Spin Exchange and Recombination in a Gas of Atomic Hydrogen at 1.2 K

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We report an accurate measurement of the longitudinal spin-exchange broadening cross section for the $\Delta F = 1$, $\Delta m_F = 0$ hyperfine transition of the hydrogen atom at 1.2 K. The result, $\overline{\sigma} = 0.51(2)$ Å^2, is the first of its kind which is sufficiently accurate to clearly demonstrate disagreement with theory. Resolution of this discrepancy is relevant to the understanding of cold atom collisions and may involve a revision of the long range part of the *ab initio* H atom pair potentials. A by-product of our work is an improved measurement of the two body recombination rate constant $k = 1.9(1) \times 10^{-33}$ cm^6/s for the gas phase reaction H + H + ^{4}He $\rightarrow$ H$_2$ + ^{4}He.

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Recent experimental evidence obtained using a cryogenic hydrogen maser indicates that serious discrepancies exist between measured and calculated hydrogen atom (H) spin-exchange cross sections at subkelvin temperatures [1–3]. This is of concern given the remarkable accuracy to which the relevant interatomic potentials are known [4] and the degree of sophistication to which the theoretical description of the problem has been advanced [5,6]. In light of the traditional role played by the H atom as a prototype system for the understanding of atomic processes, the resolution of these inconsistencies is essential to the understanding of cold atom collisions [7]. The demonstrated sensitivity of various cross sections to the details of the potentials [3,5,6,8,9] suggests that the new data may prove valuable during future refinements of *ab initio* H-H potentials. In particular, the low energy collisions characteristic of these new measurements probe very long range interactions between H atoms.

Motivated by these observations, we have undertaken a series of measurements on a gas of hydrogen atoms at 1.2 K using pulsed hyperfine magnetic resonance techniques [10,11]. Our immediate goal was to demonstrate more directly the existence of discrepancies between theory and experiment. This has resulted in what is to date the only accurate determination of the thermally averaged longitudinal [12] spin-exchange broadening cross section ($\overline{\sigma}$) for the $\Delta F = 1$, $\Delta m_F = 0$ hyperfine transition at cryogenic temperatures [13]. We report a value for $\overline{\sigma}$ which is in significant disagreement with theory yet consistent with previous results [3]. Moreover, the accuracy of our result for $\overline{\sigma}$ is such that it should provide an excellent measure against which future modifications of H atom potentials may be gauged. Before proceeding, we note that in terms of the notation whereby the four hyperfine states of the ground electronic state of the hydrogen atom are labeled $|a\rangle$, $|b\rangle$, $|c\rangle$, and $|d\rangle$ in order of increasing energy in low magnetic fields, the $\Delta F = 1$, $\Delta m_F = 0$ transition corresponds to the *a-c* transition.

A number of authors have treated the hydrogen atom spin-exchange problem in the degenerate internal states (DIS) approximation [8,9,15,16] in which hyperfine interactions are neglected in comparison to electron exchange interactions during collision. In general, good agreement [17] is obtained between both frequency shift and broadening cross sections calculated in this manner and experiments carried out at temperatures above 77 K [18]. At lower temperatures a rather dramatic reduction in the spin-exchange relaxation rate is observed [19,20]. Although accurate data do not exist, qualitative agreement between measured relaxation rates, and calculated spin-exchange broadening cross sections, has been demonstrated at temperatures down to 4 K [9,20]. At yet lower temperatures the DIS approximation cannot be expected to give accurate results [21] and one is forced to consider nonadiabatic effects [5,6].

Stoof *et al.* [6,22] examined spin-exchange and dipolar relaxation in atomic hydrogen under conditions relevant to a number of low temperature experimental situations. Unlike the DIS regime the longitudinal and transverse spin-exchange relaxation rates [23] are no longer simply related via the identity $1/T_1^{\text{se}} = 2/T_2^{\text{se}}$. At low temperatures and zero magnetic field, relaxation is dominated by three spin-exchange processes which drive the populations of the $|a\rangle$ and $|c\rangle$ states towards thermal equilibrium (TE). One finds that

$$\frac{d}{dt}(n_a - n_c) = -2(2G_{aa \rightarrow cc} + G_{aa \rightarrow bd})n_a^2$$
$$+ 2(2G_{cc \rightarrow aa} + G_{cc \rightarrow bd})n_c^2$$
$$+ 2(G_{bd \rightarrow aa} - G_{bd \rightarrow cc})n_b n_d, \quad (1)$$

