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Muonium atom spin exchange with alkali-metal vapors: Mu+Cs

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The thermally averaged total electron spin-flip cross sections ($\sigma_{\rm SF}$) for Mu-Cs have been measured in a 2 atm N_2 moderator at 543, 566, and 643 K using the muon-spin-rotation technique. Within an overall experimental error of ±15%, the measured cross sections can be taken as temperature independent, $\sigma_{\rm SF}=39.7\pm6.0\times10^{-16}$ cm^2, though there may be a trend to decreased values at the lower temperatures. This average value is considerably lower than either the early calculated results of Dalgarno and Rudge [Proc. R. Soc. London Ser. A **286**, 519 (1965)] or the more recent ones of Cole and Olson [Phys. Rev. A **31**, 2137 (1985)] for the corresponding H-Cs collisions, indicating a dramatic isotope effect.

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I. INTRODUCTION

First recognized by Bates [1] and Purcell and Field [2] as the dominant mechanism for the establishment of the spin temperature of H atoms in the upper atmosphere and in outer space, electron-spin exchange (SE) is one of the most fundamental of quantum processes. It is not only amenable to theoretical calculations in that it can be viewed as a quasielastic scattering process, but it is also important in many branches of chemistry and physics such as optical pumping, masers, plasmas, and astrophysics. Electron-spin exchange has been studied experimentally in many H-atom systems in the gas phase, such as H-H [3–6], H-O_2 and H-NO [4,7,8], Mu-O_2 and Mu-NO [9–11], H-A [12–15], as well as A-A [16–19], utilizing techniques such as masers, electron-spin resonance (ESR), microwave absorption, optical pumping, and muon spin rotation (μSR). Here Mu refers to the atomic bound states of a positive muon and an electron, the muonium atom (Mu=μ^+e^-), and A represents an alkali-metal atom. Spin exchange of atomic H (D) with alkali metals has been employed to produce polarized hydrogen, deuterium, and other atoms [12,14,15,20–23], which have many applications including cyclotron ion sources [14,15,22] and possibly spin-polarized fusion [12]. Accurate knowledge of electron-spin-exchange cross sections for such systems is therefore valuable to both theorists and experimentalists alike.

Measured total thermal electron-spin-exchange cross sections [referred to elsewhere [9,24,25] and in this work as spin-flip (SF) cross sections (one could distinguish a spin-exchange interaction and a spin-flip cross section; a spin-exchange interaction could lead to the exchange of either like or unlike spins, the latter giving rise to a measurable spin-flip cross section)] $\sigma_{\rm SF}(T)$ between muonium and cesium in the gas phase are reported herein. The primary motivation for these experiments is to compare the experimental cross sections for Mu-Cs with available theoretical calculations for H-Cs [26,27] and to investigate the isotopic mass dependence, if any, of the spin-exchange process for collisions of H atoms with alkali metals. Since the mass of Mu is only $\frac{1}{9}$ that of a hydrogen atom, the μSR technique provides a more stringent test of possible isotope effects in spin-flip cross sections than any other isotope.

To our knowledge, there are no reported studies to date of any H-atom isotope effects in spin exchange other than the comparisons between H [4,7,8] and Mu [9–11] spin exchange with O_2 and NO molecules. Studies of H (D) with A are reportedly underway [12,13], but here the mass difference is only a factor of 2. In our previous studies it was found that the experimental Mu-O_2 and Mu-NO spin-flip cross sections were considerably *reduced* compared to the corresponding experimental H-atom cross sections [8–10,24], by almost a factor of 3 on average. The theoretical comparisons of H-H and Mu-H by Shizgal [28], in which large isotope effects favoring Mu-H scattering at low temperatures were predicted, and those of Aquilanti and co-workers [9,29] comparing Mu-O_2 and H-O_2 spin-flip cross sections are the only calculations of isotope effects in H-atom spin exchange. Moreover, theoretical calculations failed completely to account for the experimental H-molecule cross sections [9,29]. The calculation of spin-flip cross sections for atom-molecule scattering (H-NO and H-O_2) is complicated by poorly known potential-energy surfaces. The simplest spin-exchange process is unquestionably that between two spin-$\frac{1}{2}$ atoms, the most fundamental of which is H-H (or Mu-H) scattering. Calculations of Mu-H and H-H electron-spin-flip cross sections have been performed by Shizgal [28], Koyama and Baird [30], Berlinsky and Shizgal [31], and Allison [32]. Impressive agreement is obtained with the experimental results for H-H over a wide range of temperatures [5]. Large isotope effects are also predicted at *low* temperatures, due to specific resonances favoring the spin-flip cross section of Mu-H over that of H-H by a factor of 5 at 50 K [28]. However, the experimental determination of spin-flip cross sections for Mu-H is complicated by the difficulty of producing a known concentration of H atoms, even with a radical redesign of current μSR gas phase reaction vessels. This is primarily the reason why we have chosen to study electron-spin-exchange processes with the alkali metals, notably Mu-Cs interactions, in the present experiment.

There have been two theoretical calculations of H-A spin-flip cross sections, $\sigma_{\rm SF}(E)$: an early calculation by Dalgarno and Rudge [26] and a much more recent one by Cole and Olson [27]. In both cases, the alkali-metal atom is assumed to have an inert core.

