseneau

Dept. of Chemistry and TRIUMF, University of British Columbia,
Vancouver, B.C., V6T 1Y6, Canada.

Abstract

Evidence for the formation and reactivity of the positive muon
molecular ion NeMu$^+$ at room temperature in a low pressure Ne moderator to
which trace amounts of Xe, CH$_4$, NH$_3$ or He have been added, is reported.
A two component relaxation of the diamagnetic muon spin rotation (μSR)
signal is seen upon the addition of trace amounts of Xe to Ne; a fast
relaxing component with bimolecular rate constant $(3.6\pm0.6) \times 10^{-10}$ cc
atom^{-1} s^{-1} is thought to be due to thermal muonium formation in a charge
exchange process while the other slow relaxing component is attributed to
a muon transfer reaction, as in proton transfer studies. With CH$_4$ or NH$_3$
added to Ne there is, at most, only a very slow relaxation seen, even
though thermal muonium formation is expected, in analogy with Xe. These
latter results may be due to very fast, possibly tunneling assisted, muon
transfer reactions, the first time that such processes have been at all
characterized.

*Present address: Energy Mines and Resources, CANMET/ERL, Western Research
Laboratory, P.O. Box 3294, Sherwood Park, Alberta, Canada T8A 2A6.

1. Introduction

The study of both molecular ion bound states and ion-molecule reactions, particularly those involving the rare gas hydrides, has long been of interest to the chemical physics community [1-15]. The positive muon (μ^+) and its muonium atom ($Mu = \mu^+ e^-$), with a mass only 1/9 that of the proton, can be considered a useful complement to the proton in atomic and molecular physics studies [16-23]; the most recent example being the calculations of Fournier and Govers of the rovibrational levels of the μ^+ analogs of HeH^+ $(HeMu)^+$ and $NeH^+ (NeMu)^+$ [16]. In fact, within the Born-Oppenheimer approximation, the positive muon (Mu atom) is chemically identical to the proton (H atom) and its unprecedented light mass provides for the possibility of observing very large isotope effects [16, 19, 24]. In particular, a study of rare gas "muides" of the positive muon, in comparison with their protonic cousins, should provide important information on both the nature of the intramolecular potential as manifest in the spectrum and lifetimes of bound and quasi-bound rovibrational levels, and on the dynamics of specific ion-molecule reactions.

In a muon spin rotation (μSR) experiment, evidence pertaining to the formation and reactivity of μ^+ molecular ions in general can be obtained from a measurement of the amplitudes and relaxation rates of the corresponding μSR signal in a given moderator. This idea was first explored in some preliminary experiments at the now defunct 184" cyclotron in Berkeley [25] with further measurements carried out at TRIUMF in ~1978 where the molecular ions $NeMu^+$ and $HeMu^+$ were tentatively identified [17, 18]. Hughes in fact first predicted that diamagnetic muon relaxation in pure He could be due to a spin rotation interaction of $HeMu^+$ and he estimated the corresponding magnetic field to be ~30 G [22]. This would correspond, however, to a relaxation rate about an order of magnitude faster than is actually observed [17]. In refs. [17] and [18], the magnetic field, limited to <75 G, was sufficiently low and inhomogeneous over the large stopping volume of the target that a reliable measurement of the diamagnetic muon relaxation rate was compromised. We have recently constructed a set of 1.5 m diameter Helmholtz coils capable of homogeneous fields up to 300 G which allow a much more precise determination of such rates. The first studies with this apparatus characterizing

the existence and reactivity of the NeMu$^+$ molecular ion are reported herein. Comparison with the thesis data of ref. [17] is also made. The results are of importance not only to the theoretical concepts referred to above but also to an understanding in general of the actual <u>diamagnetic</u> environment of the positive muon as a result of its various thermalization processes in matter [20, 26].

2. The μSR signal in gases

Positive muons are produced with kinetic energies of about 4 MeV (or greater) and 100% longitudinally spin polarized in the decay of positive pions ($\pi^+ \to \mu^+ \nu_\mu$). After traversing beam line and gas target windows and a defining muon counter, the μ^+ enters the gas with about 2.5 MeV of energy, far greater than energies of atomic interest. Most of the muon's energy is lost in Bethe-Bloch ionization of the stopping medium until a kinetic energy of ~35 keV is reached. At this point, muonium formation begins to be important and the muon enters into a series of charge exchange cycles with the moderator M,

$$\mu^+ + M \xrightarrow{\sigma_{10}} Mu + M^+$$

$$e^- + M + \mu^+ \xleftarrow{\sigma_{01}} M + Mu \tag{1}$$

where, in analogy with proton charge exchange studies [27], σ_{10} is the cross section for electron capture (forming the muonium atom) and σ_{01} is the cross section for electron loss [17,20]. There are about 80 of these charge exchange cycles as the incident muon loses about 30 keV of energy, ultimately emerging with an energy of ~30 eV depending on the specific values of the cross sections σ_{10} and σ_{01} near the end of the charge exchange region. At these energies, the muon will either be bound in the paramagnetic muonium atom or still be free in the gas. These species then thermalize via elastic and inelastic scattering processes with the moderator gas and it is during this last stage of energy loss that hot atom or hot ion reactions are likely, placing the muon in a diamagnetic environment (e.g., as a molecular ion). The total slowing-down time in a gas like Ne or Ar is ~30 ns at 1 atm. pressure [17,20]. Much later, with a mean life $\tau_\mu = 2.2$ μs, the muon decays emitting a positron preferentially along its spin direction ($\mu^+ \to e^+ \nu_e \bar{\nu}_\mu$). It is this decay positron which is detected in the experiments.

