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Duration of hydrogen-atom spin-exchange collisions*

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Interruption of the hyperfine interaction during electron spin-exchange collisions shifts the hydrogen-atom ground-state $\Delta m_F = 0$ hyperfine transition frequency in proportion to the spin-exchange collision rate and to the average time T_D during which the exchange interaction interrupts the hyperfine interaction. Measurements of the thermal average T_D for hydrogen-hydrogen collisions at 308 °K in an atomic hydrogen maser confirm the predictions of a semiclassical theory and a numerical estimate using straight-line collision trajectories. Measurements of much longer T_D for hydrogen-atom collisions with O_2, NO, and NO_2 molecules are consistent with the formation of long-lived intermediate complexes during some collisions.

I. INTRODUCTION

Electron spin-exchange collisions between ground-state paramagnetic atoms have been treated by several authors using a model which neglects all interactions other than electron exchange during the collisions.[1-8] This model predicts small shifts of the $\Delta m_F = 0$ hyperfine transition frequency in ground-state atomic hydrogen proportional to the rate of collision with other hydrogen atoms and to the difference between the two $m_F = 0$ level populations.[5-8] Measurements of spin-exchange frequency shifts by two related techniques[9] using an atomic hydrogen maser[10-12] have confirmed the theoretical estimate[13] of the thermal average spin-exchange frequency-shift cross section λ and the theory which relates λ to the hydrogen maser oscillation frequency.[8]

This paper extends the semiclassical description of electron spin-exchange collisions to first order in the hyperfine interaction during collisions, in order to include additional terms of order $\omega_0 T_D$ times the zero-order terms, where ω_0 is the ground-state hyperfine transition frequency and T_D is the average time during which a spin-exchange collision interrupts the hyperfine interaction. For hydrogen-hydrogen collisions at room temperature $\omega_0 T_D \simeq 2\times10^{-3}$, so that the additional terms are relatively small, but they predict appreciable shifts of the $\Delta m_F = 0$ atomic-hydrogen maser oscillation frequency which are distinguishable from the shifts proportional to λ because of having a different dependence on the hydrogen-atom level populations. In addition, shifts proportional to collision duration occur for hydrogen-atom collisions with any paramagnetic atom or molecule, whereas the model which neglects the hyperfine interaction during collisions predicts shifts of the $\Delta m_F = 0$ hydrogen hyperfine transition only for collisions with other hydrogen atoms.[14]

The semiclassical formulation of spin-exchange frequency shifts developed by Bender[5] is extended in Sec. II to include hyperfine interactions during collisions, and the size of the additional shift of the $\Delta m_F = 0$ hydrogen hyperfine transition frequency is estimated using undeflected collision paths. Section III relates this theory to the frequency of a hydrogen maser oscillating on the $\Delta m_F = 0$ transition and presents experimental results for hydrogen-hydrogen collisions. Measurements of collisions between hydrogen atoms and paramagnetic molecules are described in Sec. IV. Preliminary results for this work have been reported previously.[15,16]

II. HYDROGEN-HYDROGEN SPIN-EXCHANGE FREQUENCY SHIFTS

The semiclassical model of a collision between two ground-state hydrogen atoms assumes that the nuclei follow distinguishable, classical paths and that the time evolution of the $2^4 = 16$ combined electron and proton spin states is determined by an effective spin Hamiltonian[1-3,5,7]

$$H(t) = E_T P_T + E_S P_S + V . \tag{1}$$

E_T is the triplet-state hydrogen-hydrogen interaction energy, and P_T is a 16×16 element matrix operator which projects out of the full set of spin states the part which is symmetric with respect to interchanging electron spins. E_S and P_S are the singlet-state interaction energy and projection operator, respectively, and V stands for everything else in the effective spin Hamiltonian. E_T, E_S, and V vary with time as the internuclear separation R changes during the collision.

We solve the Schrödinger equation for the Hamiltonian (1) by time-dependent perturbation theory with $E_T P_T + E_S P_S$ as the unperturbed collision Hamiltonian and V included only to first order. The evolution of spin states from time t_- well before the collision to time t_+ long afterwards is described by a spin evolution operator $U(t_+, t_-) = U_0(t_+, t_-)U_I(t_+, t_-)$, where

$$U_0(t_+, t_-) = \exp\left(-\frac{i}{\hbar}\int_{t_-}^{t_+} E_S\, dt'\right) P_S + \exp\left(-\frac{i}{\hbar}\int_{t_-}^{t_+} E_T\, dt'\right) P_T \qquad (2)$$

is the usual solution[1,2,5] ignoring effects other than the exchange interaction during collisions, and

$$U_I(t_+, t_-) = 1 - \frac{i}{\hbar}\int_{t_-}^{t_+} U_0^\dagger(\tau, t_-)V(\tau)U_0(\tau, t_-)\, d\tau . \qquad (3)$$