With the exceptions of reports of H-Na spin exchange [14] and the work cited in Refs. [12,15], to the best of our knowledge, no other H-atom experiments have been carried out on these simple spin-$\frac{1}{2}$ systems. Ueno *et al.* [14] measured the H-Na spin-flip cross sections as part of a development program to produce polarized proton beams by optical pumping. These authors were able to measure the forward-scattering ($<1.1°$) *differential* cross section for H-Na spin exchange. They also calculated both total and differential cross sections with the total cross section agreeing with those of Cole and Olson, but the calculated value for the differential cross sections was a factor of 7 lower than their experimental values. Since their total cross section calculation agrees with those of Cole and Olson, the level of disagreement between theory and experiment for the differential cross section is surprising, since the theory should be highly accurate, at least given the approximation of no core-excitation channels. What are needed as well, therefore, are *total* cross section measurements. It could be that a core-excitation process is more important than heretofore realized, likely manifest in the repulsive part of the interaction potential, which would show up most dramatically in the forward-scattering amplitude. In this context, it can be remarked that similar contributions to the (exact) H-H scattering potential are nonexistent, possibly accounting for the aforementioned exemplary agreement between theory and experiment [5,28,32]. The discrepancy between experiment and theory for H-Na spin-flip cross sections is an important motivation, then, for the study of total Mu-Cs spin-flip cross sections, as reported herein.

In comparison with theory, a point of further interest in the present experiment is the possibility that the Mu-Cs atom spin-flip cross sections may be sensitive to breakdown in the Born-Oppenheimer approximation, more so than the corresponding H-Cs atom collisions. This is because Mu probes the spin-exchange process at higher velocities (factor of 3) than does hydrogen, so that the usual approximation of a separation of electron and nuclear motions in the interaction potential may be less valid for Mu reactions than for H. This question is of general interest for Mu reactivity studies. The possibility of electronic nonadiabatic reactions resulting from breakdowns in the Born-Oppenheimer approximation in the Mu(H)+K system has been discussed by Garrett, Truhlar, and Melius [33], and McKenna and Webster have discussed the effects for muon-substituted H_2^+ molecular ions [34]. In both calculations, the effects are small. It is noted that, compared with other Mu–alkali-metal systems, the ionization potential of Cs (3.89 eV) is the smallest, meaning that the outermost electron has the lowest orbital velocity.

Finally, it can be mentioned that the μSR technique enjoys a distinct experimental advantage over other techniques: only *one* probe atom exists in the target vessel at any time. Hence there is no possibility of probe-probe interactions, a correction for which can be necessary in other techniques such as H masers and ESR.

II. EXPERIMENT

A. μSR technique

The μSR technique in general [35,36], and its application to the study of chemistry and physics in gases [9–11,25,37–42], is well established. The positive muon is produced 100% longitudinally spin polarized, and during its slowing down process from 4 MeV (for surface μ^+) to thermal energies, this polarization is maintained, until the onset of Mu formation via cyclic charge exchange with the moderator [25,35,37,40]. The initial 100% spin polarization of the μ^+ in Mu is then shared with the electron via the μ^+-e^- hyperfine interaction and consequently is time-dependent, leading to effective 50% depolarization of the muon when the experimental time resolution of more than one nanosecond is taken into account. In a weak (<10 G) transverse field, the observable μ^+ polarization retained in triplet Mu, $|\alpha_\mu,\alpha_e\rangle$, is manifest by the time histogram of detected positrons ($\mu^+ \to e^+ \nu_e \bar{\nu}_\mu$), $N(t)$; this is described by the modulation of the muonium frequency superimposed upon the decay of the muon and can be fit to the following form:

$$N(t)=N_0 e^{-t/\tau_\mu}[1+S(t)]+B \ , \tag{1}$$

where N_0 is a normalization factor, τ_μ is the muon lifetime (2.197 μs), B is a constant to account for time-independent background, and $S(t)$ is the μSR "signal," often defined by

$$S(t)=A_{\rm Mu}e^{-\lambda t}\cos(\omega_{\rm Mu}t-\phi_{\rm Mu})+A_D\cos(\omega_D t+\phi_D) \ . \tag{2}$$

The first term corresponds to the muonium signal: $A_{\rm Mu}$ is the initial amplitude of muonium precession, λ is a relaxation (damping) rate corresponding to the interaction of Mu with its environment, $\omega_{\rm Mu}$ is the muonium Larmor frequency ($\nu_{\rm Mu}=\omega_{\rm Mu}/2\pi=1.39$ MHz/G), and $\phi_{\rm Mu}$ is the initial phase of the muonium precession signal. The second term in Eq. (2) corresponds to the signal for muons in diamagnetic environments, where A_D is the initial amplitude of the diamagnetic precession, ω_D is its Larmor frequency ($\nu_D=0.0136$ MHz/G), and ϕ_D is the initial phase of this precession signal. In an N_2 moderator, at 1 atm pressure, $A_{\rm Mu}$ corresponds to about 85% of incident μ^+ thermalizing as Mu, while A_D corresponds to 15% of incident μ^+ thermalizing in a diamagnetic environment [25,37,40] (in fact, as an $N_2\mu^+$ molecular ion [41]). No relaxation of the diamagnetic signal was visible in the experiment. Rather, we are concerned with the first term in Eq. (2) and particularly with its relaxation rate λ. It should be noted that Mu has thermalized before reaction since thermalization times are of the order of tens of nanoseconds [37,40,42], whereas reaction times ($1/\lambda$) are of the order of microseconds.

In the presence of unpolarized Cs vapor, electron-spin flip between Mu and Cs causes a loss of muonium polarization. In an electron-spin-flip interaction, an α electron on one atom (e.g., Mu) is exchanged with a β electron on the other (e.g., Cs). In their brief encounter, the state vector $|\alpha\beta\rangle$ in the atom-atom interaction is not an eigenstate of the spin Hamiltonian, and as such evolves in time, emerging as the state $|\beta\alpha\rangle$. When the time between collisions (of order 100 ns here) is longer than the hyperfine mixing time in muonium (0.22 ns), this electron-spin flip may destroy the coherence of the muon precession in the muonium atom and cause a depolarization of the experimental precession signal. This well-known relaxation process is discussed further below; its effect on damping the μSR signal is illustrated in Fig. 1.