The basic experimental technique has been described in detail
elsewhere [17, 20, 21] and only its salient features will be mentioned
here. The muon beam was stopped in a gas target containing 99.99% pure
Ne at pressures near 1 atm to which trace amounts (~100 ppm) of Xe, He,
NH_3 or CH_4 were added. The concentrations of these reactant gases were
determined by dilution, having first measured their pressures in a small
standard volume (~10 cc), and then sweeping them into the much larger
target vessel (~30 ℓ) with moderator gas. This target vessel was placed
in the centre of a Helmholtz coil arrangement which provided a magnetic
field transverse to the muon spin in the range ~1 G to ~300 G. In a
diamagnetic environment the muon spin precesses essentially as a free
muon (chemical shifts in a μSR experiment are on the order of 10 ppm
[28], too small to be measured with standard techniques) with a gryomag-
netic ratio γ_μ = 13.55 kHz G^{-1}, whereas paramagnetic Mu precesses
essentially as an S=1 electron, with γ_{Mu} = 1.39 MHz G^{-1}. In a given
magnetic field then, Mu precession is 103 times faster than diamagnetic
muon precession so that these different magnetic environments can easily
be distinguished; in practice, experiments are usually conducted in a
field of about 8 G for the observation of Mu precession and in >100 G
field for the observation of diamagnetic muon precession. In this
article we report on measurements of muon precession in diamagnetic en-
vironment only. Since decay positrons are emitted preferentially along
the muon spin direction, a counter telescope fixed in the plane of pre-
cession registers events with maximum probability each time the muon spin
sweeps past, giving rise to a μSR "signal", S(t). In practice, two
separate counter telescopes were utilized, giving independent sets of
data in both "Top" and "Bottom" histograms. Examples are shown in fig. 1
(a typical result from the top set of counters) for diamagnetic muon
precession in pure Ne at 1300 torr pressure in a field of 288 G and in
fig. 2 for the same Ne doped with 0.26 torr (200 ppm) of Xe.

Data of the type seen in fig. 1 can be fit to a single
exponential (λ_1) in the usual manner [17, 20], but in the case of fig. 2
it is clear that there is a second component present which necessitates a
fit to a more general form of the μSR signal S(t), given by

$$S(t) = A_1 e^{-\lambda_1 t} \cos(\omega t + \phi) + A_2 e^{-\lambda_2 t} \cos(\omega t + \phi) . \qquad (2)$$

where A_1, λ_1 and A_2, λ_2 are the amplitudes and relaxations for both com-
ponents and ω, ϕ are the corresponding Larmor frequencies ($\omega = 2\pi\nu$) and
initial phases (actually found to be the same for both components),
respectively. The solid lines shown in figs. 1 and 2 are χ^2 fits to the
data. It is important to note that there can be only one muon in the
system at a time and hence there can be no possibility of any muon-muon
interactions giving rise to spin relaxation.

3. Results

It can be seen in fig. 1 that there is a very slight relaxation
($\lambda_1 = 0.024 \pm 0.002 \ \mu s^{-1}$) of the muon signal in pure Ne but, as in
ref. [17], this is probably still dominated by field inhomogeneity
effects. The Helmholtz coils have been designed to give a homogeneity of
0.01% over the large muon stopping region but the harsh magnetic environ-
ment at the end of the beam line reduced this to about 0.1%. We are
currently trying to improve this situation. While it has not yet been
possible then to measure intrinsic muon relaxation in pure gases, we are
able to examine the effect of trace amounts of added reactants (X) as
manifest in an increased relaxation rate relative to the background value
λ_0 seen in the absence of reactant. Results have been obtained for Xe and
CH_4 added to Ne at 1300 torr and 1500 torr total pressures, for Xe added
to Ne at 900 torr and also for Xe/He mixtures added to Ne at 1300 torr
total pressure. Reference is also made to earlier data [17] obtained for
pure He and for NH_3 added to Ne. Representative results of the fits of
eq. (2) to the present data obtained by adding Xe and Xe/He to Ne at
1300 torr total pressure are given in table 1. The effect of added Xe is
dramatically illustrated by the comparison of figs. 1 and 2. There are,
as noted above, two relaxations apparent in fig. 2, a slow relaxation (λ_1
$= 0.035 \pm 0.008 \ \mu s^{-1}$) and a much faster one ($\lambda_2 = 2.80 \pm 0.24 \ \mu s^{-1}$). Similar
results were obtained at different Xe concentrations. These data
represent the first observation of two markedly distinct diamagnetic muon
relaxation rates in a gas sample. Although the value of λ_1 is admittedly
near the lower limit of detectability, it is larger than that seen in

pure Ne (fig. 1) and moreover exhibits a trend with increasing Xe
concentration (fig. 3).

There is an additional effect apparent in comparing figs. 1 and 2,
namely in the initial amplitude of the μSR signal. Upon the addition of
200 ppm Xe, the initial amplitude $(A_1 + A_1)$ is reduced by almost a factor
of three (table 1). This is due to epithermal Mu formation in the charge
exchange process $\mu^+ + Xe \rightarrow Mu + Xe^+$, as discussed in detail in ref. [20].
The observed diamagnetic amplitude decreases with increasing Xe concen-
tration becoming asymptotic to zero (after ~10% corrections for muon
stops in the walls of the target vessel) at concentrations ~400 ppm,
corresponding to the 100% Mu fraction seen in the pure gas [20]. Very
similar results were seen with added CH_4 and NH_3 although in these cases
the diamagnetic amplitudes were asymptotic to ~10% of their maximum
values corresponding again to the same fractions observed in pure gases.
It should be emphasized that the relaxations λ_1 and λ_2 are due to thermal
processes since these occur on time scales much longer than the
thermalization time of ~30 ns.