As a first approximation to the effects of including the hyperfine interaction during the collision, we assume

$$V = \hbar\omega_0(\vec{I}_1 \cdot \vec{S}_1 + \vec{I}_2 \cdot \vec{S}_2) = \hbar\omega_0 O , \qquad (4)$$

with $\vec{I}_{1,2}$ and $\vec{S}_{1,2}$ the nuclear and electron spins of the two colliding atoms and $\hbar\omega_0$ the unperturbed hydrogen hyperfine transition energy. We neglect the anisotropic hyperfine interaction, the cross-term hyperfine interaction proportional to $\vec{I}_1 \cdot \vec{S}_2 + \vec{I}_2 \cdot \vec{S}_1$, and perturbations of the direct hyperfine interaction due to electron wave-function overlap. These effects are responsible for the hyperfine frequency shifts of paramagnetic atoms caused by collisions with diamagnetic buffer gases, and such shifts are two or three orders of magnitude smaller than the shifts of interest here.[17] The spin-orbit interaction vanishes to first order when averaged over the direction of the collision plane. The electron spin-spin interaction has no first-order $\Delta m_F = 0$ transition matrix elements, and it commutes with the exchange interaction, so that including it would only introduce slight orientation dependences to E_T and E_S. The only remaining time dependence is provided by assuming undeflected classical paths for the atomic nuclei and using the numerical singlet and triplet interaction potentials calculated by Kolos and Wolniewicz.[18]

Following Bender,[5] we calculate the spin space density matrix $\rho(t_+)$ immediately after a spin-exchange collision in terms of the density matrix $\rho(t_-)$ immediately before the collision from

$$\rho(t_+) = \mathrm{Tr}\{U[\rho(t_-) \times \rho(t_-)]U^\dagger\} , \qquad (5)$$

where $\rho(t_-) \times \rho(t_-)$ is the direct product of the density matrices describing the colliding atoms just before the collisions and Tr{ } indicates a trace over the spin states of the second atom. The change of the density matrix due to the collision, integrated over impact parameters and averaged over the thermal distribution of collision velocities, then provides the effects of collisions on the atomic level populations and the widths and frequencies of transitions between levels.[5]

We find that the frequency of the $\Delta m_F = 0$ ground-state hyperfine transition is shifted by collisions by the usual shift proportional to λ plus an additional shift

$$\delta\omega_{42} = -\tfrac{1}{4}\omega_0 T_D[1 - \tfrac{1}{2}(\rho_{22} - \rho_{44})]T_{\mathrm{H}}^{-1} . \qquad (6)$$

$T_{\mathrm{H}}^{-1} = n(\mathrm{H})\bar{v}\sigma$ is the hydrogen-hydrogen electron spin-exchange collision rate, where $n(\mathrm{H})$ is the hydrogen-atom density, $\bar{v}$ is the mean collision velocity, and σ is the thermal average spin-flip cross section.[6,19-23] $\rho_{22} - \rho_{44}$ is the $\Delta m_F = 0$ transition level population difference (see Fig. 1 for notation).

$$T_D = (\bar{v}\sigma)^{-1}\left\langle v \int_0^\infty T_s(v, b) 2\pi b\, db \right\rangle_v \qquad (7)$$

is the average over collision velocities v and impact parameters b of

$$T_s(v, b) = 2\int_{t_-}^{t_+} \cos(\Delta/2)[\cos(\Delta/2) - \cos(\Delta/2 - \theta)]\, dt , \qquad (8)$$

with

$$\hbar\theta(t) = \int_{t_-}^{t} (E_T - E_s)\, dt' \quad \text{and} \quad \Delta = \theta(t_+) .$$

The dependence on v and b is due to the dependence of E_T and E_s on the choice of classical path. For v and b such that Δ is small there is no T_s. For v and b such that $\Delta \gg 1$ there is no contribution to T_s for times before θ has grown to the order of unity nor after θ has reached to within the order of unity of its final value Δ. For intermediate times

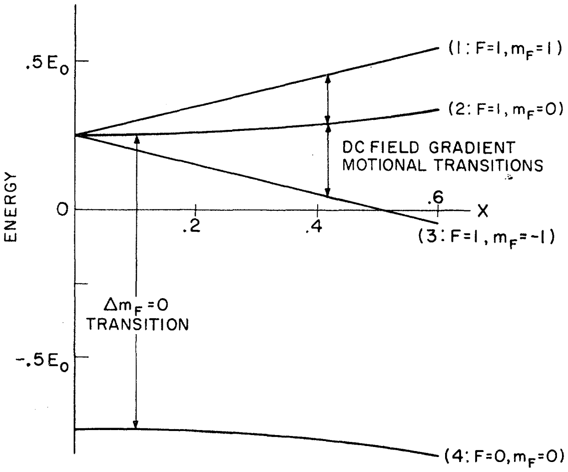

FIG. 1. Atomic hydrogen ground-state energy levels in an applied magnetic field B_0. $X = -(g_J - g_I)\mu_0 B_0/E_0$, where E_0 is the zero-magnetic-field hyperfine interaction energy. State labels are assigned according to energy.