B. Target vessel and gas handling

The target vessel is a nickel-plated stainless-steel cylinder with inner dimensions of 20×63.5 cm^2 (total volume 20.3 liters) and a nickel window of 2.5 cm diameter and 0.05 mm thickness to allow the entrance of the muon beam. The window is positioned well inside the target vessel (2 cm from the flange), and aluminized Mylar is employed as a second window placed at the outside of the flange to ensure the temperature of the inside window is not lower than that of the system.

There are two ports on the other end. One is exclusively for Cs input. The other one is for sampling and gas handling. A schematic arrangement of the target and gas-handling system is shown in Fig. 2.

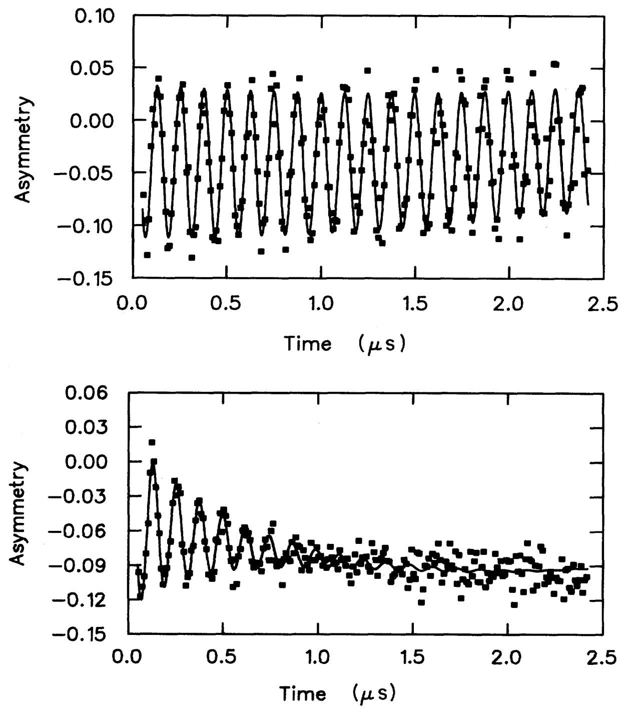

FIG. 1. Experimental μSR signal after removal of normalization, decay, and background. The top spectrum was obtained in 1500 Torr pure N_2 moderator at 566 K. The bottom spectrum was for the same conditions but with an added 9.9×10^{14} molecules/cm^3 of Cs (21 ppm).

The system is first thoroughly cleaned and evacuated to better than 10^{-6} Torr and heated (by heating tapes) above the operating temperature for more than 24 h before an experiment. The coldest spot in the system is purposely the Cs boiler, a container made of pure nickel that is temperature controlled to stabilize at a set value determined by the desired Cs concentration in the reaction vessel. For each run the boiler, previously loaded with 99.95% pure Cs (Strem Chemicals), is opened to the target vessel long enough to establish an equilibrium Cs vapor pressure in the system before it is closed. Temperature fluctuations during this period are less than 0.5 °C. Pure dry N_2 gas is then slowly let into the target vessel up to a certain total pressure, typically 2 atm in these experiments. During the data taking, the temperature inside the reaction vessel is monitored and maintained at a constant and homogeneous value, which is significantly (> 50 K) higher than the boiler temperature. All temperatures are measured by thermocouples.

C. Cs Density

Since the muonium relaxation rate is dependent on the Cs number density, the concentration of Cs atoms in the target vessel must be known accurately in order to reliably extract the spin-flip cross sections of interest. Several intrusive methods have been developed to measure Cs vapor pressure (density) [43–45]. However, they would all greatly complicate the present experiment and, moreover, in most cases require a calibration (by vapor pressure curves), so that their accuracy is no better than that of the known vapor pressure curve. These methods were deemed not worthwhile in this experiment. Instead, we made direct use of the Cs vapor pressure curve of Taylor and Langmuir [43] for a given boiler temperature, to calculate the concentration of Cs inside the target vessel. Although 50 years old, this Cs vapor pressure curve has recently been verified as accurate to within a few percent near 500 K [44]. Vapor pressure curves have, in fact, been used in a variety of experimental situations [13,16,17,19], but our impression is that the absolute accuracy of the curves for the alkali metals (includ-

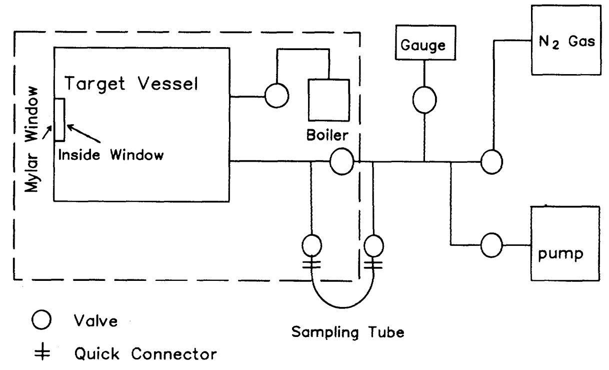

FIG. 2. Gas-handling system and target vessel for Mu-Cs spin-exchange experiment. Area in the dashed line is kept above the boiler temperature, except for the sampling tube.

ing Cs) is not well established, particularly in a metal environment in the presence of a foreign gas, which is the present experimental situation. Independent determinations of the alkali concentrations at given temperatures seem to be rarely carried out, although they could be essential to an accurate determination of $\sigma_{\mathrm{SF}}(T)$. Consequently, a further means of determining the concentration of Cs atoms in the present experiment was desirable.

