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D. G. Fleming, J. H. Brewer, D. M. Garner, A.E. Pifer,
T. Bowen, D. A. Delise, and K. M. Crowe

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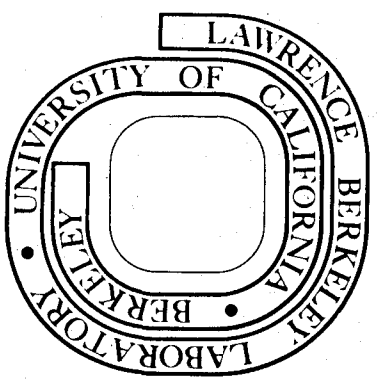

DISCLAIMER

Muonium Chemistry in Gases: $Mu + Br_2$

D.G. Fleming, J.H. Brewer and D.M. Garner, TRIUMF and Department of Chemistry, University of British Columbia, Vancouver, B.C. Canada, V6T 1W5, and

A.E. Pifer, T. Bowen, and D.A. Delise, Dept. of Physics, University of Arizona, Tucson, Arizona, U.S.A., 85721, and

K.M. Crowe, Department of Physics and Lawrence Berkeley Laboratory, University of California, Berkeley, California, U.S.A., 94720.

ABSTRACT

We report a precise measurement of the rate of reaction of muonium atoms with bromine molecules in an argon moderator gas at 1 atmosphere and 23°C The bimolecular rate constant is $k = (2.4 \pm 0.3) \times 10^{11}$ ℓ/mole-sec, ten times higher than that for the analogous reaction of hydrogen atoms. Since muonium can properly be treated as a light isotope of hydrogen, this comparison has potential significance to the theory of absolute reaction rates. The technique is described and the results discussed.

1. INTRODUCTION

Muonium (Mu) is an analogue of the H atom with the proton nucleus replaced by a positive muon (μ^+). The chemical properties of Mu and H atoms are virtually identical,[1] with one exception: the mass of Mu is only about 1/9 that of the H atom. Mu can thus be thought of as an ultralight "isotope" of the H atom. Consequently, the chemical reactions of Mu provide a unique context in which to examine dynamic isotope effects in chemical kinetics--in particular, quantum mechanical tunnelling.[2]

Chemical reactions of muonium in the liquid phase have been studied by the μ^+ depolarization technique.[1,3] The rate constants obtained are consistently higher than those measured for the analogous reactions of hydrogen atoms, and in some cases suggest dramatic tunnelling effects. However, the kinetics of liquid phase reactions are complicated by diffusion, etc., and an unambiguous quantitative interpretation of those results is not yet feasible. The obvious extension of such studies to the gas phase has long been hampered by experimental difficulties, but recent improvements in technique have greatly facilitated these measurements. We report here the results of an experiment in which we measured the room temperature rate constant for reaction of Mu with trace amounts of Br_2 in $\sim$1 atm of Ar moderator gas.

2. THE MUON BEAM

Positive muons arise in the decay of pions, which are generally produced by bombardment of a suitable material with protons of incident energy at least equivalent to the rest mass of the pion, 140 MeV. In this experiment, the 740 MeV proton beam of the 184 in. Cyclotron at the Lawrence Berkeley Laboratory was focussed on a Cu target. Pions produced in the resultant nuclear interactions then decay via the weak interaction (with a mean lifetime of 26 nsec), according to the process

$$\pi^+ \rightarrow \mu^+ + \nu_\mu \quad . \tag{1}$$

The kinetic energy of the outgoing μ^+ in the rest frame of the π^+ is 4.1 MeV. Since the pion has zero spin and the spin 1/2 neutrino (ν_μ) has definite negative helicity (spin antiparallel to its momentum), the conservation of angular momentum forces the spin 1/2 μ^+ to also have 100% "backward" longitudinal polarization in the rest frame of the π^+.

To our knowledge all previous muon beams were derived from pions decaying in flight, so that the decay kinematics had to be transformed into a moving frame, and special techniques used to obtain a polarized muon beam.[4] The resulting disadvantages (from the viewpoint of gas phase muonium studies) were: (a) reduced polarization (typically 75%); (b) higher momentum (typically $p_\mu \sim 100$ MeV/c); and (c) large spread in momentum (typically $\Delta p_\mu \sim 20$ MeV/c). For gas phase studies with such "conventional" muon beams, it was generally necessary to use

high-pressure (30-50 atm) gas targets in order to have a substantial fraction of the muons stop in the gas.[5] We know of only one instance in which such a beam was used to study Mu in gases near 1 atm.[6]

In our experiment, muons were collected into a beam from pions decaying at rest in the surface of the production target. This technique was developed by a University of Arizona group working at Berkeley,[7] and is referred to as the "Arizona mode." The resulting μ^+ beam is nearly monoenergetic at a momentum of 29.8 MeV/c, and is nearly 100% polarized. By the time the beam has traversed several thin counters and vacuum windows to reach the gas stopping target, its kinetic energy has dropped from 4.1 MeV to about 2 MeV. The range of these muons is about 12 inches of Ar gas at 1 atmosphere, with a range straggling of a few inches.