the second term of Eq. (8) washes out, and for $\Delta \gg 1$ the average of $\cos^2(\Delta/2)$ over small increments of velocity is one-half, so that T_s is essentially the time during which "strong" spin-exchange collisions are "strong" in the sense originally introduced by Wittke and Dicke.[2]

Integrating Eq. (8) along straight-line classical paths using numerical potentials[18] and averaging over impact parameters and velocities, we find that for hydrogen-hydrogen collisions at room temperature $T_D(308\,^\circ\mathrm{K}) \simeq 1.6\times 10^{-13}$ sec, and $T_D(77\,^\circ\mathrm{K}) \simeq 4.0\times 10^{-13}$ sec.

Were we to calculate T_D using accelerated classical trajectories corresponding to the interaction potentials, we would expect shorter $T_s(v, b)$ at small b because of the accelerations. On the other hand, we would expect contributions to T_s for larger impact parameters and somewhat longer $T_s \times (v, b)$ at these impact parameters because of orbiting.[24] There would be a very small additional frequency shift proportional to $\rho_{22} + 3\rho_{44}$ and the difference between the duration of singlet collisions and the duration of triplet collisions. The semiclassical estimate using accelerated classical paths and making some correction for centrifugal barrier penetration might be larger or smaller than the straight-path estimate. It would still suffer from the deficiencies of the semiclassical picture, which ignores the identity of the hydrogen nuclei, the distortion of the electron wave functions at small internuclear separations, and the details of the interaction at large internuclear separations, which has been treated theoretically for the static case by Harriman *et al.*[25] The semiclassical model suggests the major dependence on level populations of the frequency shifts because of interruption of hyperfine interaction during electron exchange collisions, and the straight-path value for T_D suggests the order of magnitude of the coefficient.

We have also estimated the effects of hyperfine interaction interruption on the level populations and the width of the $\Delta m_F = 0$ transition using straight classical paths. We find an additional contribution to the $\Delta m_F = 0$ linewidth of order $+2 \times 10^{-4}(3\rho_{44} - \rho_{22})$ times the usual spin-exchange contribution to T_2^{-1}. A similar calculation for $\rho_{22} - \rho_{44}$ predicts an additional relaxation rate of order $+8\times 10^{-4}(\rho_{11}\rho_{33} - \rho_{44}^2)$ times the usual spin-exchange contribution to T_1^{-1}. These effects are negligible at the present state of experimental comparisons of T_1^{-1} and T_2^{-1} relaxation rates.[26]

III. HYDROGEN-HYDROGEN COLLISION SHIFTS IN THE HYDROGEN MASER

Shifts of the $\Delta m_F = 0$ oscillation frequency of an atomic hydrogen maser due to spin-exchange effects other than interruption of the hyperfine interaction during collisions have been described in detail previously.[8,9] When the maser microwave cavity is tuned well within its resonance width, the oscillation frequency ω is pulled from its density-independent value ω_0 by [Ref. 9, Eq. (3)]

$$\omega - \omega_0 = [(2Q/\omega_0)(\omega_c - \omega_0) - \alpha\lambda]\, \tau_2^{-1}, \tag{9}$$

where Q is the microwave-cavity quality factor, ω_c is the cavity resonance frequency, and $(\pi\tau_2)^{-1}$ is the $\Delta m_F = 0$ transition resonance linewidth (in Hz), including a term $(2\pi T_H)^{-1}$ due to spin-exchange collisions plus terms due to other broadening mechanisms.[27] $\alpha = (\bar{v}/16\pi)(\hbar/\mu_0^2)(V_c/\eta Q V_b)$, where μ_0 is a Bohr magneton and $\eta V_b/V_c$ is a filling factor relating the energy stored in the cavity to the amplitude of rf field driving the $\Delta m_F = 0$ transition.[11,12] Interruption of the hyperfine interaction during spin-exchange collisions between hydrogen atoms introduces additional shifts characterized by Eq. (6), which when added give

$$\omega - \omega_0 = [(2Q/\omega_0)(\omega_c - \omega_0) - \alpha\lambda']\tau_2^{-1} + \epsilon_{\mathrm{H}} T_{\mathrm{H}}^{-1}, \tag{10}$$