To check the Cs density, a known volume of gas in the target vessel was pumped out through a sampling tube filled with glass wool and immersed in liquid nitrogen. During sampling, the pressure inside the target vessel was kept higher than 100 Torr to prevent Cs coming off the walls. Cs vapor condensed in the tube and was then washed out with distilled water and titrated against a standard HCl solution. Results of these titrations were used to verify the Cs concentration predicted from the vapor pressure curve. Some results of off-line tests are listed in Table I. Two different moderator pressures, 1 atm and 2 atm, were employed in these off-line tests, though the actual data taking was carried out at 2 atm pressure. As can be seen from Table I, the titration data agree with the vapor pressure curve to within about 10%. The differences are likely due to losses of Cs during sampling and washing. The slight decrease of Cs titrated at 1500 Torr has been shown to be a consequence of slower sampling. The comparisons in Table I show that the vapor pressure curve [43] is indeed reliable for our system, and consequently Cs densities are calculated from these vapor pressures only. It is noted from the titration data that there could be a systematic error of ±10% (or less), possibly higher at the higher pressures.

The presence of Cs dimers, Cs_2, inside the reaction vessel could contribute to an error in the Cs density as well as contributing to a damping of the μSR signal due to chemical reactions, forming CsMu. However, the dimer is only about 0.5% of [Cs] at 560 K under saturated pressure without a foreign gas [46]. It would be less in the target vessel since Cs is not saturated there, although a three-body association reaction could conceivably occur at higher moderator pressures, 2 atm in this experiment. Nevertheless, we feel the contribution from dimers is minimal here.

TABLE I. Cs vapor pressure test. The first column gives the boiler temperature and the second column the total moderator (N_2) pressure before sampling. The third column gives the total number of moles of Cs from titration. Errors are estimated systematic uncertainty of the technique. The last column shows moles calculated from the Cs vapor pressure (VP) curve of Taylor and Langmuir [43]. Errors are due to uncertainties in boiler temperature.

		Cs in the target (10^{-5} mol)	
T_b (K)	P (Torr)	Titration	VP curve
452±3	700	1.37±0.31	1.75±0.23
451±3	1501	1.30±0.31	1.75±0.23
466±3	700	3.06±0.41	3.10±0.37
466±3	1503	2.80±0.40	3.10±0.37
482±3	700	4.96±0.61	5.70±0.65
482±3	1503	4.70±0.60	5.70±0.65
488±3	702	7.00±0.86	7.15±0.78
488±3	1500	6.61±0.81	7.15±0.78
507±3	705	12.9±1.5	13.9±1.4
507±3	701	13.1±1.5	13.9±1.4
507±3	1500	11.9±1.5	13.9±1.4

There is some discussion in the literature on the *total* pressure dependence of saturated Cs vapor pressure, which causes some concern in experiments relying on data from vapor pressure curves [16,17]. In our case, however, the Cs is saturated when there is *no* moderator gas present. The vessel is pressurized only after the boiler (and the coldest spot) is isolated from it. Therefore the Cs is no longer saturated when the total pressure is changed, and hence the Cs density should not be affected by a change in the moderator pressure. Our off-line tests (Table I) also showed very little total pressure dependence.

Another possible, albeit very unlikely, source of error could be a slow reaction of $\mathrm{Cs}+\mathrm{N}_2$. However, while there is some evidence of a very slow reaction of Li or Mg with N_2, there appears to be no information on any reactivity of Cs with N_2 [47]. It is worth noting here that the boiler and the target vessel are free of N_2 when loading Cs, so any reaction involving N_2 can only occur after the boiler is closed, which could conceivably reduce the Cs density in the vessel, though this is very unlikely over the approximately 2-h time period when Cs is in contact with N_2. Furthermore, the product of this reaction would be expected to be $\mathrm{Cs}_3\mathrm{N}$ [47], a virtual impossibility at the Cs density of the present experiment. Moreover, our time-dependence studies (i.e., consecutive runs on the same gas over a time period of 4 h) showed that the relaxation rates were independent of time, indicating that the effect of any competing reactions is insignificant. No time dependence was detected in off-line titration tests either. Generally, the titration results gave good agreement with expectations from the vapor pressure curve (Table I).

Thus, the uncertainty in the Cs number density will be primarily due to an uncertainty in the *boiler* temperature. At 440–510 K, this is well below 3 K, yielding an uncertainty in the Cs density of $\lesssim 13\%$ (Table I).

III. RESULTS AND DISCUSSION

The experimentally observed depolarization rate (λ) of the μSR signal [Eq. (2) and Fig. 1] is a function of the thermal spin-flip cross section [9,11,24,25] and can be written in the form

$$\lambda=\lambda_0+\lambda_1 \,. \tag{3}$$

Here λ_0 is some background relaxation due to contributions such as field inhomogeneity and chemical impurities, while λ_1 is a measure of muon depolarization due to electron-spin flip between Mu and Cs atoms. It is λ_1 that is of interest here. λ_1 is proportional to the thermal-spin-flip cross section at temperature T, $\sigma_{\mathrm{SF}}(T)$, which is defined by

$$\sigma_{\mathrm{SF}}(T)=\frac{1}{(k_B T)^2}\int_0^\infty \sigma_{\mathrm{SF}}(E)Ee^{-E/k_B T}dE \,. \tag{4}$$

In a weak transverse field (< 10 G), and with an $s=\frac{1}{2}$ (Cs) collision partner, λ_1 is given by [9,24,25]

$$\lambda_1=\tfrac{1}{2}\lambda_{\mathrm{SF}}=\tfrac{1}{2}n\bar{v}\sigma_{\mathrm{SF}}(T)\ , \qquad (5)$$

where λ_{SF} is the rate of spin-flip interaction, n is the number density of Cs atoms, and $\bar{v}$ is the thermal velocity ($\bar{v}=\sqrt{8k_BT/\pi\mu}$, where k_B is Boltzmann's constant and μ is the reduced mass of the colliding atoms).