where the rate constants $G_{\alpha\beta \rightarrow \gamma\delta}$ describe the exchange processes $\alpha\beta \rightarrow \gamma\delta$ [22], and the n_i represent the density of atoms in the various hyperfine states. For temperatures of order 1 K and small deviations from TE, the approximations $G_{aa \rightarrow bd} \approx G_{cc \rightarrow bd}$, $G_{\alpha\beta \rightarrow \gamma\delta} \approx G_{\gamma\delta \rightarrow \alpha\beta}$, and $n_a + n_c \approx n/2$, where n is the total H

atom density, are valid and Eq. (1) can be written in the form

$$\frac{d}{dt}(n_a - n_c) = -\overline{\sigma}\,\overline{v}n(n_a - n_c),\qquad(2)$$

where $\overline{v}$ is the thermally averaged relative collision velocity. Comparing Eqs. (1) and (2) we identify the longitudinal spin-exchange relaxation rate

$$1/T_1^{se} = \overline{\sigma}\,\overline{v}n = (2G_{cc\to aa} + G_{bd\to aa})n.\qquad(3)$$

It is convenient to discuss the analysis of our experiment in terms of the fictitious spin 1/2 analogy in which the time evolution of the atomic density matrix is likened to the time evolution of the magnetic moment of a fictitious spin 1/2 particle. Within this framework, the longitudinal spin magnetization of an ensemble of these fictitious particles in a magnetic field is analogous to the population difference between atoms in the $|a\rangle$ and $|c\rangle$ states. Details can be found in an appendix to Ref. [11].

Our measurement of the spin-exchange relaxation rate $1/T_1^{se}$ using hyperfine magnetic resonance techniques is based upon the use of a finite train of π-$\pi/2$ tipping pulse pairs. Each π pulse in the train inverts the effective spin magnetization M_z of the sample which subsequently relaxes back towards its TE value M_0. The free induction decay (FID) response of the atoms to the $\pi/2$ pulse then provides a measure of the amplitude of M_z a time Δt following the π pulse. Pulse pairs are separated by a time interval much longer than T_1 so that TE is achieved prior to each new π pulse. In the absence of other processes, one expects the longitudinal magnetization to recover according to

$$M_z = M_0[1 - 2\exp(-\Delta t/T_1)]\qquad(4)$$

from which T_1 may be determined by measuring M_z as a function of Δt. In general, T_1 will contain contributions from one body processes as well as spin exchange. That is, $1/T_1 = 1/T_1^{se} + \Gamma_0$ where Γ_0 accounts for relaxation processes which are independent of n.

This procedure is complicated by recombination events which reduce the atomic density over the course of the measurement. The two body gas phase recombination reaction $H + H + {}^4He \to H_2 + {}^4He$ causes the atomic density n to decay such that

$$\frac{1}{n(t)} = \frac{1}{n_0}\left(1 + \frac{1}{\tau_0}\right),\qquad(5)$$

where $\tau_0 = 1/kn_{He}n_0$ is a time characteristic of the decay [10,11]: τ_0 is inversely proportional to the H atom density n_0 at time $t = 0$, the ${}^4He$ atom density n_{He}, and the two body gas phase recombination rate constant k.

One can use this information to calculate what M_0 was at the time of the ith π-$\pi/2$ pulse pair if it is subsequently measured using a single $\pi/2$ pulse a time τ_i later (again $\tau_i \gg T_1$ to allow the system to reach TE). If the atomic density remains constant on the time scale

of each interpulse spacing Δt_i, then

$$\ln\left[1 - \chi_i\frac{M_z}{M_0}\right] = -\Delta t_i\left[\frac{1}{\chi_i T_1^{se}} + \Gamma_0\right] + \ln(2),\quad(6)$$

where $0 < \chi_i = 1 - \tau_i/\tau_0 < 1$ describes the decrease in M_0 over the course of time due to recombination. Here M_0 and τ_0 implicitly refer to the values of these quantities at the time of the single $\pi/2$ pulse. Likewise $1/T_1^{se}$ is the spin-exchange relaxation rate which corresponds to the atomic density at that time.

Most of the experimental details pertinent to the measurements we describe have been reported in detail elsewhere [11]. A sealed Pyrex glass cell containing a mixture of H_2 and ${}^4He$ gases is cooled to temperatures of order 1 K in a pumped liquid ${}^4He$ (ℓ-${}^4He$) bath. The temperature of this bath and consequently that of the cell is measured and regulated to within 0.1 mK by monitoring the vapor pressure of the ℓ-${}^4He$. The temperature within the cell can be monitored very precisely by observing the ${}^4He$ buffer gas shift [11]. A pulsed 50 MHz oscillator is used to dissociate H_2 molecules adsorbed to the inner walls of the cell. Sufficient ${}^4He$ is added to the cell prior to sealing to form a saturated superfluid film of ℓ-${}^4He$ within the cell. This film suppresses adsorption of H atoms to the cell walls.