3. THE "MSR" TECHNIQUE

The μ^+ itself is an unstable particle (2.20 μsec mean lifetime), decaying via the weak interaction according to

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu \ . \qquad (2)$$

Due to the nonconservation of parity implicit in the definite helicity of neutrinos, the e^+ tends to exit along the μ^+ spin direction. In general, the number of positrons emitted at an angle θ with respect to the muon spin direction is given by[8-10]

$$\frac{dN_e}{d\Omega} \sim (1+a \cos \theta.) \qquad (3)$$

The asymmetry, a, is a function of the energy of the emitted e^+, with an average value of 1/3, and a maximum value of 1 (for positrons of maximum energy, 52 MeV).[8]

Muons stopped in a magnetic field perpendicular to their polarization precess at their Larmor frequency, $\omega_\mu = \gamma_\mu B$, where $\gamma_\mu = 8.5 \times 10^4$ rad/sec-gauss. If a very small positron counter is fixed in the plane of precession at an angle ϕ_o to the initial muon spin direction, the angle between the μ^+ spin and the e^+ detector when the muon decays at time t will be $\phi_o + \omega_\mu t$. The probability of detecting the positron is then proportional to $dN_e/d\Omega$ in Eq. (3), with $\theta = \phi_o + \omega_\mu t$. Thus, for the whole ensemble of stopped muons, the number of detected positrons will rise and fall in time as the μ^+ polarization sweeps past the counter--reflecting the Larmor precession of the muons and the pattern

of their decay positrons. Of course, real detectors have finite dimensions, and there are various solid angle corrections to Eq. (3). There are also corrections due to target geometry and beam polarization. In practice, these can all be absorbed into the empirical asymmetry, A_μ.

Since A_μ is proportional to the muon polarization (there is no asymmetry in the decay of muons with randomly oriented spins), it is easy to monitor the magnitude and time dependence of the muon polarization by this method. This has been called the "μ^+SR" technique (for μ^+ Spin Rotation), by analogy with NMR and ESR methods. The technique is very similar to nuclear Perturbed Angular Correlation studies. The associated study of μ^+ depolarization mechanisms and local magnetic fields in various media forms the basis of a broad area of research.[9]

We introduce the new notation "MSR" (for Muonium Spin Rotation) to emphasize the distinction between the technique used in this experiment and that used in liquid phase studies of the chemical reactions of muonium:[1] whereas in the liquid phase one is forced to look for precession of muons in diamagnetic environments, here we observe the precession of Mu atoms themselves.

In the Mu atom, the spins of the μ^+ and the e^- are coupled together by the hyperfine interaction, which may be thought of as the effect of the field (B_0 = 1593 G) due to the μ^+ magnetic moment upon the magnetic moment of the e^-.[10] In weak fields ($B \ll B_0$), this interaction "locks" the muon and electron spins together to form a net spin of 0 (singlet) or 1 (triplet). In the triplet state, the net spin

is twice that of the free muon, while the net magnetic moment is approximately that of the electron, which is about 207 times larger than the muon's. The notable result is that the Mu atom triplet state precesses about 103 times faster than the free muon in the same magnetic field, as long as the field is too weak to compete with the hyperfine field, B_0. This fast precession is reflected in the positron distribution from muons in muonium atoms.

Positive muons stopped in most gas targets thermalize almost exclusively as Mu atoms.[10] None of the muon polarization is lost in the slowing down process,[9,10] so the muonium ensemble is made up from fully polarized muons and completely unpolarized electrons. The initial spin states of Mu are thus 50% $|\alpha_\mu\alpha_e\rangle$ and 50% $|\alpha_\mu\beta_e\rangle$, where α and β represent spins parallel and antiparallel to the quantization axis. In zero field, the stationary states of the μ^+e^- spin system are the singlet state, $|F=0,M=0\rangle = 1/\sqrt{2}\,[|\alpha_\mu\beta_e\rangle - |\beta_\mu\alpha_e\rangle]$, and the three triplet states, $|F=1,M=+1\rangle = |\alpha_\mu\alpha_e\rangle$, $|F=1,M=0\rangle = 1/\sqrt{2}\,[|\alpha_\mu\beta_e\rangle + |\beta_\mu\alpha_e\rangle]$, and $|F=1,M=-1\rangle = |\beta_\mu\beta_e\rangle$. Here F refers to the total spin and M is the total magnetic quantum number. The first half of the muonium ensemble is therefore constant (in zero field); the second half, however, is in a superposition of the two M=0 eigenstates: $|\alpha_\mu\beta_e\rangle = 1/\sqrt{2}[|F=0,M=0\rangle + |F=1,M=0\rangle]$. It therefore oscillates between $|\alpha_\mu\beta_e\rangle$ and $|\beta_\mu\alpha_e\rangle$ at the Mu hyperfine frequency, $\omega_0 = 2.8\times10^{10}$ rad/sec. Such a high frequency cannot be resolved experimentally, so this half of the ensemble appears to be completely depolarized.[3,9]

In finite transverse field, neither state is a perfect eigenstate, and the general time dependence of the muon polarization takes on a rather complicated form.[9] However, as long as the field is very weak ($B<<B_0$), one can consider the external field to be a small perturbation upon the triplet state, causing coherent precession at the muonium Larmor frequency, $\omega_{Mu} = 103\ \omega_\mu$. The positron detection probability thus acquires another term of the form of Eq. (3), except with a new empirical asymmetry A_{Mu} and with $\theta = \phi_o + \omega_{Mu} t$.