Experimentally, $\sigma_{\mathrm{SF}}(T)$ is determined by measuring λ at several values of n at a given temperature and fitting to Eqs. (3) and (5). This is illustrated in Fig. 3 for data taken at 566 K. Each data point in Fig. 3 took one or two hours to measure. Two positron counter arrays were used to give two histograms of positron events (two to three million counts in each to give less than 10% statistical error in the relaxation rate), which were fit separately. The average of the two fits is taken as the relaxation rate and plotted in Fig. 3. Results for $\sigma_{\mathrm{SF}}(T)$ at different temperatures are recorded in Table II, which compares the data with the theoretical calculations of Dalgarno and Rudge [26] and Cole and Olson [27]. The total cross sections are calculated using Eq. (4) and the parameters given in Ref. [26] for the former and estimated from the reaction rate curve given in Ref. [27] for the latter. The values given in Table II are four times the cross sections in Ref. [27], which are defined as $\frac{1}{4}\sigma_{\mathrm{SF}}$. This comparison is shown in Fig. 4 as well. The three higher-temperature data points (Table II) agree within (random) errors (note the reproducibility at 565 and 566 K), but the lowest-temperature point at 543 K seems considerably below the trend in the data. However, considering the possibility of a 10% systematic uncertainty in the Cs density, as described earlier, giving rise then to an overall uncertainty of $\lesssim\pm15\%$ (i.e., $\pm6\times10^{-16}$ cm^2), we cannot state conclusively that the lowest-temperature data point is anomalously low, but rather that the data exhibit a temperature dependence not inconsistent with the theoretical calculations (both calculated temperature dependences give rise to only about a 2% decrease in cross sections over the range of our data). It can be noted that the possible decrease in $\sigma_{\mathrm{SF}}(T)$ at the lower temperatures is also seen in the Mu-O_2 data [9]. A simple average of the Mu-Cs results in Table II gives $\sigma_{\mathrm{SF}}=39.7\pm6.0\times10^{-16}$ cm^2, taking into account the overall uncertainty.

TABLE II. Spin-flip cross sections.

T	$\sigma_{\mathrm{SF}}^{\mathrm{expt}}$ (Mu)	$\sigma_{\mathrm{SF}}^{\mathrm{theor}}$ (H)	
(K)	(10^{-16} cm^2)	Ref. [26]	Ref. [27]
543±3[a]	35.9±1.8[b]	59.4	99
565±3	41.2±1.6	59.2	98
566±3	42.3±1.8	59.2	98
643±3	39.5±2.6	58.6	97

[a] T uncertainty is $\lesssim\pm3$ K, which has little effect on the calculation of the Cs number density in the target vessel.

[b] Quoted errors are one standard deviation from the fits of Eqs. (3) and (5) to the data. Estimated systematic errors are about 10%, mainly due to uncertainties in the Cs density from the boiler temperature (Table I).

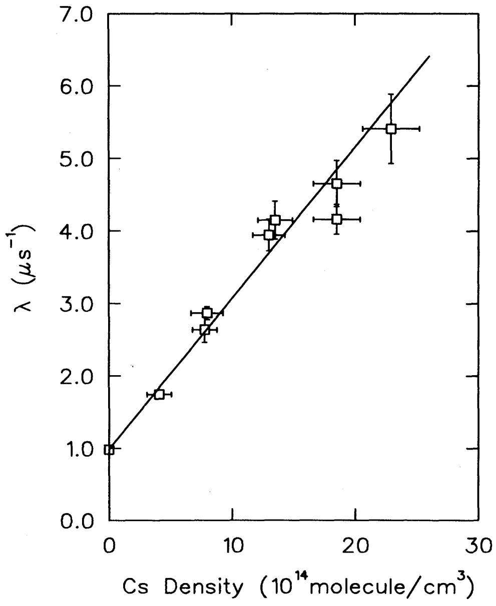

FIG. 3. Spin-relaxation rate λ vs Cs number density at 566 K and an N_2 moderator pressure of 2 atm. The vertical error bars are due to counting statistics; the horizontal errors are due to uncertainty in Cs density (see discussion in the text). The spin-flip cross section $\sigma_{\mathrm{SF}}(T)$ is obtained from the slope and Eq. (5) is equal to $(42\pm2)\times10^{-16}$ cm^2. Here the quoted error (±5%) is statistical only.

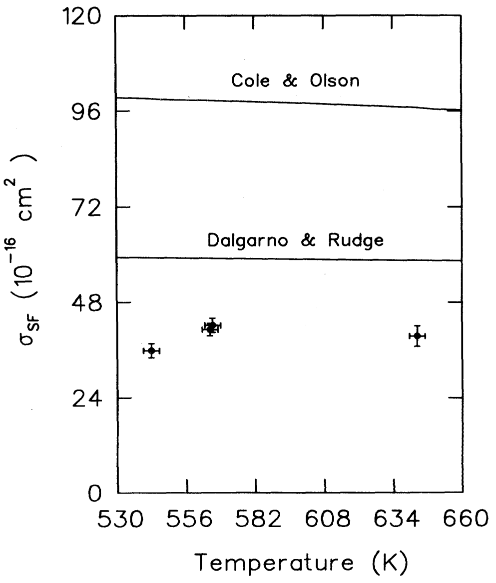

FIG. 4. Spin-flip cross sections $\sigma_{\mathrm{SF}}(T)$. Solid lines are calculations for H-Cs. The vertical errors on the experimental points are one standard deviation from the fits of Eq. (5) to the data. Systematic errors are 10%; the horizontal errors are estimated temperature uncertainties, as discussed in the text.