Averaged results of the relaxations found in top and bottom
histograms (table 1) are plotted as a function of Xe concentration for
both λ_1 and λ_2 in figs. 3 and 4, respectively. As in muonium reaction
studies [19, 21], these data can be described by the straight line

$$\lambda = \lambda_0 + k \, [X] \qquad (3)$$

where λ_0 is the background relaxation referred to above, [X] is the
concentration of the added reactant and k is the bimolecular rate
constant. The fit to the slow relaxation data in fig. 3 gives
$k_1 = (1.8 \pm 0.4) \times 10^{-12}$ cc atom^{-1} s^{-1} while the fast relaxation data in
fig. 4 gives $k_2 = (3.0 \pm 0.3) \times 10^{-10}$ cc atom^{-1} s^{-1} for the solid line fit
shown. Similar experiments were carried out for CH_4 added to Ne but in
this case only a single very slow relaxation essentially consistent with
zero was observed $(k_1 \sim (0.5 \pm 0.3) \times 10^{-12}$ cc molec^{-1} s$^{-1})$. Similarly, in
our earlier study of NH_3 added to Ne [17] only a single slow relaxation
was seen; these data are given in fig. 5 $(k_1 = (5 \pm 2) \times 10^{-12}$ cc molec^{-1}
s$^{-1})$. It is to be noted in fig. 3 that the value of λ_0 is the same as

in pure Ne (λ_0 = 0.024±0.002 μs^{-1}) while in fig. 4 it is a factor of about 30 larger when taken as the intercept consistent with the best straight line fit (χ^2 = 1.4). If the fit (dashed line) is forced to include the pure Ne value for λ_0 (which seems physically correct) we find k_2 = (4.2±0.3) × 10^{-10} cc atom s^{-1} but at the expense of essentially having to ignore the first data point and with a considerably worse fit (χ^2 = 6.6). This could mean that there has been an error in determining the concentration of this first point or possibly that there is an additional much faster component present in the data. We prefer to quote at this time an average of the above two values (with an expanded error) giving k_2 = (3.6±0.6) × 10^{-10} cc $atom^{-1}$ s^{-1} for the fast relaxing component of fig. 2, pending a series of further experiments at lower Xe concentrations over a range of different total pressures.

The present relaxation data for Xe and CH_4 differ considerably though from that reported in an earlier study [17,18]. As noted above, the apparatus used then gave a considerably less homogeneous and also lower magnitude (~70 G) magnetic field. The lower field in particular rendered the observation of very fast diamagnetic muon relaxation rates (as in fig. 4) virtually impossible. Nevertheless, despite the difficulties in that earlier study we can be confident of certain trends in comparison with the present data; in particular, the absence of any fast muon relaxation in the case of NH_3 added to Ne (fig. 5). A summary of rate constants found from the muon relaxation data in Xe, CH_4 and NH_3 doped Ne is given in table 2.
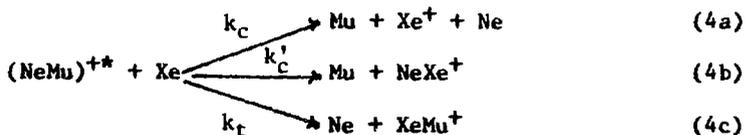
4. Discussion

There are two quantities relevant to an understanding of these data: the proton affinity (PA) and ionization potential (IP) of the reactant X in comparison with the IP of Mu itself (13.6 eV). These values are compared in table 3. Consider now the consequences of the collision of a free muon at thermal energies with any of the reactants of table 3. Muonium must form since the energy defect for the charge exchange process $\mu^+ + X \rightarrow Mu + X^+$ is exothermic ($\Delta E < 0$) in every case. Although such

charge exchange processes are not "resonant" in the sense of $\Delta E = 0$, we still expect 100% thermal Mu formation for $X = Xe$, CH_4 or NH_3, consistent with the extrapolation of large proton charge exchange cross sections to the thermal energy regime for these cases [20,27]. Moreover, the polarizabilities of Xe, NH_3 and CH_4 are all large [29] and the (Langevin) rates for the collision process $\mu^+ + X$ for a __free__ muon are all expected to be $\sim 10^{-8}$ cc atom^{-1} s^{-1}; hence the probability of thermal Mu formation should be very similar for all three reactants. Muonium precesses in the (288 G) magnetic field 103 times faster than the free muon, and thus __thermal__ Mu formation will lead to loss of phase coherence in the observed µSR signal and hence a relaxation of this signal. The fact that a fast relaxation is seen __only__ for the case of Xe in Ne establishes that the muon cannot be free in the gas but must be bound in a diamagnetic environment, most likely as the $NeMu^+$ molecular ion. Other diamagnetic species are possible, XMu^+ with reactant X and in the case of the molecular reactants, molecules like $MuCH_3$ may be formed as a consequence· of hot atom reactions. However, these possibilities are regarded as extremely unlikely in view of the much higher chance of collisions with the Ne moderator ($\sim 10^4$) during the thermalization processes of the muon in the gas. Moreover, in the pure gases, no diamagnetic signal is seen in Xe and in the cases of CH_4 and NH_3 hot atom reactions clearly have low probabilities [20].

4.1 Reactivity of the NeMu$^+$ ion

The binding energy of the μ^+ in $NeMu^+$ (and in $HeMu)^+$ can be estimated from the known values for NeH^+ and HeH^+ [10] using a simple harmonic zero point mass correction [17]. However, accurate values have been calculated in ref. [16] and these are given in table 4 along with the corresponding values for the hydride ions. Note the enormous isotope effect of the much lighter mass muon ($m_\mu - 1/9 \, m_p$). This has the consequence that the rovibrational level density in $NeMu^+$ ($HeMu)^+$ is about an order of magnitude less than in their protonic analogs.

The two-component relaxation seen for Xe in Ne in fig. 2 can be understood in terms of the following reaction scheme,