with $\epsilon_{\mathrm{H}} = -\frac{1}{4}\omega_0 T_D$ and $\lambda' = \lambda + 2\epsilon_{\mathrm{H}}\sigma$ slightly changed from the usual spin-exchange frequency-shift cross section by the Eq. (6) term proportional to $\rho_{22} - \rho_{44}$. The usual method of tuning the maser microwave cavity[12] is to tune it so that there is no variation of oscillation frequency ω with spin-exchange collision rate T_{H}^{-1}. When that has been done, the spin-exchange tuned cavity frequency ω_{ct} and spin-exchange tuned oscillation frequency ω_t become

$$\omega_{ct} - \omega_0 = (\omega_0/Q)(\tfrac{1}{2}\alpha\lambda' - \epsilon_{\mathrm{H}}), \tag{11}$$

$$\omega_t - \omega_0 = -2\epsilon_{\mathrm{H}}(\tau_2^{-1} - \tfrac{1}{2}T_{\mathrm{H}}^{-1}). \tag{12}$$

The usual spin-exchange tuning procedure does not leave the oscillation frequency tuned to the value it would have in the absence of both cavity pulling and spin-exchange collisions, as was suggested by the earlier spin-exchange theory.[8,28] However, the error is of the order of $\frac{1}{5}$ the usual spin-exchange frequency shift and does not affect the accuracy of any experimental results published to date.[29] Note that the oscillation frequency is shifted from its density-independent value by an amount proportional to ϵ_{H} and that part of the linewidth not contributed by spin-exchange collisions. The variation of tuned oscillation frequency with density-independent linewidth suggests that the coefficient ϵ_{H} can be measured experimentally by varying some noncollision contribution to the linewidth. We have made such a measurement using relaxation by transverse magnetic field gradients to vary the density-independent linewidth.

Figure 2 is a schematic of the apparatus, which is similar to that described in detail previously.[12] Molecular hydrogen is dissociated in the rf discharge shown at bottom center in Fig. 2. Atoms emerging vertically upwards into the vacuum system pass through a state-selecting magnet which throws out of the beam the atoms in the lower two hyperfine spin states and focuses atoms in the upper two spin states into a spherical storage bottle. The bottle is centered axially in a cylindrical microwave cavity operating in the TE_{011} mode and tuned to the frequency of the $\Delta m_F = 0$ hyperfine transition. The cavity is surrounded by an aluminum bell jar, a solenoid producing a variable vertical dc magnetic field, and three concentric molypermalloy magnetic shields. Three ten-turn coils of wire wound on the outside of the bell jar provide changes of dc magnetic field gradient. The usual storage bottle entrance stem is replaced by a multitube collimator in order to eliminate motional averaging frequency shifts of the type discussed by Brenner.[30]

Atoms radiating on the $\Delta m_F = 0$ hyperfine transition can also undergo $\Delta F = 0$, $\Delta m_F = \pm 1$ transitions due to motion through transverse dc magnetic field gradients (Fig. 1). These motional transitions contribute a term independent of level populations to the linewidth $(\pi\tau_2)^{-1}$ of the $\Delta m_F = 0$ transition.[11,31,32] They also introduce[16,33-35] a frequency pulling proportional to the spin-exchange collision rate T_H^{-1}, so that the equation for density-dependent frequency shifts becomes [Ref. 16, Eq. (5)]

$$\omega - \omega_0 = [(2Q/\omega_0)(\omega_c - \omega_0) - \alpha\lambda'](T_0^{-1} + T_M^{-1} + \tfrac{1}{2}T_H^{-1}) + \epsilon_H T_H^{-1} + \epsilon_M T_H^{-1} . \qquad (13)$$

T_M^{-1} is the motional transition contribution to τ_2^{-1} and T_0^{-1} is the residual contribution due to atom-surface collisions and flow out of the storage bottle. ϵ_M is of order zero to 10^{-2}, depending on the configuration of dc and rf magnetic field gradients in the storage bottle. ϵ_M and T_M^{-1} vanish at average dc magnetic fields high enough for the frequencies of the $\Delta F = 0$ transitions to be large compared to the rate at which the atoms bounce back and forth in the magnetic field gradients.[11,16] In that case the spin-exchange tuned cavity and oscillation frequencies are as given in Eqs. (11) and (12). At low average magnetic fields in the presence of residual or applied transverse magnetic field gradients the tuned cavity and oscillation frequencies are[36]

$$\omega_{ct} - \omega_0 = (\omega_0/Q)(\tfrac{1}{2}\alpha\lambda' - \epsilon_H - \epsilon_M) , \qquad (14)$$

$$\omega_t - \omega_0 = -2(\epsilon_H + \epsilon_M)(T_0^{-1} + T_M^{-1}) . \qquad (15)$$