The analysis above assumes that only spin flip contributes to relaxation of the Mu precession signal. Chemical reactions, in which the μ^+ is placed in a different magnetic environment, would also contribute to the transverse field relaxation rate. A possible diamagnetic channel in these experiments is the formation of CsMu ("muide"), the muon analog of CsH. This could form either through a molecular collision with Cs and a moderator (N_2) molecule, or directly via reaction with Cs dimers, though, as stated, the concentration of the latter is believed to be negligible. Traditionally, chemical reactions are distinguished from spin exchange by measuring total pressure dependence and relaxation rate in a *longitudinal* magnetic field [10,11,39,48]. Recently, Senba has found that chemical reaction is also distinguishable from spin exchange in a *transverse* field [50]. This has, in principle, always been possible via the "residual polarization" technique [35,39], but in Senba's recent treatment, separation of these two contributions is due to the fact that the chemical reaction is field independent while the observable relaxation rate due to spin exchange is field dependent. More specifically, the factor of $\frac{1}{2}$ in Eq. (5) is only true for *weak* transverse fields, but not true for intermediate fields where two-frequency muonium precession is observable. This characteristic "heartbeat" signal of muonium has been known for decades and has been studied and used to determine the magnitude of the hyperfine splitting of the muonium atom in matter [49]. However, the dependence of the observed two-frequency relaxation rate on the spin-flip rate has never been investigated in detail.

It has been shown [25] that the muon spin polarization in muonium after n spin-flip collisions at times $t_1,t_2,t_3,\ldots,t_n$ can be expressed by

$$P_n(t)=G(t-t_n)G(t_n-t_{n-1})\cdots G(t_2-t_1)G(t_1-t_0)\ . \tag{6}$$

In low transverse fields, $G(t)$ takes the form

$$G(t)=\tfrac{1}{2}e^{i\omega_{\mathrm{Mu}}t}\ . \tag{7}$$

Therefore,

$$P_n(t)=(\tfrac{1}{2})^{n+1}e^{i\omega_{\mathrm{Mu}}t}\ . \tag{8}$$

The probability that there are exactly n spin-flip collisions between $t_0=0$ and t is given by $\exp(-\lambda_{\mathrm{SF}}t)(\lambda_{\mathrm{SF}}t)^n/n!$, assuming a Poisson distribution. The weighted average muon spin polarization observed at t is expressed by

$$P(t)=\sum_{n=0}^{\infty}e^{-\lambda_{\mathrm{SF}}t}\frac{(\lambda_{\mathrm{SF}}t)^n}{n!}(\tfrac{1}{2})^{n+1}e^{i\omega_{\mathrm{Mu}}t}=\tfrac{1}{2}e^{-\lambda_{\mathrm{SF}}t/2}e^{i\omega_{\mathrm{Mu}}t}\ . \tag{9}$$

Note that this $P(t)$ corresponds to the first term in Eq. (2), with the observable amplitude A_{Mu} empirically determined.

At a field $B\gtrsim 20$ G, one can observe two frequencies with typically about 1 ns experimental resolution, and then the time evolution of the muon spin can be approximately expressed by

$$G(t)=\tfrac{1}{4}e^{i(\omega_{\mathrm{Mu}}+\Omega)t}+\tfrac{1}{4}e^{i(\omega_{\mathrm{Mu}}-\Omega)t}\ , \tag{10}$$

where $\Omega=\omega_0[(x^2+1)^{1/2}-1]/2$ and $x=B/B_0$, with B_0 being 1585 G for a (free) Mu atom. Thus,

$$P_n(t)=(\tfrac{1}{4})^{n+1}e^{i(\omega_{\mathrm{Mu}}+\Omega)t}+(\tfrac{1}{4})^{n+1}e^{i(\omega_{\mathrm{Mu}}-\Omega)t}+H(t_1,t_2,\ldots,t_n,t,\Omega)\ . \tag{11}$$

The cross term $H(t_1,t_2,\ldots,t_n,t,\Omega)$ can be shown to vanish after statistical averaging if $8\Omega>\lambda_{\mathrm{SF}}$ (true for fields $\gtrsim 20$ G) [50]. The polarization at t is then

$$\begin{aligned}P(t)&=\sum_{n=0}^{\infty}e^{-\lambda_{\mathrm{SF}}t}\frac{(\lambda_{\mathrm{SF}}t)^n}{n!}(\tfrac{1}{4})^{n+1}\\&\quad\times[e^{i(\omega_{\mathrm{Mu}}+\Omega)t}+e^{i(\omega_{\mathrm{Mu}}-\Omega)t}]\\&=e^{-\lambda_{\mathrm{SF}}t}e^{\lambda_{\mathrm{SF}}t/4}(\tfrac{1}{4})[e^{i(\omega_{\mathrm{Mu}}+\Omega)t}+e^{i(\omega_{\mathrm{Mu}}-\Omega)t}]\\&=\tfrac{1}{4}e^{-3\lambda_{\mathrm{SF}}t/4}[e^{i(\omega_{\mathrm{Mu}}+\Omega)t}+e^{i(\omega_{\mathrm{Mu}}-\Omega)t}]\ .\end{aligned} \tag{12}$$

The same result can be obtained using the Boltzmann-equation approach given in Ref. [24].

More intuitively, Eq. (6) together with Eq. (10) implies that only $\frac{1}{4}$ of the polarization survives each spin flip at intermediate fields. The polarization lost in a spin-flip collision is, therefore $1-\frac{1}{4}=\frac{3}{4}$, which is the factor in the decay exponent of Eq. (12). This can be understood in more general terms from the complete expression for Eq. (10), which actually contains four frequencies, two of which are averaged to zero by the experimental time resolution. After a spin-flip collision, the muonium atom could be in any of the four eigenstates of the spin Hamiltonian with equal probability, just as if it were newly formed, and therefore precesses with one of the four possible associated frequencies. If only one of these frequencies is monitored, after a spin-flip collision the muon will precess with the same frequency but with a probability of $\frac{1}{4}$. Since the interaction time (typically of order of picoseconds) is very small compared to the hyperfine mixing time (220 ps), the signal will precess coherently with the same probability, $\frac{1}{4}$. The effective rate of loss of the muonium signal is therefore $\frac{3}{4}\lambda_{\mathrm{SF}}$, as in the intermediate-field case of Eq. (12). However, if two of the four frequencies are degenerate and cannot be distinguished experimentally, as in the weak-field case, the probability of coherent precession after a collision is doubled, i.e., $\frac{1}{2}$. The effective loss of signal is then $\frac{1}{2}\lambda_{\mathrm{SF}}$, as in Eq. (9).