Of course, the time distribution of decay positrons also falls off exponentially, due to the decay of the muons. In addition , each oscillatory term may have an exponential damping if the component of the muon ensemble with which it is associated is disappearing or being depolarized. In particular, as free Mu atoms disappear by chemical reaction, the muonium "signal" is damped. The general form of the positron time distribution is then

$$\frac{dN_e(t)}{d\Omega} = N_o\{BG + e^{-t/\tau_\mu}[1 + A_\mu e^{-\lambda_\mu t}\cos(\omega_\mu t + \phi_o) + A_{Mu} e^{-\lambda t}\cos(\omega_{Mu} t + \phi_o)]\}, \quad (4)$$

where N_o = a normalization factor, BG = time-independent background from accidental counts, etc., τ_μ = the muon lifetime, 2.20 μsec, A_μ and A_{Mu} are the experimental asymmetries from the muon and muonium signals, respectively, λ_μ and λ are the rates of decay of those signals, ω_μ and ω_{Mu} are the muon and muonium precession frequencies, and ϕ_o is the initial phase of the precession.

The usual experimental technique used in MSR studies is as follows: some sort of ultrafast "clock" is started when a muon enters the target and stopped if and when the muon's decay positron is observed in the e^+ counter. The measured time interval is stored in a time histogram. This process is repeated until a time spectrum is obtained, which can be compared with the form (4) by a fitting programme on a computer.

In this paper we are primarily concerned with measurements of λ, the rate of disappearance of the muonium signal. This damping can be due either to spin relaxation in the free Mu atoms or to removal of muons from the free muonium environment by chemical reactions.[9] Both effects have been studied briefly by Mobley et al.[5] at high pressures. In this experiment we have avoided spin interactions and concentrated upon the simple bimolecular reaction

$$Mu + Br_2 \xrightarrow{k_{Mu}} MuBr + Br \qquad (5)$$

4. EXPERIMENTAL DETAILS

The target and counters were arranged as shown in Fig. 2: incident muons triggered a three-fold coincidence in counters B1 (not shown), B2 and B3 sending a "μ-stop" = B1·B2·B3 pulse to the "start" input of a time digitizing multichannel analyzer. The two sets of counter telescopes (Left and Right) situated at 90° to the incident μ^+ beam were used to detect decay positrons. Two thick (2 inch) graphite absorbers between the outside e^+ counters served to reduce accidentals and to discriminate against low-energy decay positrons, thereby raising the experimental asymmetry.[8-10] The e^+ signature, either "e_L" = L1·L2·L3 or "e_R" = R1·R2·R3 was sent to the "stop" input of the analyzer, and the resultant digitized time interval was routed to the appropriate time histogram (Left or Right). Each histogram was divided into 256 bins of 20 nsec/bin. The resultant time spectra of Left and Right positrons will be referred to as L(t) and R(t).

For each target, Left and Right time spectra were accumulated simultaneously; then the magnetic field was reversed and the process repeated. Uninteresting aspects of the time distributions were thus cancelled out by defining the "signal", S(t), as

$$S(t) = N_1\left(\frac{L(t) - R(t)}{L(t) + R(t)}\right)_{\uparrow} + N_2\left(\frac{R(t) - L(t)}{L(t) + R(t)}\right)_{\downarrow} \qquad (6)$$

where N_1 and N_2 are statistical normalization constants ($N_1 + N_2 = 1$) proportional to the total number of events with field up (↑) and field down

(↓), respectively. If we neglect the very small L/R differences in BG and if $\phi_o = \pm \pi/2$, we can expect S(t) to be given by

$$S(t) = A_\mu e^{-\lambda_\mu t} \sin(\omega_\mu t) + A_{Mu} e^{-\lambda t} \sin(\omega_{Mu} t). \quad (7)$$

Fig. 1a shows S(t) for muons stopping in 1 atm. of pure argon in a transverse magnetic field of 2G. At this low field the free μ^+ precession is so slow that it can be approximated by a linear correction on the 2.2 μsec time scale dictated by the muon decay.

The magnetic field was provided by a pair of Helmholtz coils 24 in. in diameter. A Hewlett Packard Model 3539 magnetometer probe was used to monitor the field at the center of the coils, which was set to 2.0 ± 0.05 G. The field is expected to be somewhat less uniform at the edges of the target region; the effect of such nonuniformity would be to cause a constant "extra" relaxation rate added to the fundamental value of λ.

The gas target consisted of an Al cylinder of $7\frac{3}{4}$ in. diameter by $26\frac{1}{2}$ in. length, closed at one end by a plate incorporating the gas and pressure fittings, and at the other end by a 2 mil Mylar window, through which the μ^+ beam entered. The gas volume was approximately 20.5 liters. The reagent grade Ar moderator gas was kept slightly below atmospheric pressure to avoid flexing the thin window. Oxygen impurities in the argon were stated to be less than 5 ppm, and this purity proved entirely adequate for our purposes, so no further purification was attempted; several runs with ultrapure Ar gave virtually identical results.