$$k_c \longrightarrow Mu + Xe^+ + Ne \qquad (4a)$$

$$(NeMu)^{+*} + Xe \overset{k_c'}{\longleftarrow} Mu + NeXe^+ \qquad (4b)$$

$$k_t \longrightarrow Ne + XeMu^+ \qquad (4c)$$

where $k_c(k_c')$ and k_t are meant to denote bimolecular rate constants for charge exchange and muon transfer processes, respectively. The difference between channels (4a) and (4b) is in the formation, or not, of a bound $NeXe^+$ complex. Such complexes are expected to have binding energies ~1 eV [30] and a two-body final state is perhaps more likely from the point of view of available phase space. Although we could not distinguish (4a) from (4b), the production of muonium by either channel (or both) results in the immediate loss of phase coherence as the muon is transferred from the diamagnetic molecular ion environment to paramagnetic muonium. As such it provides a ready explanation for the very fast relaxation seen upon $NeMu^+ + Xe$ collisions (fig. 2) with the corresponding rate constant k_2 (fig. 4) being identified with either k_c or k_c' or their sum. On the other hand, reaction (4c), the muon analog of a proton transfer reaction, is the precursor for the observed slow relaxation component of fig. 2. One would indeed not expect this latter process to give rise to any appreciable relaxation of the µSR signal because the muon again finds itself in a diamagnetic environment. Thus, µSR does not provide a direct observation of the process corresponding to k_t. However, table 1 shows the amplitudes A_1 and A_2 to be comparable, indicating that the branching ratio of reactions (4a) and/or (4b) and (4c) is about 0.5, from which it may be inferred that $k_t \approx (k_c + k_c')$. Indeed, it is frequently the case that charge transfer and proton transfer proceed with comparable rates at low energies [31]. On the other hand, as noted already, there is a discernable trend to increasing λ_1 with increasing Xe concentration in fig. 3, giving rate constant k_1. This relaxation could conceivably be due to a spin rotation interaction of $XeMu^+$ - Xe collision complexes, in analogy with NMR studies in other rare gas systems [32]. It must be understood that $k_1 \neq k_t$; k_t corresponds to the relatively fast but not directly observable muon transfer reaction (4c), whereas k_1 corresponds to the subsequent slow relaxation of the $XeMu^+$ molecular ion which is only just observable. In order to be able to make more

definitive statements of the meaning of k_1, we will have to improve the
effective homogeneity of our apparatus by something like a factor of
ten.

From the values in tables 3 and 4 it can be seen that reaction (4a)
from the ground state of the NeMu$^+$ ion is endothermic by 0.4 eV (the
corresponding HeMu$^+$ would be endothermic by 0.1 eV). Hence, any
observed fast relaxation in collisions with Xe due to this reaction must
be due to NeMu$^+$ in an excited state (as denoted by the *), with an
excitation energy > 0.4 eV (it is unlikely that electronically excited
Xe* would play any role). On the other hand, reaction (4b) would be
exothermic even from the ground state by ∼0.6 eV, depending on the bind-
ing energy of the NeXe$^+$ ion [30]. Regardless of the nature of the
final state in (4a) or (4b) it seems likely that NeMu$^+$ would form in a
long-lived ($\tau > \tau_\mu = 2.2$ μs) excited state. This is typical of a variety
of formation processes of rare gas hydrides [5-7,31]. From the calcula-
tions of ref. [16] there are a large number of bound states which satisfy
this requirement as well as a long-lived v=0 J=1 quasibound state
($\tau = 4.2 \times 10^{-6}$ s). The radiative lifetime of the bound states are all
expected to be much longer than the muon lifetime, of order 100 μs in
both HeMu$^+$ and in NeMu$^+$, based on the calculations of ref. [13], [14] and
[16] and on the measured values of refs. [5] and [6].

Corroborating evidence for the formation and reactivity of (NeMu$^+$)* in
an excited state was obtained by adding trace amounts of He to the Ne/Xe
reaction mixture, illustrated by the μSR signal in fig. 6. This was
obtained at 1300 torr Ne total pressure with added Xe and He at 200 ppm
and 100 ppm, respectively. In comparison with fig. 2, one notes a
dramatic decrease in the amplitude of the fast component. The relaxa-
tions, however, are essentially (within 2 standard deviations) unchanged.
Similar effects were seen in a 35 ppm Xe/Ne mixture to which 17 ppm He
was added. Results for the corresponding amplitudes are given in table 1.
These particular mixtures were chosen to reflect essentially equal rates
for NeMu$^+$-Xe and NeMu$^+$-He collisions. The results are understandable in
terms of efficient vibrational-translational (V-T) energy transfer in a
competition between NuMu)$^{+ *}$-Xe and (NeMu)$^{+ *}$-He collisions, placing the

$(NeMu^+)^*$ in a non-relaxing state at a lower excitation energy. Such
processes are known in general to be very efficient for small light atoms
[1,33], particularly for He atoms; the simplistic explanation in the
present case being that the velocity of the faster-moving He atom is
better matched to the vibrational period of the molecular ion than is the
Ne atom. Indeed, in ref. [17], it was found that even in the case of Xe
added to He itself there was essentially zero diamagnetic muon relaxa-
tion, in marked contrast to Ne (fig. 2), which can again be understood in
terms of an efficient V-T energy transfer, in this case of $(HeMu^+)^*$-He
collisions.

The experimentally averaged thermal rate constant $k_2 = (3.6\pm0.6) \times 10^{-10}$ cc atom^{-1} s^{-1} for the process $(NeMu)^{+*} + Xe \rightarrow Mu + Xe^+$ (fig. 4) is
about a factor of three lower than the classical Langevin rate, k_L
(table 2). It is well known though that the Langevin limit is for a par-
ticularly simple type of ion-molecule interaction (induced dipole) and
there can be many additional factors involved, affecting even the
classical reaction rate [1, 2, 34]. Moreover, the overall reaction rate
reflects the particular topology of a given reaction channel and can
generally be expected to be different (usually smaller) than the maximum
encounter rate. Indeed the present result of $k_L/k_2 \sim 3$ for reaction (4a)
and/or (4b) is not atypical of a wide variety of thermal ion molecule
reactions in that experimentally determined rate constants agree with the
calculated Langevin values to within a factor of 2 or 3 [2-4, 7, 35]; in
most cases, in fact, k_L gives the maximum thermal rate constant found
experimentally.

The most surprising result emerging from the present experiments is
the lack of any fast relaxation seen for NeMu$^+$ in the presence of either
X=CH$_4$ or NH$_3$ (fig. 5). In the case of the analog of (4a), reaction with
CH$_4$ is endothermic by 0.8 eV but with NH$_3$ it is exoergic even from the
g.s. of $(NeMu)^+$; the analogs of (4b) would presumably be exoergic from the
$(NeMu)^+_{g.s.}$ in both cases (if the products are indeed formed). At this
point it is worth recalling that observation of the collision process
$(NeMu)^{+*} + X$ is possible only if it results in Mu formation ($k_2 = k_c + k_c'$);
the competitive channel (k_t) forming the XMu$^+$ molecular ion (4c) leads
to a very small relaxation (with Xe). In fact, for both X = CH$_4$ and NH$_3$,

the measured rate constant corresponding to this slow relaxation is ef-
fectively consistent with zero, particularly in the case of CH_4 (table 2).
The fact that there is <u>no fast</u> component seen for both $X=CH_4$ and NH_3 is a
strong indication of the existence of very fast muon tranfer reactions.
In order for us not to be able to observe the expected Mu formation
channel, μ^+ transfer from $NeMu^+$ to CH_4 (or NH_3) must occur on a time scale
<100 ns at the lowest concentrations. This corresponds to a bimolecular
rate constant $k > 7 \times 10^{-9}$ cc $molec^{-1}$ s^{-1}, which is at least a factor of 5
<u>faster</u> than the Langevin rate, k_L (table 2); the corresponding cross
section would be of order 100 $Å^2$.