In contrast to spin exchange, a chemical reaction will destroy the coherence of muon precession completely due to the change in muon precession frequency from the four possible free muonium frequencies. Thus, the polarization decay rate due to chemical reaction is equal to the chemical reaction rate and is not dependent at all upon the applied magnetic field.

Since the exponential decay factor for $P(t)$ due to spin exchange changes from $\frac{1}{2}$ to $\frac{3}{4}$ at intermediate fields, and does not change for chemical reactions, the measurement of $P(t)$ at both weak (6 G) and intermediate fields (35 G) for the same gas conditions at the same temperature will allow both the spin-exchange and chemical reaction rates to be determined. From measurements conducted at both fields, it was found that there was *no* significant chemical reaction contribution to the Mu-Cs relaxation rate. Hence we conclude that only spin exchange contributes to the relaxation of the Mu signal.

At present, there are no theoretical calculations available for Mu-Cs spin-exchange collisions. As noted, spin-flip cross sections for H-Cs have been calculated by Dalgarno and Rudge [26] and by Cole and Olson [27], giving values of 59×10^{-16} cm^2 and 98×10^{-16} cm^2 at 560 K, respectively (Table II). Theoretical calculations of the spin-flip cross sections for H-A collisions have traditionally assumed that the core electrons can be treated as closed shells [26,27,51]. The first calculations of spin exchange for H-A as well as for A-A were those of Dalgarno and Rudge [26], who used asymptotic expansion methods to determine the difference potential between the $X\,^1\Sigma$ and $a\,^3\Sigma$ molecular states and the straight-line trajectory method to estimate the cross sections. Chang and Walker [51], using semiclassical and partial-wave analysis, also calculated the spin-flip cross sections for A-A collisions. The more recent calculations by Cole and Olson [27] for H-A collisions have used a pseudopotential molecular-structure method to calculate the interaction potentials and a full quantal *S*-matrix technique, as well as a straight-line trajectory method, to determine the spin-flip cross sections. The quantal method included contributions from the quasibound states (or "orbiting resonances"), which are absent in the straight-line method. Both the Chang and Walker [51] and the Cole and Olson [27] calculations find that Dalgarno and Rudge underestimate the spin-flip cross sections by 10% (H-Li and Li-Li) to 40% (H-Cs and Cs-Cs).

There are no direct measurements of H-A total cross sections that have been published to compare with these calculations. There are, however, a number of experimental results available for Cs-Cs collisions [16,17,18], which mostly range over $(2.0-2.4)\times10^{-14}$ cm^2, with more recent data [16,17] giving values of 1.4×10^{-14} and 1.5×10^{-14} cm^2, respectively. All these values are in relatively good agreement with Dalgarno and Rudge's calculation of 2.0×10^{-14} cm^2. In comparison, Chang and Walker's calculation gives 2.8×10^{-14} cm^2. Since Dalgarno and Rudge's method requires that the difference between the ionization potentials (IP) of the colliding partners is small, it is expected that their results for H-Cs (it has the largest IP difference among all H-A collision partners) are not nearly as accurate as for Cs-Cs collisions. This suggests that Cole and Olson's calculation for H-Cs collisions is the most accurate. However, as mentioned earlier, the experimental differential spin-flip cross section of H-Na at 300 K was found to be *seven* times larger than the theoretical calculations in Ref. [14], the total cross section of which agreed with those of Cole and Olson, suggesting that the latter calculations underestimate the true values. Spin-flip reaction rates for H-Rb collisions have also been estimated from H-atom polarizations in an optical pumping experiment [12]. It is suggested therein that Cole and Olson also underestimate the reaction rate but by a factor of 2 in this case, in the same direction as the results of Ref. [14]. Total spin-flip cross sections of H-Na for a fast (2 keV) H beam incident on a Na target have also been evaluated from proton polarizations, and these are in reasonably good agreement with extrapolations of Cole and Olson's calculations [15,52]. This may be fortuitous, though, since the method used in these calculations is presumably not accurate at large (>2.5 eV) collisional energies because core-core interactions are not treated correctly. Our assessment is that the agreement between experimental and theoretical values of *thermal* H-A spin-flip cross sections, insofar as comparison can be made [12,14], seems generally to be poor, with the calculations of Cole and Olson in particular *underestimating* the cross sections.

Our measured Mu-Cs thermal spin-flip cross sections are significantly lower than the *calculated* H-Cs values: two-thirds of the lower value of Dalgarno and Rudge, and less than half of the presumably more accurate value of Cole and Olson (Table II, Fig. 4), indicating a significant isotopic effect. As mentioned above, if Cole and Olson's calculations do in fact underestimate the H-A spin-flip cross sections, then the magnitude of this isotope effect could be greater still. The same trend has also been seen in the cases of Mu-O_2 versus H-O_2 and Mu-NO versus H-NO spin-exchange scattering [8–10,24], where the ratio of $\sigma_{\rm SF}({\rm Mu}):\sigma_{\rm SF}({\rm H})$ is about 1:3 for both cases.