The cell is located along the axis of a 1420 MHz split ring resonator which is used for magnetic resonance studies. A 6 mT longitudinal magnetic field with first order gradient correction provides a homogeneous bias field which effectively isolates the a-c transition from neighboring transitions. Stray fields from external sources are largely eliminated by magnetic shields which surround the cryostat; the residual static field transverse to the axis of the resonator was determined to be less than 35 nT by nulling the longitudinal field and measuring the frequency of the a-b and a-d transitions.

The power radiated by the H atoms following a magnetic resonance tipping pulse is determined following a careful calibration of all components of the microwave detection system. The atomic density is subsequently determined knowing the quality factor Q of the resonator and the filling factor η for the cell-resonator geometry. The absolute calibration of the density depends upon the product ηQ which can be determined by measuring the length of time and resonant microwave power required to invert the $|a\rangle$ and $|c\rangle$ state populations with a π tipping pulse. For the particular cell used in this work we find $\eta Q = 512(19)$. This last step is crucial to the accurate determination of atomic densities.

An independent measurement of the filling factor using a perturbation technique wherein small Teflon and metallic spheres are passed throughout the volume occupied by the cell [24] yields $\eta = 0.280(11)$. When combined with a direct measurement of the quality factor of the critically coupled resonator, we find $\eta Q = 515(21)$, in excellent agreement with the value reported above. A third measure of this product is obtained by fitting the FID response of
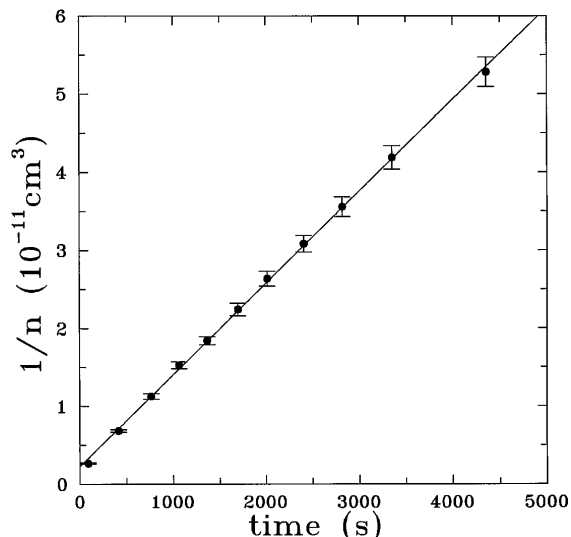
FIG. 1. Measurement of the recombination rate constant k for the two body gas phase recombination reaction H + H + ^{4}He → H_2 + ^{4}He at 1.23 K. The slope of the fit to the data yields the product kn_{He} [cf. Eq. (5)]; n_{He} is accurately determined from vapor pressure measurements.

the atoms to a numerically integrated solution of the differential equations describing the decay using measured values of T_1 [11]. The form of this decay is determined primarily by radiation damping and can thus be used to determine the coupling ηQ between the atoms and the resonator. The result of such an analysis is again in excellent agreement with the values quoted above.

In Fig. 1 we plot an example of the inverse of the measured H atom density following a single rf discharge pulse as a function of time. Knowing the ^{4}He vapor density, the slope of a least squares fit of the data to a straight line [cf. Eq. (5)] yields a measure of the two body recombination rate constant k. We find $k = 1.9(1) \times 10^{-33}$ cm^6/s at 1.23 K, in agreement with the value 1.8×10^{-33} cm^6/s calculated by Greben et al. at 1 K [25]. This result is considerably more accurate than that reported by Hardy et al. [10] primarily because of improved ^{4}He vapor pressure measurements and temperature regulation [11]. Measurements similar to the one shown in Fig. 1 but at different temperatures (^{4}He atom densities) reproduce this result very well, indicating that the recombination rate is indeed proportional to the ^{4}He density, and that this reaction is the only significant recombination process within the cell.

The density independent relaxation rate Γ_0 is determined by examining the response of the atomic system to the pulse sequence described above in the low density regime where recombination can be neglected [cf. Eq. (4)]. It is found that $\Gamma_0 \approx 0.2$ s^{-1} but that the exact value changes from discharge to discharge. The analysis of data obtained at higher densities is illustrated in Fig. 2 [cf. Eq. (6)]. The triangles represent an analysis in which both recombination and density independent

relaxation are ignored (i.e., $\chi_i = 1$, $\Gamma_0 = 0$). The same data are replotted after the effects of recombination (finite measured χ_i) are included (circles) and after both recombination and density independent relaxation (measured Γ_0) are included (squares). The slope of a fit to the data yields a measure of the spin-exchange relaxation rate $1/T_1^{se}$ at $n = 8.9 \times 10^{10}$ cm^{-3}. An extrapolation of the fit to $\Delta t = 0$ passes very closely to ln2, providing a useful check of the analysis. Similar agreement is obtained for all of the data we collected. A compilation of relaxation rates measured in this fashion is presented in Fig. 3 as a function of the H atom density. The slope of a fit to these data yields a value $\overline{\sigma} = 0.51(2)$ Å^2 at 1.23 K. We note that the data shown in Fig. 3 were obtained following a single discharge to illustrate the fact that a single measured value of Γ_0 is sufficient to describe a wide range of data. We emphasize that changes in Γ_0 do not affect the value determined for $\overline{\sigma}$ in this manner to within the stated accuracy of the measurement.