Classically, a trend to increased muon transfer in the order
$X=NH_3 > CH_4 > Xe$ is expected on the basis of the proton affinities
given in table 3 (the corresponding muon affinities can be expected to
show the same trends); i.e., in the direction of increasing exothermicity,
in analogy with proton transfer reactions [3,4,7], particularly from rare
gas hydride ions. However, the dramatic dichotomy seen in the present
study between $X=Xe$ on the one hand and $X=CH_4$ and NH_3 on the other cannot
be explained on this basis. Although polyatomic molecules generally have
larger PA's and hence tend to exhibit faster ion-molecule reaction rates
than diatomics or atoms do, these are still rarely faster than the
Langevin rates [4,7]. It is to be noted though that molecular quadrupole
moments and even intrinsic dipole moments can have important effects on
the classical charge-induced dipole interaction [36,37], the NH_3 molecule
itself being a case in point. Even in these cases, though variational
theories can yield upper bounds for rate constants well in excess of the
Langevin ones [36], the best agreement with experiment in the thermal
energy regime is again within a factor of two of the simple Langevin
rate. To our knowledge there is no precedent for a proton (muon) trans-
fer reaction in the gas phase at <u>thermal energies</u> which is >5x faster
than the Langevin rate (protonation reactions in liquid media, particu-
larly the Gartenhaus mechanism in water, can be regarded as special cases
of <u>intra</u> molecular proton transfer reactions which are known to be very
fast in certain systems [38]). All of the above-mentioned calculations
are classical in origin and the fact that we see such an enhanced transfer
rate in the case of the positive muon may indicate a significant effect

of muon tunneling in the NeMu$^+$ + CH$_4$ (NH$_3$) collision process. The utility of the light muon mass as a probe of quantum tunneling in muonium reactivity is well established [19,24] but the above processes may represent the first time that similar effects have been characterized in muon transfer reactions.

There are a number of other possible explanations that should also be considered, all of which seem less likely to us though than a fast muon transfer reaction. Vibrational excitation and curve crossing (surface hopping) phenomena can have dramatic effects on both charge exchange and proton transfer reactions at different kinetic energies [31], particularly vibrational excitation at low (thermal) energies, promoting resonant ($\Delta E=0$) charge transfer. By contrast, vibrational excitation is expected to have relatively little effect on proton (muon) transfer at these energies. As alluded to above, highly rovibrational excited states of (NeMu)$^{+*}$ [16] may well facilitate resonant charge transfer in the (NeMu)$^{+*}$ + X collision process, regardless of whether a Ne molecular ion bound state is again formed in the product channel (4b) or not. Perhaps there is a very efficient V-T (or V-V) energy transfer in the case of collisions of both NH$_3$ and CH$_3$ with (NeMu)$^{+*}$, as is known to be the case for several small molecules in other reactive systems [39]. If this were true, however, the corresponding cross sections would have to be considerably larger than those in (NeMu)$^{+*}$-He collisions since we still observe a fast relaxation (with reduced amplitude) in (NeMu)$^{+*}$/Xe/He mixtures, as discussed already (fig. 6). Such large cross sections seem unlikely in view of the previously mentioned efficiency for He in promoting V-T relaxation [33] (although V-V transfer is of course not possible in collisions with He). It is also conceivable that radiation damage effects initiated by fragmentation reactions of energetic charged particle beams in molecular gases [40] could sufficiently affect the environment of the muon that thermal Mu formation in subsequent collisions (e.g., with radiation produced H$_2$) would no longer be possible. However, in view of the intensity of our ~3 MeV beam (<10^5 μ^+ per second) such a process would seem to be extremely unlikely. Finally, if the muon were bound in a diamagnetic chemical bond as a result of hot atom reactions during its slow-

ing-down process forming, e.g., MuCH$_3$ (or MuNH$_2$), subsequent collisions with CH$_4$ (or NH$_3$) at thermal energies would not effect any change in the muon polarization, except possibly on the very slow time scale of NMR relaxation times seen in similar systems [32,41]. Again though, as noted earlier, such a process is regarded as very unlikely in the present study where only ~100 ppm amounts of CH$_4$ (or NH$_3$) have been added to Ne moderator, compared to earlier studies in the pure molecular gases where ~90% of incident muons thermalize as paramagnetic muonium [20].

4.2 Formation of the NeMu$^+$ ion

The mechanism of the formation of NeMu$^+$ (and other rare gas "muides") is not clear at this time but it seems that there are basically only two possibilities,

$$\mu^+ + Ne \rightarrow (NeMu)^{+*} + h\nu , \tag{5a}$$

$$Mu + Ne^* \rightarrow (NeMu)^{+*} + e^- . \tag{5b}$$
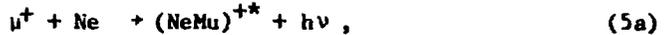
These reactions are only likely to occur with appreciable probabilities well after the charge exchange regime, in the energy range from ~20 eV to $k_B T$ [20]. In the case of reaction (5a), which might involve a termomolecular encounter, the relative energy must be low enough to allow sufficient time for reaction to occur. In particular, recent studies of orbiting resonances in the He-H$^+$ system [12] suggest that HeMu$^+$ (and hence probably also NeMu$^+$) would form with appreciable cross section only at kinetic energies < 0.5 eV. Larger molecular complexes of the rare gas hydrides are also well known [15], but their formation is regarded as extremely unlikely in the present context (similar complexes formed in negative muon capture [42] proceed by a totally different mechanism). Consideration of the energetics for Mu + Ne and Mu + Ne$^+$ (and similarly for He) indicate further that reaction (5b) is only likely to occur if the Ne(He) atom has been placed in an excited state by collision with the Mu atom, notably in a metastable S state. In this case, the reaction scheme depicted below is expected to occur at low (~20 eV) incident Mu energies,

$$Mu(\sim 20 \text{ eV}) + Ne \rightarrow Mu(\sim 2 \text{ eV}) + Ne^* (3S) \rightarrow (NeMu)^{+*} + e^- . \tag{6}$$

Further experiments, particularly on the pressure dependence of the

signal amplitudes in Ne/Xe mixtures (so that both a paramagnetic Mu and diamagnetic muon fraction can be seen) are required. It may even be possible in future experiments to detect the optical transition from the Ne^*(3S state, using single photon uv detectors.