Changes of ϵ_M due to changes of dc magnetic field intensity and configuration produce changes of both the tuned cavity frequency and the tuned oscillation frequency. Comparing the tuned cavity and oscillation frequencies at some relatively high magnetic field (25 mOe), where ϵ_M and T_M^{-1} vanish, to their values at some relatively low magnetic field (4–10 mOe), the change of tuned cavity frequency $\Delta\omega_{ct}$ and change of tuned oscillation frequency $\Delta\omega_t$ are related by

$$\Delta\omega_t = -2\epsilon_H T_M^{-1} + (2Q/\omega_0)\Delta\omega_{ct}(T_0^{-1} + T_M^{-1}) . \qquad (16)$$

Values of $\Delta\omega_t$ produced in this way were measured to a few parts in $10^{-14}\omega_0$ by comparing the oscillation frequency to that of a second hydrogen maser. Corrections for the change of average dc magnetic field were made using measured values of the $(F=1, m_F=0)$ to $(F=1, m_F=-1)$ transition frequency.[28] Small additional corrections to $\Delta\omega_t$ were made for estimated changes of ω_0 with changing magnetic field gradients at low magnetic fields due to the quadratic dependence of the $\Delta m_F = 0$ transition frequency on average dc magnetic field.

Companion values of $\Delta\omega_{ct}$ were measured to a few parts in $10^{-5}(\omega_0/Q)$ by detecting with a lock-in amplifier the cavity response to an external signal

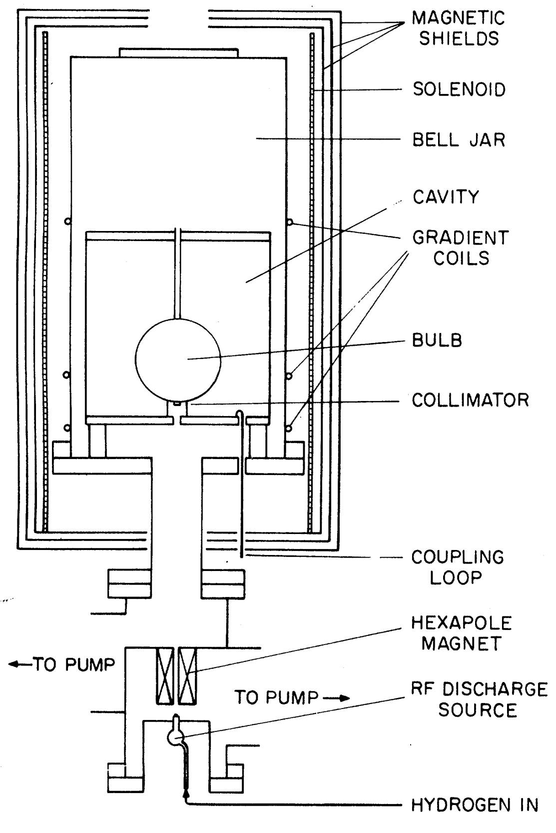

FIG. 2. Schematic diagram of the apparatus.

switched at 5 Hz to alternate sides of the cavity resonance.[9] Changes of oscillation frequency ω with cavity frequency ω_c directly measure τ_2^{-1} [Eq. (13)]. Values of T_M^{-1} companion to $\Delta\omega_t$ and $\Delta\omega_{ct}$ were measured to a few percent by measuring the change of τ_2^{-1} from the low magnetic field configuration to the higher reference configuration while holding the hydrogen-atom beam intensity fixed. Associated values of T_M^{-1}, $\Delta\omega_t$, and $\Delta\omega_{ct}$ were fitted to Eq. (16) with ϵ_H and T_0^{-1} as fitted parameters and with weights derived from accumulated uncertainties due to oscillation frequency fluctuations, cavity frequency drift, and drift of the hydrogen atom beam intensity. Results for both a 5-in.- and a 7-in.-diameter storage bottle are given in Table I. The fitted values of ϵ_H agree to well within the errors, and the fitted values of T_0^{-1} agree with the values labeled $(T_0^{-1})_{\text{expt}}$, which were measured by an independent method described in the Appendix.