The μ^+ beam was first stopped in pure Ar gas, and the signal S(t) from about 200,000 events (~3 hrs. running time) was fitted to Eq. (7) to yield a value for $\lambda = \lambda_o$ representing "background" relaxation due to field inhomogeneities, minute O_2 impurities, and/or any unknown relaxation phenomena unrelated to the chemical relaxation to be studied. The value obtained was

$$\lambda_o = 0.19 \pm 0.04 \ \mu sec^{-1}. \tag{8}$$

Later runs on pure Ar yielded relaxation rates statistically equivalent to this value; this served as a consistency check on the gas system and the basic technique. Subsequent targets were prepared by adding measured amounts of Br_2. The fitted value of λ for a given run is the sum of the "background" relaxation rate λ_o and the relaxation rate λ_r due exclusively to "chemical" relaxation:

$$\lambda = \lambda_o + \lambda_r \tag{9}$$

Measured Br_2 impurities were introduced by utilizing the natural vapor pressure of $Br_2(\ell)$. A sample of reagent grade $Br(\ell)$ from Malinckrodt Chemicals was placed in a vial with a small amount of KBr (to consume any Cl_2 impurities), and degassed. Bromine vapor at -11°C (salt/ice bath) was then admitted into a previously evaculated bulb of known volume (20.1 cc). The Br_2 in this bulb was flushed with argon into the previously purged and evacuated target container, bringing the pressure up to just under 1 atm. In some runs, several "standard bulbs" of Br_2 vapor were added to obtain the desired Br_2 concentration, while in other runs the Br_2 concentration was diluted by pumping out some fraction of the gas in the target vessel and refilling with pure argon. All data were taken at 23°C.

5. RESULTS

Using the simple technique described above, we varied the Br_2 concentration in the range ~10-100 ppm for a series of runs spanning a period of several months at the Lawrence Berkeley Laboratory. The resulting time distributions were fitted to Eq. (7) and best values of λ determined for each concentration; the results, listed in Table 1, are plotted in Fig. 3. As can be seen from Fig. 3, two points are out of line with the trend of the rest of the data. These points were taken during poor field regulation caused by an unstable power supply. As mentioned earlier, field inhomogeneities (either in time or in position) cause an increased "background" relaxation rate λ_o. The bad points are therefore not included in the fits, but are shown to illustrate this effect. The largest sources of error are thought to be in the measurement of the temperature of the $Br_2(\ell)$ (estimated to be ~1°C), and in the values of the vapor pressure of $Br_2(\ell)$ reported in the literature, which for some temperatures varied by up to 30%.[11]

The "chemical" relaxation rate λ_r is taken to be due exclusively to the removal of free Mu atoms by chemical reaction. Since there is never more than one Mu atom in the target at the same time, what we actually observe in the relaxation of the muonium precession signal is the statistical probability of a given Mu atom surviving reaction for a given length of time. It is logical to presume a constant probability of reaction per unit time, so that if Mu(t) represents the probability that a given Mu atom has survived for a time t, then $dMu(t)/dt = -\lambda_r\, Mu(t)$. This probability therefore decays exponentially:

$$Mu(t) = Mu(0)\, e^{-\lambda_r t} \tag{10}$$

Thus λ_r is a pseudo-first order rate constant, related to the bi-molecular rate constant k_{Mu} characterizing Eq. (5) in the usual manner:

$$\lambda_r = k_{Mu}[Br_2], \tag{11}$$

where $[Br_2]$ represents the Br_2 concentration. The data shown in Fig. 3 are therefore fitted to Eq. (9) using Eq. (11), with the line shown on the graph corresponding to the best fitted value,

$$k_{Mu} = (2.4 \pm 0.3) \times 10^{11}\ \text{ℓ/mole-sec.} \tag{12}$$

6. COMPARISON WITH H ATOM DATA

A survey of the literature reveals that the rate constant for the H atom reaction analogous to (5),

$$H + Br_2 \xrightarrow{k_H} HBr + Br \quad , \tag{12}$$

has never been directly measured. Values reported for k_H were derived from determinations of k'_H for the reaction

$$H + HBr \xrightarrow{k'_H} H_2 + Br \tag{13}$$

and measured ratios of k_H/k'_H. The latter measurements were generally made at high temperatures (>500°K). Furthermore, there is no unanimous agreement among the various authors about any of these values. For the sake of comparison, we have estimated a value of $k_H = (2.2 \pm 1.5 \times 10^{10})$ ℓ/mole-sec. at 295°K, as a critical average of the results of Refs. 12, 13 and 14. The rate constant for deuterium atoms is also interesting for comparison. A simple calculation using the thermodynamic data of Ref. 15 and the kinetic data from Refs. 13, 14 and 16 yields an estimate of $k_D = (6.1 \pm 3.2 \times 10^{9})$ ℓ/mole-sec. at 295°K for the reaction

$$D + Br_2 \xrightarrow{k_D} DBr + Br \tag{14}$$

Within the framework of a simple collision theory[2,17] of bimolecular gas phase reactions, the overall rate constant (averaged over thermal velocities) has the form

$$k \sim \bar{v} \, (\sigma_A + \sigma_B)^2 \quad \exp(-E_a/RT) \quad , \tag{15}$$

where $\bar{v}$ is the mean relative velocity, σ_A and σ_B are the diameters of the reactants (treated as "hard spheres"), and E_a is an activation energy. Since the atomic sizes of D, H and Mu are virtually identical,[10] any difference in their rates of reaction with the same partner must be contained in the mass dependence of $\bar{v}$ and/or E_a. The masses of Mu and H differ by a factor of 9, so $\bar{v} = (8k_BT/\pi\mu)^{1/2}$ (μ being the reduced mass, essentially equal to m_{Mu} in this case) will be 3 times faster for Mu than for H at the same temperature -- thus predicting a trivial rate enhancement by the same factor of three. Similarly, from kinetic effects alone we expect $k_D = 0.7\ k_H$. This "kinetic isotope effect" is not interesting; besides, it fails to account completely for the ratios of 0.28 and 10.9 obtained for $\frac{k_D}{k_H}$ and $\frac{k_{Mu}}{k_H}$, respectively.