5. Concluding remarks

Further work is in progress, including a study of both the temperature and pressure dependence of the reactivity with Xe, CH_4 and NH_3, in helium, neon and argon moderators. Experiments in both pure and mixed molecular gases are also planned with improved field homogeneity in order to properly compare NMR [31,41] and μSR relaxation phenomena. Here it is the slow time scale that is of interest (cf. fig. 3) and since proton relaxations in gases are proportional to γ_p^2 (or γ_p^4 for certain spin rotation interactions), there should be a large enhancement seen if a proton is replaced by a positive muon ($\gamma_\mu/\gamma_p = 3.18$). As such, the study of slow μSR relaxation phenomena in gases is capable of providing valuable further tests of the basic theory of NMR relaxation.

It is hoped that the present results will stimulate some theoretical calculations of ion-molecule reactions involving the positive muon; in particular, whether the proposed mechanism of significant muon tunneling is correct or not. These reactions may be very suitable as an example of H-L-H (heavy-light-heavy) systems which are currently being studied via hyper-spherical and Delve's coordinate transformations [43]. It would also be of considerable interest to have some theoretical guidance on the formation process of $NeMu^+$ and indeed on the formation of positive muon molecular ions in general.

References

[1] Electronic and ionic impact phenomena, Vol. III, Chap. 19, H.S.W. Massey, E.H.S. Burhop and H.D. Gilbody (Clarendon Press, Oxford, 1971).

[2] Kinetics of ion-molecule reactions, NATO Advanced Study Series, Vol. 40B, ed. P. Ausloos (Plenum, New York, 1978).

[3] K.R. Ryan and I.G. Graham, J. Chem. Phys. 59 (1973) 4260.

[4] D.K. Bohme, G.I. MacKay and H.I. Schiff, J. Chem. Phys. 73 (1980) 4976 and references to earlier papers contained therein; R. Walder and J.L. Franklin, Int. J. Mass. Spect. and Ion Phys. 36 (1980) 4976.

[5] J.M. Peek, Physica 64 (1973) 93; J. Schopman, P.G. Fournier and J. Los, ibid. 63 (1973) 518; J. Schopman and J. Los, ibid. 48 (1970) 190.

[6] A. Carrington, J. Buttenshaw, R.A. Kennedy and T.P. Softley, Molec. Phys. 44 (1981) 1233; D.E. Tolliver, G.A. Kyrala and W.H. Wing, Phys. Rev. Lett. 43 (1979) 1719; P. Bernath and T. Amano, ibid. 48 (1982) 20.

[7] H. Villinger, J.H. Futrell, F. Howorka, N. Duric and W. Lindinger, J. Chem. Phys. 76 (1982) 3529.

[8] D.M. Bishop and L.M. Cheung, J. Chem. Phys. 76 (1982) 2492, and earlier papers referenced therein; T.A. Green, H.H. Michels and J.C. Browne, J. Chem. Phys. 69 (1978) 101, and references to earlier papers therein.

[9] W.A. Chupka and M.E. Russell, J. Chem. Phys. 49 (1968) 5426.

[10] A. Henglein, J. Phys. Chem. 76 (1972) 3883; H.P. Weise, H.U. Mittman, A. Ding and A. Henglein, Z. Naturforsch. 26A (1971) 1122; W.G. Rich et al., Phys. Rev. 4A (1971) 2253.

[11] M. Wong, P. Bernath and T. Amano, J. Chem. Phys. 77 (1982) 693.

[12] M. Konrad and F. Linder, J. Phys. B. At. Mol. Phys. 15 (1982) L405.

[13] L. Dabrowski and G. Herzberg, Trans. N.Y. Acad. Sci. 38 (1977) 14.

[14] V. Bondybey, P.K. Pearson and H.F. Schaefer, J. Chem. Phys. 57 (1972) 1123; K. Vasudevan, Mol. Phys. 30 (1975) 437; S. Peyerimhoff, J. Chem. Phys. 43 (1968) 998.

[15] B.N. Pettit, K. Jacobson and R.L. Matcha, J. Chem. Phys. 72 (1980) 2892, and references to previous papers therein.

[16] P.G. Fournier and B.L. Govers, J. Phys.-Lettres 43 (1982) 483.

[17] R.J. Mikula, Ph.D. thesis, Univ. of British Columbia, 1981, unpublished.

[18] R.J. Mikula et al., Hyp. Int. 6 (1979) 379.

[19] D.G. Fleming, Proc. of XII ICPEAC, Gatlinburg, Tenn., 1981 ed. S. Datz (North-Holland, Amsterdam, 1982), p. 297; D.M. Garner, Ph.D. thesis, Univ. of British Columbia, 1979, unpublished.

[20] D.G. Fleming, R.J. Mikula and D.M. Garner, Phys. Rev. 26A (1982) 2527, and references contained therein.

[21] R.J. Mikula, D.M. Garner and D.G. Fleming, J. Chem. Phys. 75 (1981) 5362; D.G. Fleming, R.J. Mikula and D.M. Garner, J. Chem. Phys. 73 (1980) 2751.

[22] V.W. Hughes, Phys. Rev. 108 (1958) 1106.

[23] R.D. Stambaugh et al., Phys. Rev. Lett. 33 (1974) 568;
R.D. Stambaugh, Ph.D. thesis, Yale University, 1972, unpublished.