The fits to ϵ_H are most conveniently illustrated by defining a corrected oscillation frequency change

$$\Gamma = \Delta\omega_t - (2Q/\omega_0)\Delta\omega_{ct}(T_0^{-1} + T_M^{-1}) , \qquad (17)$$

which can be calculated for each of the low-magnetic-field configuration measurements using $(T_0^{-1})_{\text{expt}}$ and the measured values of $\Delta\omega_t$, $\Delta\omega_{ct}$, and T_M^{-1}. Plots of $\Gamma/2\pi$ against $(\pi T_M)^{-1}$ for both storage bottles are shown in Fig. 3. According to Eqs. (16) and (17), the experimental points should be randomly distributed about a straight line passing through the origin and having slope $-\epsilon_H$: fits to straight lines passing through the origin give essentially the same values of ϵ_H as in Table I. The alternative hypothesis of a systematic offset of $\Gamma/2\pi$ but zero slope (no term in ϵ_H) is not consistent with the data. Allowing for a systematic offset of $\Gamma/2\pi$ in addition to the term in ϵ_H does not give better fits. Consequently, we take as the best experimental estimate of ϵ_H the weighted average of the fits ignoring such systematic offsets and add to the statistical uncertainty an independent estimate of the effects of systematic errors. The result is $\epsilon_H = -4.04(35)\times 10^{-4}$ at mean storage bottle temperature 308(3) °K. The assigned error (35) is one standard deviation from the mean and includes statistical uncertainty (18), (12) uncertainty due to estimated errors in $\Delta\omega_t$ proportional to T_M^{-1}, and (27) uncertainty due to estimated errors in $\Delta\omega_t$ not proportional to T_M^{-1}. The errors proportional to T_M^{-1} are due primarily to uncertainties in the corrections to ω_0 for quadratic field averaging and are taken to be the weighted average of one-half each correction. The errors not proportional to T_M^{-1} are due primarily to uncertainties in the corrections of ω_0 for average dc magnetic field.

TABLE I. Values of frequency shift parameter ϵ_H and density-independent linewidth $(\pi T_0)^{-1}$ fitted to Eq. (16) using data from two storage bottles. Comparison values $(\pi T_0)^{-1}_{\text{expt}}$ were measured as described in the Appendix. Errors are one standard deviation from the mean.

Storage bottle diameter (in.)	5	7
$(\epsilon_H)_{\text{fit}} \times 10^4$	−3.98(27)	−4.09(24)
$(\pi T_0)^{-1}_{\text{fit}}$ (Hz)	0.727(19)	0.350(10)
$(\pi T_0)^{-1}_{\text{expt}}$ (Hz)	0.730(10)	0.344(09)

The accuracy of such corrections has been carefully studied by Brenner, using a similar geometry and somewhat higher magnetic fields.[37] Comparing our magnetic field amplitudes and $\Delta F = 0$ transition linewidths to his, we estimate the error in ϵ_H from this source to be equivalent to a systematic offset of $\Gamma/2\pi$ equal to 10^{-5} Hz.

The agreement of this experimental result for ϵ_H with the semiclassical estimate supports the approximate validity of the semiclassical picture, but it would be interesting to see the degree to which a fully quantum-mechanical treatment of spin-exchange collisions to first order in the hyperfine interaction during collisions is consistent with Eq. (6) and the present experimental value

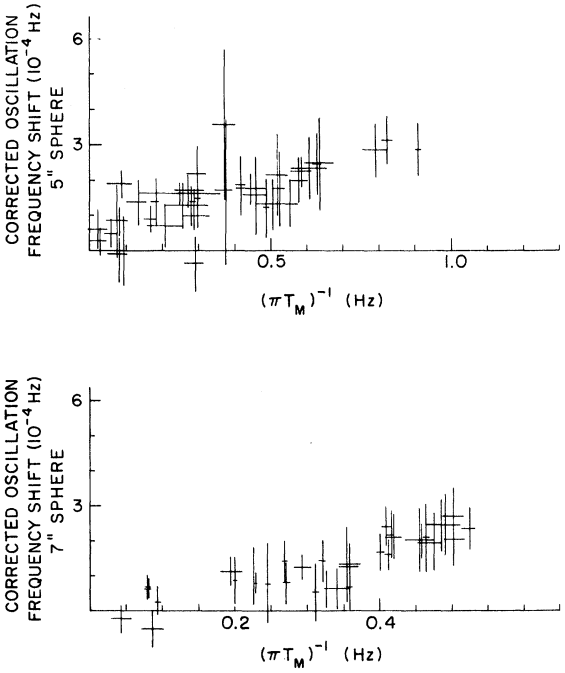

FIG. 3. Corrected oscillation frequency shift $\Gamma/2\pi$ plotted against motional transition contribution to the resonance linewidth. Equation (16) predicts a straight line passing through the origin with slope $-\epsilon_H$.

of ϵ_H. Experimentally, it would be interesting to extend the measurements to other temperatures and to confirm the room-temperature value by another technique. One alternative method is to change the density-independent part of the linewidth by changing the rate at which atoms leave the storage bottle. The change of density-independent linewidth is potentially somewhat larger, and the systematic errors are somewhat different. An experiment to determine ϵ_H by this technique is under way at Harvard University.[38]