The residual factors of 0.4 and 3.6 point to a "dynamic isotope effect" which can only be contained in the activation energy. One can easily imagine two such effects, not completely separable: a semi-classical one involving a change in force constants between reactants and products (zero-point motion change), and a purely quantum mechanical one involving tunnelling through the potential barrier which is reflected in the activation energy. There have been numerous discussions of these concepts in the literature[2,17, 18] and we make no attempt at any definitive description here. However, a brief review of the basic aspects of the tunnelling process is in order.

The simplest physical interpretation of tunnelling is that an incident particle (wave) is transmitted through the potential barrier for incident kinetic energies less than the barrier height, rather than

being completely reflected as demanded classically. Various models and "self-consistent" calculations have been considered for the radial form of the potential barrier. The one-dimensional square well, while physically untenable, is a useful example for illustrative purposes. In this case, the probability of tunnelling can be written

$$P \sim \exp\left(\frac{-2R\sqrt{2\mu c^2 (V_o - T)}}{\hbar c}\right) \qquad (16)$$

where R is the barrier width, μ is the reduced mass, and $V_o - T$ is the deficit by which the incident kinetic energy T falls below the potential barrier V_o. The average of this difference, particularly for high barriers, is just the activation energy E_a. We do not wish to defend the validity of Eq. (16), but merely to point out that most tunnelling calculations predict some type of exponential dependence (such as a WKB integral) or other dramatic dependence upon the mass of the light reactant. In this sense even Eq. (16) may be useful in predicting the ratio of two rates in which only the light mass differs. Such arguments have played a role in comparisons of D and H atom reactions,[2,17] where the masses of the light atoms differ by a factor of two; reactions of Mu and H, whose masses differ by a factor of nine, are potentially far more sensitive to the presence of quantum tunnelling than any processes heretofore studied.[19]

It will be noted that even in the case of tunnelling there is a dramatic dependence of the rate upon the activation energy $E_a = \langle V_o - T \rangle_{eff.}$

Since V_o is the barrier height minus the zero-point energy, differences in force constants will generally affect V_o and thus E_a and the rate. The activation energy for the reaction $H + Br_2 \rightarrow HBr + Br$ is reported[12] to be ~0.9 kcal/mole. This is a very small value (essentially k_BT at room temperature); if the Mu, H and D reactions have the same E_a, tunnelling could not be expected to be very significant compared with normal thermal activation at room temperature.[20] Indeed, Eq. (16) predicts no difference between H and Mu reactions, for E_a = 0.9 and a 1 Å barrier. Thus we will probably have to look to differences in zero-point motion in the "collision complexes" HBr_2^* and $MuBr_2^*$ [18] to account for differences in E_a leading to the "dynamic factor" of 3.6 in the rate ratio, k_{Mu}/k_H. This prediction will be tested by studying the temperature dependence (if any) of the muonium reaction rate.

7. SUMMARY AND PROSPECTUS

To our knowledge, this is the first measurement of the rate of a chemical reaction of the Mu atom in the gas phase at low pressure, and by far the least uncertain at any pressure. This was made possible by a new type of μ^+ beam which stops completely in a few inches of gas at 1 atmosphere.

The rate constant we measured is about ten times faster than that for the corresponding reaction of the hydrogen atom, whose only ostensible difference is in its mass. A factor of 3 is expected due to the increased collision frequency of the lighter Mu atom; the additional factor of 3.6 deserves closer examination. Due to the very low activation energy expected for this reaction, quantum mechanical tunnelling probably plays a minor role; we suspect that studies of the temperature dependence of this reaction will reveal an activaton energy lower than that for the H atom reaction, probably due to a higher zero-point energy.

A programme of "survey" experiments on the gas phase reactions of Mu has been completed at the 184 in. Cyclotron in Berkeley. These were intended to break the ground for an extensive series of in-depth studies on the MSR Facility at TRIUMF, a new high-intensity meson-producing accelerator in Vancouver, British Columbia. The MSR Facility is expected to become operational in 1975-76, and will permit detailed measurements of the chemical reactions of Mu in gases and liquids, as well as various solid state studies with μ^+ and μ^-. The ultimate comparison between a large body of Mu and H atom rates is sure to have an impact on our understanding of chemical reaction processes.

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19. The study of positronium (Ps) chemistry [V.I. Goldanskii, At. Energy Review 6 (1968) 3; H.J. Ache, Angew. Chem. internat. Edit. 11 (1972) 179; L.J. Bartal, J.B. Nicholas and H.J. Ache, J. Phys. Chem. 76 (1972) 1124], might be considered an exception to this statement. However, the Ps (e^+e^-) atom, having no nucleus, is a rather poor analogue of the H atom in any but the most general sense. Comparisons of Ps and H are likely to be fruitful in a qualitative sense, but the same quantitative model is unlikely to describe both.

20. Preliminary results for the Mu + Cl_2 reaction indicate that it is~20 times faster than the analagous H + Cl_2 reaction. In this case, E_a = 3.5 kcal/mole, and a large tunnelling enhancement might be expected.