We can estimate $\sigma_{\rm SF}^{\rm Mu}(T)$ from the straight-line trajectory methods [26,27]. In the calculation by Dalgarno and Rudge, the difference potential (between singlet and triplet) is only dependent on the ionization potentials of the colliding partners, and since Mu has essentially the same IP as H, Mu-Cs should have roughly the same spin-flip cross sections as H-Cs at the same velocity. Although in Cole and Olson's calculation a more realistic potential is assumed, the spin-flip cross section in both cases is represented by

$$[\sigma_{\rm SF}(v)]^{1/2}=a-b\ln(v)\ . \tag{13}$$

If H-Cs and Mu-Cs would have the same parameters *a* and *b*, then the thermally averaged cross section of Mu-Cs would be expected to be less than that of H-Cs at the same temperature, because its velocity distribution is shifted to higher values ($\bar{v}_{\rm Mu}\approx3\bar{v}_{\rm H}$). If for H-Cs one can write, at energy *E*,

$$[\sigma_{\rm SF}^{\rm H}(E)]^{1/2}=A-B\ln(E)\ , \tag{14}$$

where *A* and *B* are constants depending on *a*, *b*, and $\mu_{\rm H}$, the reduced mass of H-Cs, then for Mu-Cs,

$$[\sigma_{\rm SF}^{\rm Mu}(E)]^{1/2}=A-B\ln(\mu_{\rm H}/\mu_{\rm Mu})-B\ln(E)\ , \tag{15}$$

with $\mu_{\rm Mu}$ being the reduced mass of Mu-Cs. Using Eqs. (4) and (15) and Dalgarno and Rudge's parameters for H-Cs, $\sigma_{\rm SF}^{\rm Mu}(T)$ is calculated to be 52×10^{-16} cm^2 at 560 K. Though this is within 20% of the experimental value (Table II), it is recalled that their calculations are expected to *underestimate* this cross section. Similarly, from considerations of velocity distribution effects only, it is determined that Cole and Olson's method gives $\sigma_{\rm SF}^{\rm Mu}(T)\approx85\times10^{-16}$ cm^2 at the same temperature, in considerable disagreement with the experimental data (Table II). In comparison with both the H-atom and Mu-atom values in Table II, then, it seems clear that these calculations do *not* account for the isotope effect seen here, though a trend to a decreased spin-flip cross section for Mu is indicated. At thermal energies, the contributions from orbiting resonances do appear to be significant [27]. Furthermore, these contributions only depend on singlet potentials and are very sensitive to small changes in potential curves and reduced masses [30,31,53]. Therefore, an accurate calculation of the Mu-Cs potential-energy curve is necessary for a precise evaluation of spin-flip cross sections.

The quantum total spin-flip cross section for spin-$\frac{1}{2}$ collision partners at energy E, independent of nuclear spin and final hyperfine state, is defined [19,26,32] by

$$\sigma_{\mathrm{SF}}(E)=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2(\delta_l^3-\delta_l^1)\ , \tag{16}$$

where $k=\mu v/\hbar$ is the incident wave number, and δ_l^3 and δ_l^1 are the phase shifts for scattering from the interaction potentials for triplet and singlet states. The difference in phase shift, $\Delta_l=\delta_l^3-\delta_l^1$, will disappear at large separations, indicating that there will be a maximum number ($l_{\max}$) of partial waves that could contribute to the cross section, contained as well as in the semiclassical approximations of Eq. (15). Since Mu is lighter than the H atom by a factor of 9, the maximum number of partial waves for Mu is about three times less than H at a given energy, assuming both have the same interaction potentials. The isotope effect discussed above is likely a reflection of the sampling of fewer partial waves in the Mu scattering process [9,24] as well as different resonance structures, but accurate theoretical calculations are required to confirm this.

Comparisons of this nature between Mu- and H-atom spin-flip cross sections could prove valuable in determining intermolecular potentials of short and intermediate range between H atoms and various dopants, since only the H-H spin-exchange potential is accurately known [28,30–32,54]. Interestingly, in the calculations of Ref. [28], a dramatic isotope effect is predicted in Mu-H versus H-H spin exchange at *low* temperatures, but it is one in which $\sigma_{\mathrm{SF}}^{\mathrm{Mu}}$ is actually considerably *larger* than $\sigma_{\mathrm{SF}}^{\mathrm{H}}$, just opposite to the situation reported here (and in Refs. [9,11]). This is presumably due to specific resonances from the partial-wave scattering effect referred to above. It can also be noted that a random-phase approximation to Eq. (16) would predict a mass-independent cross section [9], in contrast to both the present and earlier [9,11,24] experimental results.

IV. CONCLUSIONS

The thermally averaged electron-spin-flip cross sections between Mu and Cs have been measured by the μSR technique to an overall uncertainty of less than 15%. The measured Mu-Cs cross sections are found to be less than one-half of the most recent calculated value for H-Cs [27], indicating a significant isotope effect. The actual isotope effect may be even greater if the calculated H-A spin-flip cross sections [26,27] are underestimated, as some experiments seem to indicate [12,14]. This interesting isotope effect may originate from the different sampling of partial waves and the different resonance structures of the two systems, which are very sensitive to potential-energy curves and reduced masses. Theoretical calculations of this cross section are required to compare with the experimental data and to explain the origins of this isotope effect.

An alternative method has also been developed to distinguish between spin exchange and possible chemical reactions in a μSR experiment, which may have applications to other reaction systems as well, notably those involving muon depolarization in muonium addition reactions [55].

Note added in proof. A recently published report of the Mu-Rb spin-flip cross section by Barton *et al.* [A. S. Barton *et al.*, Phys. Rev. Lett. **70**, 758 (1993)] gives $\sigma_{\mathrm{SF}}^{\text{Mu-Rb}}(T)=(136\pm17\pm25)\times10^{-16}\ \mathrm{cm}^2$ at 200 K, which is about a factor of 4 larger than ours. The polarized Rb used in their experiment could account for a factor of 2 [27]. They also assumed *no* isotope effects in σ_{SF} among Mu-Rb, $(\mu^-\mathrm{He})^+e^-$-Rb, and H-Rb, seemingly contradictory to both theory and our experimental results. To properly assess the difference between our results and theirs, though, it is necessary to know the details of their experiment and data analysis, which is not given in the paper. It can be noted that the calculated H-Rb spin-flip cross section is actually smaller (~15%) than that of H-Cs [27].

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