IV. COLLISIONS WITH OTHER PARAMAGNETIC GASES

The semiclassical treatment of collisions between hydrogen atoms and some other atomic or molecular species having electron spin is very similar to the hydrogen-hydrogen case. There are two exchange interaction projection operators and potential-energy functions, and the unperturbed hyperfine interaction operator [Eq. (4)] is the same except for the hyperfine structure constant of the second species. For collisions with something having electron spin $\frac{1}{2}$ and nuclear spin either $\frac{1}{2}$ or 1, the $\Delta m_F = 0$ hydrogen hyperfine transition frequency is shifted by

$$\delta\omega_{42} = -\tfrac{1}{3}\omega_0 T_D T_p^{-1}\,, \tag{6$'$}$$

with T_D defined as in Sec. II in terms of the spin-flip cross section and interaction potentials appropriate to this species and $(\pi T_p)^{-1}$ the contribution of added gas collisions to the $\Delta m_F = 0$ hydrogen transition linewidth.[39] The frequency shift for collisions with something having electron spin 1 and nuclear spin zero is equal to this result multiplied by $\frac{9}{8}(1 - \frac{1}{3}\rho_{00})$, where ρ_{00} is the $m_s = 0$ level population of the second species prior to the collision. When the second species is unpolarized, this factor reduces to unity.

We assume that collisions with any paramagnetic gas resemble one of the cases of electron and nuclear spin considered above. In that case the density-dependent oscillation frequency pulling of hydrogen atoms colliding with other paramagnetic atoms or molecules as they also collide with each other is

$$\begin{aligned}\omega - \omega_0 = {} & [(2Q/\omega_0)(\omega_c - \omega_0) - \alpha\lambda'] \\ & \times (T_0^{-1} + T_M^{-1} + \tfrac{1}{2}T_H^{-1} + T_p^{-1}) \\ & + \epsilon_H T_H^{-1} + \epsilon_M T_H^{-1} + 2\epsilon_p T_p^{-1}\,,\end{aligned} \tag{13$'$}$$

with $\epsilon_p = -\frac{1}{6}\omega_0 T_D$. In the presence of the added paramagnetic gas the spin-exchange tuned cavity and oscillation frequencies are

$$\omega_{ct} - \omega_0 = (\omega_0/Q)(\tfrac{1}{2}\alpha\lambda' - \epsilon_H - \epsilon_M)\,, \tag{14$'$}$$

$$\omega_t - \omega_0 = -2(\epsilon_H + \epsilon_M)(T_0^{-1} + T_M^{-1}) + 2(\epsilon_p - \epsilon_H - \epsilon_M)T_p^{-1}\,. \tag{15$'$}$$

Comparing the spin-exchange tuned oscillation or cavity frequencies with and without the added paramagnetic gas or measuring the variation of hydrogen spin-exchange tuned oscillation frequency with added gas contribution to the linewidth all measure the combination $(\epsilon_p - \epsilon_H - \epsilon_M)$. We have verified that the hydrogen spin-exchange tuned cavity frequency is independent of added gas density, and we have measured the quantity $(\epsilon_p - \epsilon_H - \epsilon_M)$ at 308 °K for the added gases O_2, NO, and NO_2 using several different storage bottles coated with FEP Teflon. Measurements at low magnetic fields were corrected for ϵ_M using measurements of the tuned cavity frequency as in the hydrogen-hydrogen measurements. The results for $\epsilon_p - \epsilon_H$ are given in Table II.

The agreement between values of $\epsilon_p - \epsilon_H$ measured for a particular added gas with different rates of collision with different Teflon storage bottle coatings is evidence that we have observed a gas phase phenomenon largely uncontaminated by anything having to do with the storage bottle coatings. Preliminary results for some fluorinated drifilm storage bottle coatings do show some evidence of variation with storage bottle coating and suggest that the added gas frequency shifts may be a useful probe of the "background spin exchange" reported by Berg[27,31] but thus far undetected in other hydrogen maser experiments.[26]

Berg has measured the spin-flip cross sections for O_2, NO, and NO_2 molecules colliding with hydrogen atoms and has found them to be roughly comparable to the hydrogen-hydrogen spin-flip cross section.[27] Given the slower mean relative collision velocity at the same temperature and the compensating factor of $\frac{2}{3}$ in the definition of ϵ_p compared to that of ϵ_H, we would expect $\epsilon_p - \epsilon_H$

TABLE II. $\epsilon_p - \epsilon_H$ for added paramagnetic gases. Errors are one standard deviation from the mean.