TABLE I. FITTED RELAXATION RATES

$[Br_2]$(μmoles/liter)	$\lambda(\mu sec^{-1})$
0.00	0.194 ± 0.029
0.00	0.171 ± 0.038
1.74 ± 0.23	0.716 ± 0.123
2.19 ± 0.24	0.706 ± 0.062
2.95 ± 0.32	0.982 ± 0.099
3.45 ± 0.44	1.21 ± 0.15
4.13 ± 0.45	1.11 ± 0.10
5.75 ± 0.61	1.43 ± 0.16
7.73 ± 0.81	2.22 ± 0.25
1.02 ± 0.09	1.46 ± 0.20[a]
4.25 ± 0.55	3.47 ± 0.58[a]

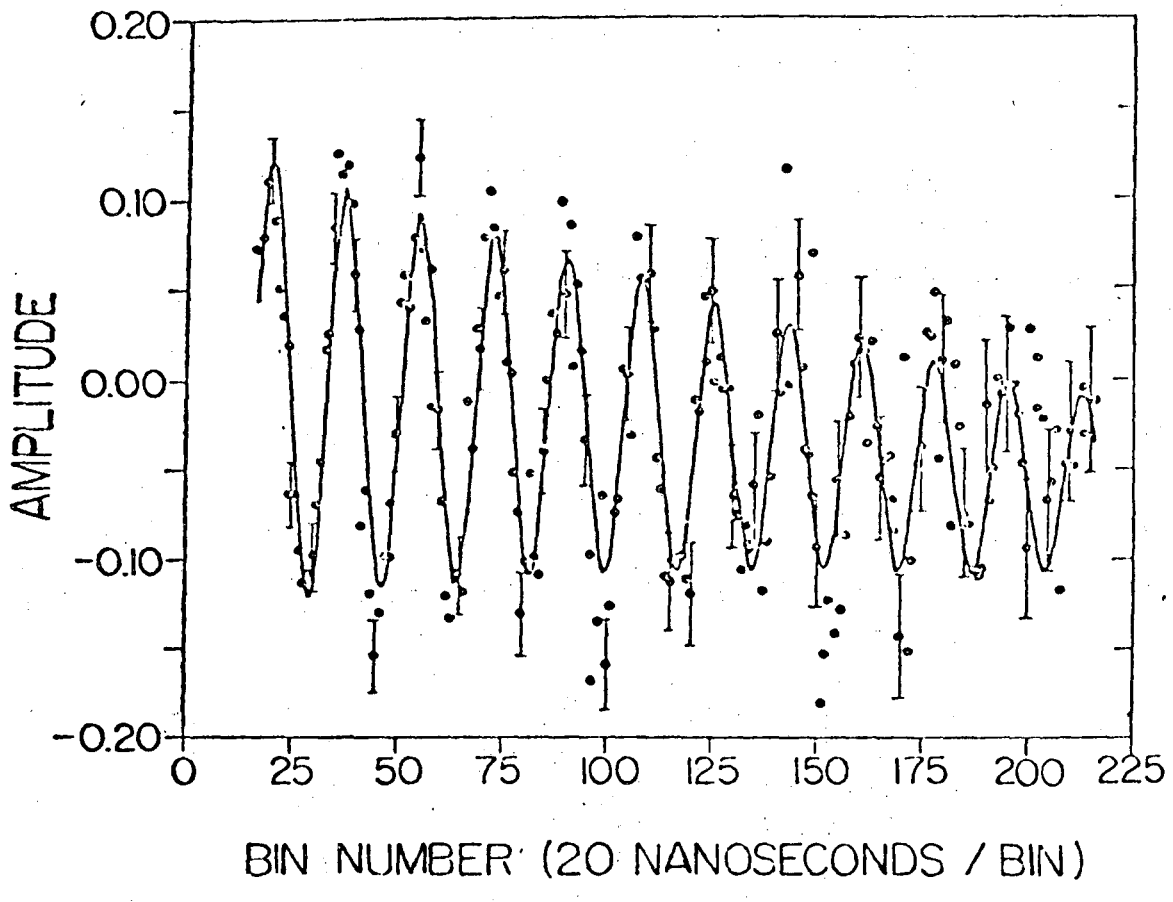
[a]deviant points (see text)

FIGURE CAPTIONS

Fig. 1 (a; top) The "signal" S(t) showing muonium precession and the background relaxation rate λ_0. The target gas is pure argon at 1 atmosphere and 23°C. Precession field is 2 G. the curve shown is a computer fit of the data to the form of Eq. (7). Error bars are primarily due to counting statistics only.
(b; bottom) A typical S(t) for a different target with ∿10 ppm of halogen reactant added to the Ar. The increased rate of relaxation of the Mu precession signal is due to the removal of free Mu atoms by chemical reaction.

Fig. 2 Diagram of the apparatus. The incident μ^+ triggers the beam counters B1 (not shown), B2 and B3 (each a 5 mil plastic scintillator); later, a decay e^+ triggers either the left (L1·L2·L3) or right (R1·R2·R3) positron telescopes. Two inch graphite absorbers were used to stop low energy e^+. The magnetic field is out of the paper (physically the vertical direction).