Our experimental result should be compared to the value $\overline{\sigma} = 0.37$ Å^2 calculated from the rate constants $G_{\alpha\beta\rightarrow\gamma\delta}$ [6,22]. We note that the theoretical prediction lies well below the experimentally determined cross section. This situation is comparable to that observed at 0.5 K where the experimentally determined transverse spin-exchange broadening cross section is larger than predicted by theory by roughly the same factor [3]. The result presented here thus lends considerable support to
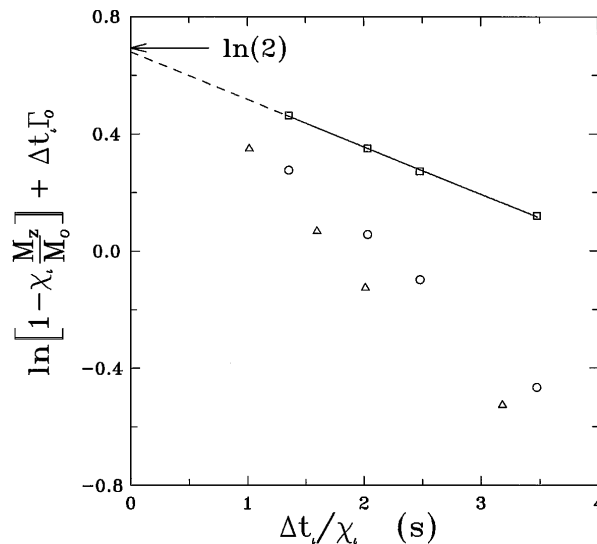

FIG. 2. Analysis of data obtained from four π-π/2 tipping pulse pairs followed by a single π/2 pulse as outlined in the text. Each datum corresponds to a measurement of the longitudinal (fictitious) magnetization a time Δt after the application of a π tipping pulse. The parameter χ_i accounts for recombination of H to form H_2 over the course of the measurement while Γ_0 represents relaxation processes which are independent of n. Triangles illustrate an analysis in which both effects are ignored ($\chi_i = 1$, $\Gamma_0 = 0$). The same data are replotted so as to correct for recombination (circles) and for both effects (squares). The slope of a fit to the data yields the longitudinal spin-exchange relaxation rate $1/T_1^{se}$ [cf. Eq. (6)].
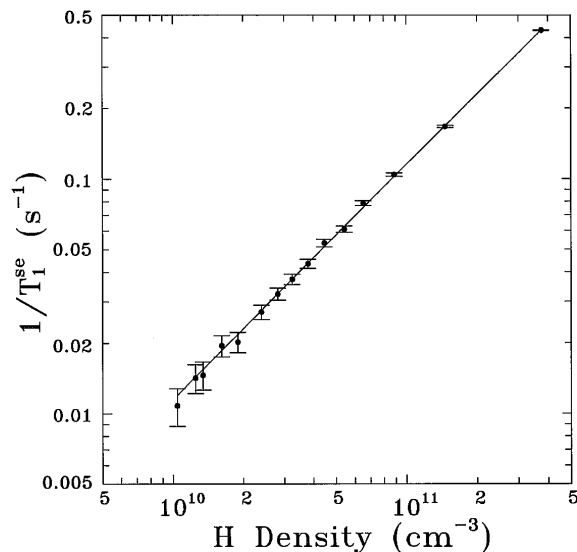
FIG. 3. Determination of the longitudinal spin-exchange relaxation cross section $\overline{\sigma}$. Each datum corresponds to a measurement of $1/T_1^{\text{se}}$ at a different H atom density as illustrated in Fig. 2. The slope of a fit to the data yields $\overline{\sigma}$ after dividing by the thermally averaged relative velocity $\overline{v}$.

the 0.5 K measurements. Based upon this observation, one may argue either that the H atom spin-exchange collision problem is not fully understood at low collision energies, or that the pair potentials used to calculate the various cross sections are not sufficiently accurate. In the latter case, the experimental results we have presented here and previously [1–3] should provide an excellent gauge against which future modifications to these potentials can be judged. In either case, resolution of these discrepancies will likely be an important step towards furthering the understanding of cold atom collisions.

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