[24] D. Bondi et al., J. Chem. Phys. 76 (1982) 4986;
J.N.L. Connor, Hyp. Int. 8 (1981) 423.

[25] J.H. Brewer et al., Proc. of IXth ICPEAC, Seattle, Washington, 1975,
Abstracts of Contributed papers (unpublished), J.S. Risley and
R. Geballe, eds., p. 157.

[26] D.C. Walker, Hyp. Int. 8 (1981) 329;
P.W. Percival, Radiochim. Acta 26 (1979) 1;
P.W. Percival, E. Roduner and H. Fischer, Chem. Phys. 32 (1978) 353.

[27] H. Tawara, At. Data Tables 22 (1978) 491;
H. Tawara and A. Russek, Rev. Mod. Phys. 45 (1973) 178.

[28] M. Camani et al., Hyp. Int. 6 (1979) 435;
M. Castro, J. Keller and A. Schenck, ibid., 439.

[29] J.B. Hasted, Physics of atomic collisions (Butterworths, London,
1964), p. 506.

[30] K.K. Huber and G. Herzberg, Constants of diatomic molecules (Van
Nostrand Press, New York, 1979), p. 455.

[31] F.A. Houle et al., J. Chem. Phys. 77 (1982) 748, and references con-
tained therein;
E.A. Gislasen, J. Chem. Phys. 57 (1972) 3396.

[32] N.D. Bhaskar, W. Hopper and T. McClelland, Phys. Rev. Lett. 49
(1982) 25;
C.H. Volk, T.M. Kwon, J.G. Mark, Y.B. Kim and J.C. Woo, Phys. Rev.
Lett. 44 (1980) 136;
H.C. Tovey, Phys. Rev. 130 (1963) 2306.

[33] G.D. Billing and D.C. Clary, Chem. Phys. Lett. 90 (1982) 27;
D.C. Clary, Chem. Phys. 65 (1982) 247, J. Chem. Phys. 75 (1981) 209;
M. Huetz-Aubert, G. Louis and J. Taine, Physica 93C (1978) 237.

[34] D.R. Bates, J. Phys. B. At. Mol. Phys. 15 (1982) L259.

[35] D.L. Albritton, Atomic and Nucl. Data Tables Vol. 22 (1978);
A.B. Rakshit et al., J. Phys. B. At. Mol. Phys. 11 (1978) 4237.

[36] W.J. Chesnavich, T. Su and M.T. Bowers, ref. 2, p. 31, and
references contained therein.

[37] W.R. Gentry, ref. 2, p. 81;
D.J. McClure, G.H. Douglass and W.R. Gentry, J. Chem. Phys. 67
(1977) 2362.

[38] See, e.g., H. Kwart, Acc. Chem. Res. 15, 401 (1982), and references
contained therein.

[39] L.S. Dzelzkains and F. Kaufman, J. Chem. Phys. 77 (1982) 3508;
G.W. Flynn, Acc. Chem. Res. 14 (1981) 334;
G.S. Arnold and I.W.M. Smith, J. Chem. Soc. Far. Trans. 2, 77 (1981)
861.

[40] A.K. Edwards et al., J. Chem. Phys. 69 (1978) 1985.

[41] D.J. Kouri, J. Chem. Phys. 69, 4999 (1978);
M. Bloom and I. Ozier, Can. J. Phys. 54 (1976) 1712;
K. Lalita, M. Bloom and J.D. Noble, Can. J. Phys. 47 (1969) 1355;
F.M. Chen and R.F. Snider, J. Chem. Phys. 50 (1969) 4082.

[42] J.E. Russell, Phys. Rev. 18A (1978) 521;
J.S. Cohen and J.N. Bardsley, Phys. Rev. 23A (1981) 46.

[43] J. Manz, E. Pollak and J. Romelt, Chem. Phys. Lett. 86 (1982) 26;
J.M. Launay and M. LeDourneuf, J. Phys. B. At. Mol. Phys. 15 (1982)
L455.

TABLE 1: The Amplitudes (A) and Relaxations (λ) of the μSR Signals
Seen Upon the Addition of Trace Xe and He to Ne, 1300 Torr

$[Xe]$[a]	$[He]$[a]	A_1[b],[c]	$\lambda_1(\mu s^{-1})$ [b]	A_2[b]	$\lambda_2(\mu s^{-1})$ [b]
0.0	0.0	.316±.002	.023±.002		
1.4±0.1(33)	0.0	.109±.005	.030±.01	.147±.006	1.24±.07
5.7±0.1(135)	0.0	.049±.003	.030±.006	.121±.004	2.63±.17
8.5±0.2(200)	0.0	.041±.002	.041±.006	.081±.004	3.28±.27
11.4±0.2(268)	0.0	.038±.002	.043±.006	.045±.004	4.34±.76
1.4±0.1(33)	0.7±0.1(17)	.124±.005	.028±.01	.109±.006	1.80±.20
8.5±0.2(200)	4.3±0.1(100)	.032±.003	.038±.008	.035±.008	4.9±2.5

a) The concentration of added Xe or He in units of 10^{15} atoms cc^{-1}, calcu-
lated from measured volumes and assuming the validity of the ideal gas law.
values in ppm given in parenthesis.
b) Obtained from the results of the fits of eq.(1) to the data, reported
in most cases as a weighted average of results from both the Top and Bottom
histograms.
c) The amplitude of the slowly relaxing signal has been corrected for muons
scattered into the walls of the target vessel. See discussion in ref. [20].

TABLE 2: Rate Constants k for the Reactions
$(NeMu)^{+*}$ + X, for X = Xe, CH_4 or NH_3

Reactant, X	$k_{exp}(10^{-10}cc\ atom^{-1}s^{-1})$ [a]	$k_L(10^{-10}cc\ atom^{-1}s^{-1})$ [b]
Xe	k_2 = (3.6±0.6) [c]	11.0
	k_1 = (.018±.004)	
CH_4	k_1 = (.005±.003) [d]	12.5
NH_3	k_1 = (.05±.02) [e]	13.3

a) Experimentally determined rate constant.
b) Classical Langevin rate constant.
c) An average of the two fits shown in fig. 4, as discussed in the text.
d) Consistent with zero.
e) From fig. 5 (taken from ref. [17]).