Fig. 3 Plot of the overall relaxation rate λ for the reaction of Mu with Br_2, as a function of the concentration of Br_2 reagent. The straight line is a minimum-χ^2 computer fit to the data, assuming that the relationship between λ_r and $[Br_2]$ is characterized by a second-order rate constant k as in Eq. (11). The two "bad" points are not included in the fit (see text).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125
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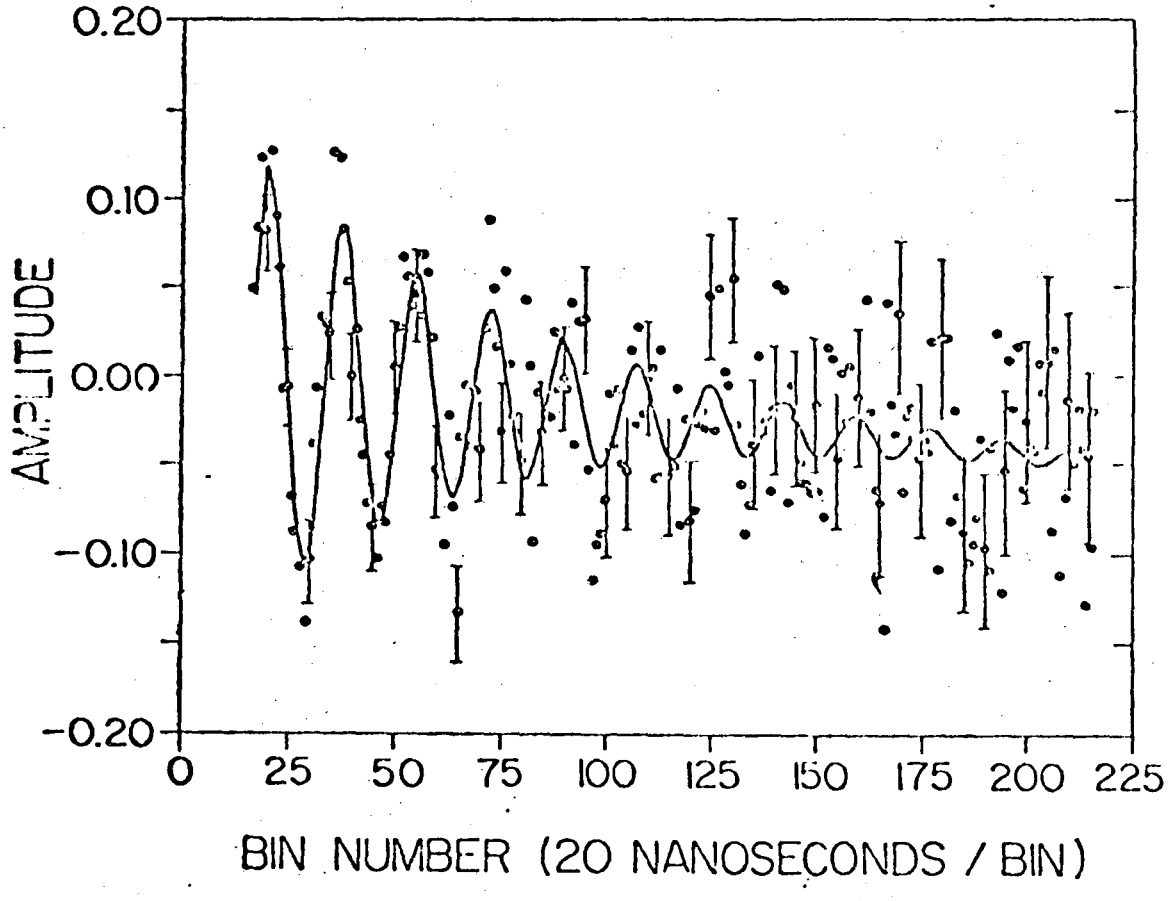
BIN NUMBER (20 NANOSECONDS / BIN)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BIN NUMBER (20 NANOSECONDS / BIN)