Added gas	Storage bottle diameter (in.)	$(\epsilon_p - \epsilon_H) \times 10^4$
O_2	$3\frac{1}{2}$	−10.00(90)
O_2	5	−10.05(26)
O_2	7	−9.70(30)
NO_2	5	−5.40(65)
NO	5	−5.85(39)
NO	7	−5.80(30)

TABLE III. Thermal average collision duration T_D for hydrogen atoms colliding with hydrogen atoms and with paramagnetic molecules. Errors are one standard deviation from the mean.

Target gas	T_D (10^{-13} sec)
H	1.81(16)
O_2	9.37(27)
NO_2	6.35(50)
NO	6.63(28)

to be small compared to ϵ_H. That it is not suggests that some mechanism prolongs the average interaction times T_D of collisions between hydrogen atoms and these paramagnetic molecules. Results for mean collision durations T_D derived from our experimental determinations of ϵ_H and $\epsilon_p - \epsilon_H$ at 308 °K are given in Table III.

The relatively long mean collision durations for hydrogen-atom collisions with O_2, NO, and NO_2 are consistent with the observations of relatively long-lived intermediate complexes in molecular beam scattering studies of reactive atoms and molecules.[40-42] Assuming that $\epsilon_p - \epsilon_H$ would be small but for the formation of some complexes and assuming that the probability of forming a complex is small, the probability of forming a complex multiplied by the lifetime of the complex is roughly $(-6/\omega_0)(\epsilon_p - \epsilon_H)$, or about 4×10^{-13} sec for NO and NO_2 and about 7×10^{-13} sec for O_2. It would be interesting to measure T_D for collisions between hydrogen atoms and some other paramagnetic atoms and radicals, including combinations which might also be amenable to molecular beam scattering experiments.

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APPENDIX: MEASUREMENT OF $(T_0^{-1})_{\text{expt}}$

The theoretical basis of the measurement is [Ref. 8, Eq. (15′)]:

$$x^2 = \frac{4}{m\tau_p T_H} - \frac{\beta}{\tau_1\tau_2}\,. \tag{A1}$$

x^2 is the square of the $\Delta m_F = 0$ transition matrix element and is proportional to the oscillation power coupled out of the hydrogen maser. $m = 16\alpha\sigma$, with α as defined in Sec. III and σ the hydrogen-hydrogen spin-flip cross section. τ_1^{-1} is the sum of all terms in the density matrix rate equations which deplete $\rho_{22} - \rho_{44}$ in proportion to itself, and τ_p^{-1} is the sum of all terms in the rate of change of the population difference not directly proportional to $\rho_{22} - \rho_{44}$. T_H^{-1} is the hydrogen-hydrogen spin-exchange collision rate, and $(\pi\tau_2)^{-1}$ is the $\Delta m_F = 0$ transition linewidth, as defined above. Finally, $\beta = 1 + Q^2(\omega_c/\omega_0 - \omega_0/\omega_c)^2$ measures the effect on the oscillation power level of mistuning the maser cavity. As in Ref. 12 but in slightly different notation we assume that $\tau_p^{-1} = s_0/T_b$ with s_0 the $\Delta m_F = 0$ transition level population difference as the atoms enter the storage bottle and T_b^{-1} the rate at which atoms escape from the bottle. As in Ref. 12 we also assume that $\tau_1^{-1} = T_b^{-1} + T_1^{-1} + T_H^{-1}$ with T_1^{-1} a relaxation rate which takes into account the effects of atom-surface collisions on the level population difference. We neglect some small spin-exchange effects due to the identity of the colliding nuclei,[6] and we ignore relaxations which affect the three $F = 1$ levels differently from the $F = 0$ level. The formulation is approximate, and it holds only at magnetic fields high enough for T_M^{-1} to effectively vanish. With these assumptions Eq. (A1) becomes

$$x^2 = -2\beta\tau_2^{-2} + \frac{8s_0}{mT_b}\,\tau_2^{-1} - \beta(T_b^{-1} + T_1^{-1} - 2T_0^{-1})\tau_2^{-1} - \frac{8s_0T_0^{-1}}{mT_b}\,. \tag{A2}$$

This result is similar to Eq. (6) of Ref. 12 except for including the effects of cavity mistuning and taking the measurable τ_2^{-1} as the independent variable instead of the hydrogen beam intensity. By fitting observed relative oscillation power levels to parabolas in τ_2^{-1} for various values of cavity mistuning, we can extract from the ratios of fitted coefficients the parameters T_0^{-1}, s_0/mT_b, and $T_b^{-1} + T_1^{-1}$. For example, these parameters for the 7-in. stemless storage bottle used in the ϵ_H experiments were $T_0^{-1} = 1.081(28)$ sec^{-1}, $s_0/mT_b = 2.19(06)$ sec^{-1}, and $T_b^{-1} + T_1^{-1} = 1.31(32)$ sec^{-1}.

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