TABLE 3: A Comparison of Ionization Potentials and Proton
Affinities for Different Reactants

Reactant(X)	I.P.(eV)[a]	ΔE(eV)[b]	P.A.(eV)[c]
Xe	12.2	1.4	5.1
CH_4	12.6	1.0	5.9
NH_3	10.8	2.8	8.9

a) Taken from the Handbook of Chemistry and Physics, 57th ed., 1976.
b) Exothermicity for the charge exchange process, $\mu^+ + X \rightarrow Mu + X^+$
c) Proton Affinity, from the data of Bohme et al., ref. [4]

TABLE 4: Dissociation Energies (eV) for the First Two
Vibrational (v=0,1; J=0) levels of $NeMu^+$ and $NeMu^+$

Ion	D_e	D_o	D_1
HeH^+ [a]	2.037	1.842	1.482
$HeMu^+$ [b]	2.037	1.532	0.734
NeH^+ [c]	2.265	2.085	1.76
$NeMu^+$ [b]	2.265	1.786	0.975

a) From ref. [13].
b) From ref. [16].
c) From refs. [9] and [11].

Figure Captions

1. The μSR signal in pure Ne at 288 G and 1300 torr pressure. The solid line is a χ^2 fit to the data assuming a single relaxation.

2. The μSR signal at 288 G in Ne at 1300 torr with 200 ppm of added Xe. The solid line is a χ^2 fit to the data assuming two different relaxations, giving λ_1 (slow) = 0.035±0.008 μs^{-1} and λ_2 (fast) = 2.80±0.24 μs^{-1}.

3. A plot of the observed relaxation λ_1 (slow) for Ne/Xe mixtures as a function of Xe concentration at 1300 torr total pressure. The points are an average of fits obtained from "Top" and "Bottom" histograms. The solid line is the best straight line fit to the data.

4. A plot of the observed relaxations λ_2 (fast) for Ne/Xe mixtures as a function of Xe concentration. The solid line is the best straight line fit ignoring the "λ_0" value for pure Ne while the dashed line is the best fit including this value. The squares represent fits to the fast relaxation at 1300 torr pressure while the diamonds were obtained at 1500 torr total pressure. Additional points obtained at 900 torr pressure agree within errors and are not shown.

5. A plot of the relaxation of the μSR signal seen in Ne/NH$_3$ mixtures at 930 torr and 70 G as a function of NH$_3$ concentration, assuming a single relaxation. The solid line is the best straight line fit to the data (taken from ref. [17]).

6. As in fig. 2 but with an additional 100 ppm of added He. Note the change in amplitude of the early time (fast) signal in comparison with fig. 2.
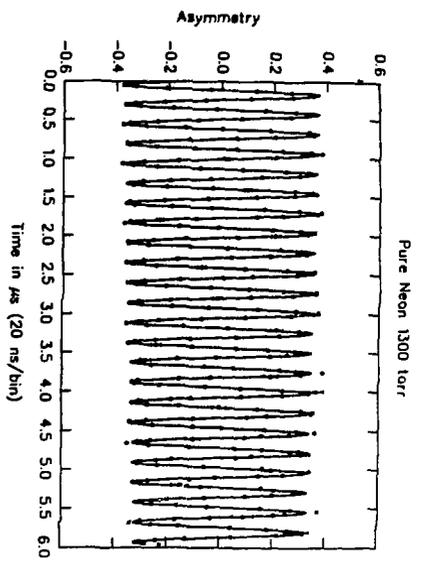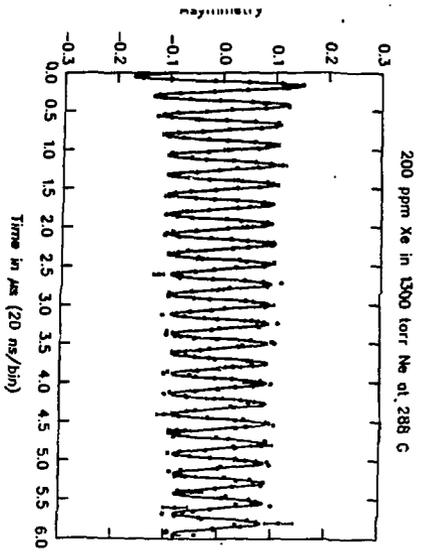
Asymmetry

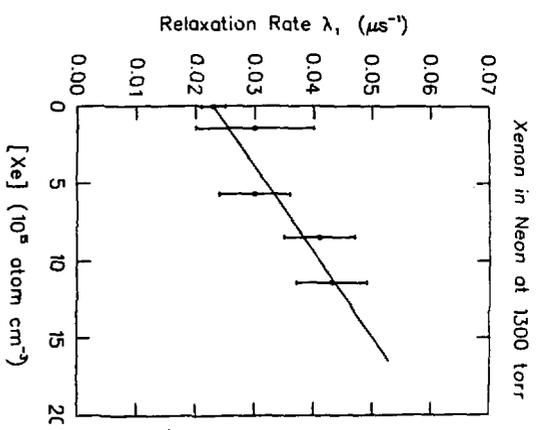Pure Neon 1300 torr

Time in μs (20 ns/bin)

Fig. 1

Asymmetry

200 ppm Xe in 1300 torr Ne at, 288 C

Time in μs (20 ns/bin)

Fig. 2

Relaxation Rate λ_1, (μs^{-1})

Xenon in Neon at 1300 torr

[Xe] (10^{15} atom cm^{-3})

Fig. 3

Relaxation Rate λ_2 (μs^{-1})

Xenon in Neon: ■=1300, ◆=1500 torr

[Xe] (10^{15} atom cm^{-3})

Fig. 4

Relaxation Rate λ_1 (μs^{-1})

Ammonia in Neon at 930 torr

[NH$_3$] (10^{15} molecule cm^{-3})

Fig. 5

Asymmetry

100 ppm He + 200 ppm Xe/1300 torr Ne

Time in μs (20 ns/bin)

Fig. 6