Fig. 1

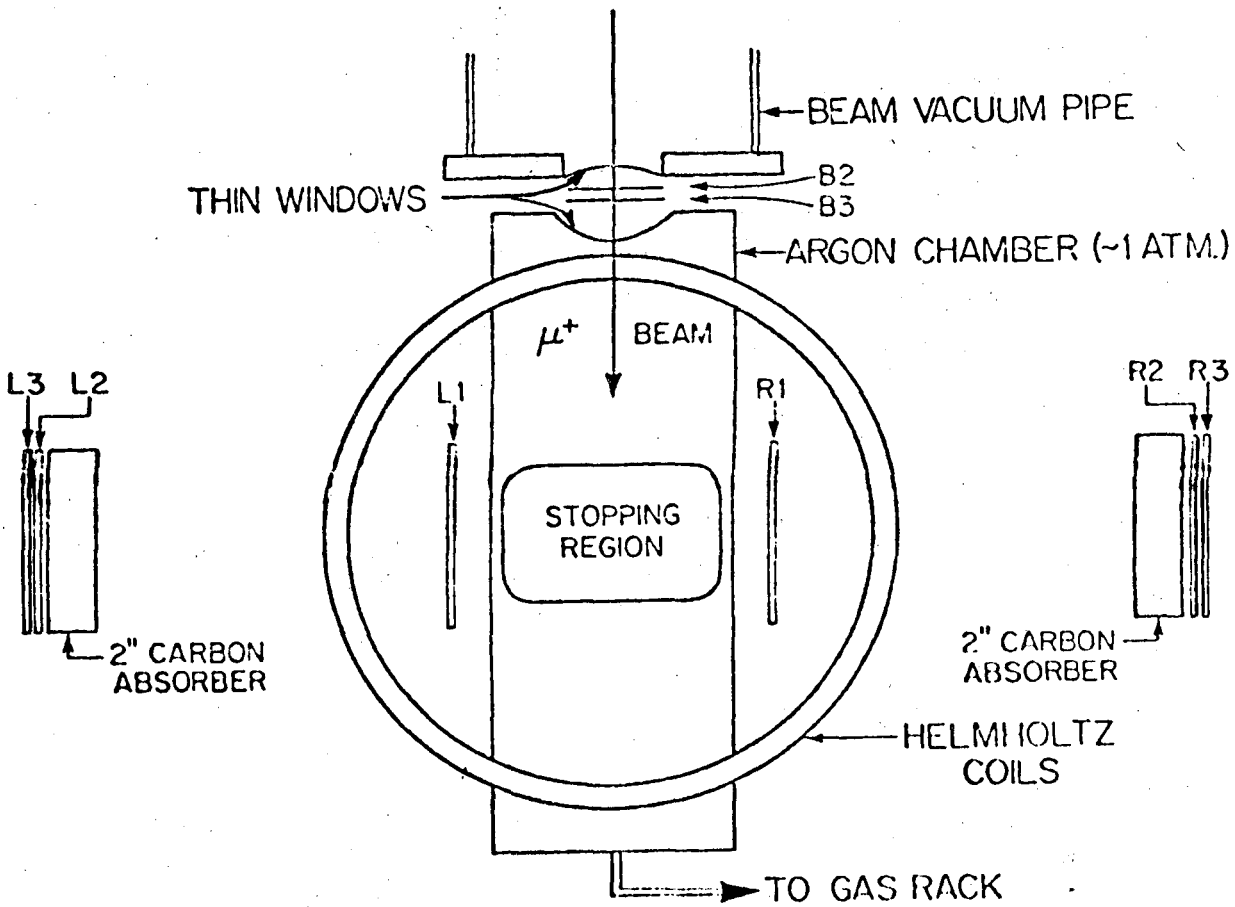

Fig. 2

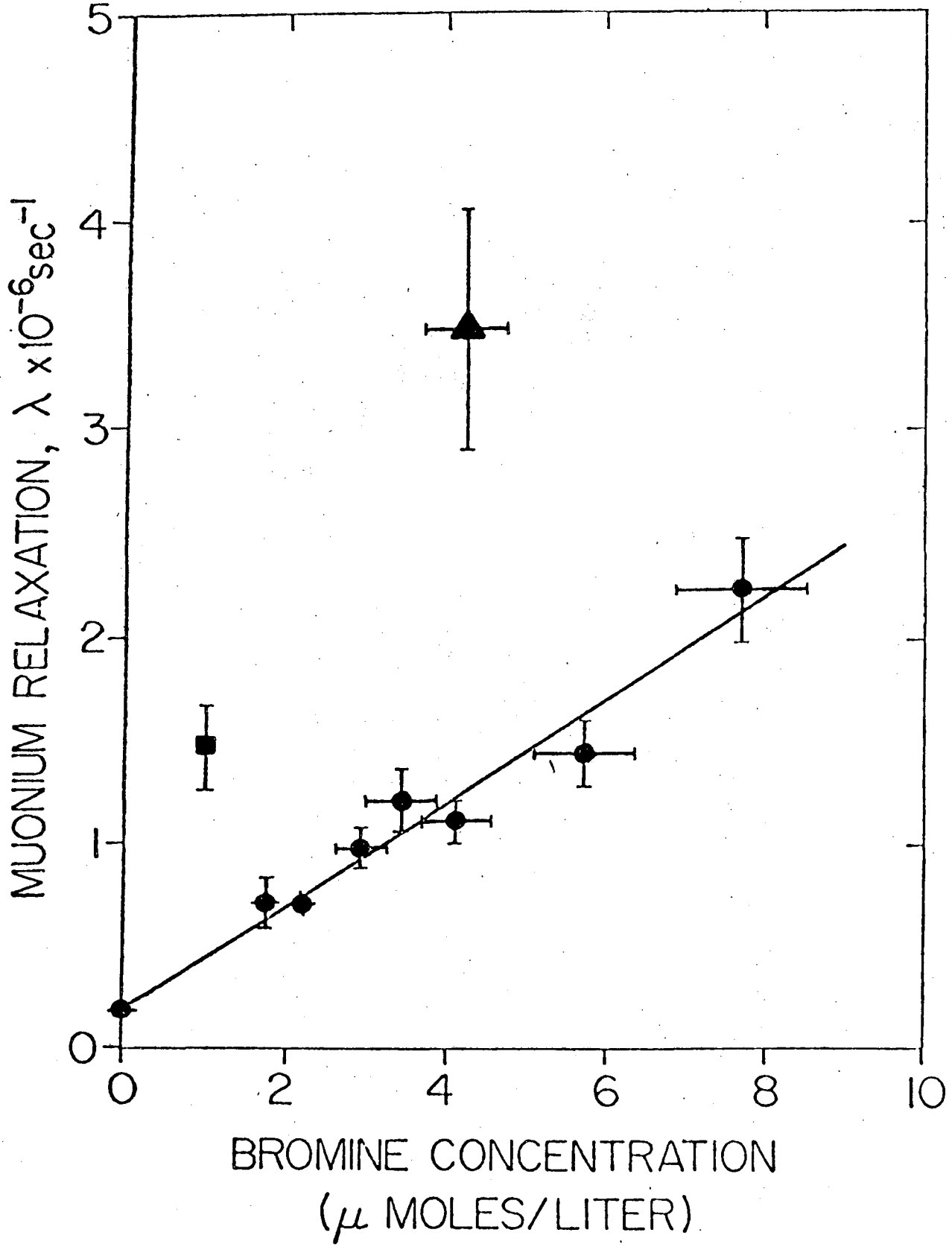
MUONIUM RELAXATION, λ x10⁻⁶sec⁻¹
0
1
2
3
4
5
0
2
4
6
8
10
BROMINE CONCENTRATION
(μ MOLES/LITER)

Fig. 3

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720