action (1). Classical deflection function calculations[7] for the ion-pair–mediated process (2) show that the impact-parameter range 2.5 Å $\lesssim b \lesssim$ 3.44 Å contributes to the rainbow feature. Hence, in this simple picture, the rainbow feature of the neutrals would yield inelasticities between ~ 1.0 and 1.6 eV.

This simple model explains the lack of elastic scattering in the rainbow region for reaction (2); but it slightly underestimates the average inelastic scattering values. Although relaxing some of our simplifying assumptions might yield a better fit to the data, the basic physics is clearly already contained in the model. One possible route to larger inelasticities involves transfer from the ion-pair intermediate surface to more highly excited neutral surfaces. The crossing radii R_c' between the ion-pair surface and higher neutral surfaces also oscillate with time. A few examples are shown in the upper portion of Fig. 4. Although the larger values of R_c' seem to imply smaller coupling matrix elements and thereby much lower adiabatic crossing probabilities,[3] there may be other factors favoring production of electronically excited states. In fact, the radial motion of the particles $[R(t)]$ relative to that of the *moving* crossing $[R_c'(t)]$ should be the radial velocity appropriate for estimating curve-crossing probabilities. In the extreme case, when the crossing sphere is expanding rapidly and parallel to $R(t)$, e.g., for $b = 2.5$ and the $2p_2$ state of Ar in Fig. 4, the interaction can be profoundly altered. Significant electronic excitation might result.

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Close-Coupling Calculations of Spin-Polarized Hydrogen-Deuterium Collisions

Yea-Hwang Uang and William C. Stwalley

Departments of Chemistry and Physics, University of Iowa, Iowa City, Iowa 52242

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Close-coupling calculations on the atomic collisions at cryogenic energies in a 100-kG magnetic field between spin-polarized hydrogen ($H_\uparrow$) and deuterium ($D_\uparrow$) have demonstrated the resonant spin-flip process postulated by Stwalley and the importance of minimizing the presence of $D_\uparrow$ in the experimental preparations of bulk $H_\uparrow$ currently in progress. Other interesting features are presented and briefly discussed including multiple Ramsauer-Townsend effects and direct electron and nuclear single– and double–spin-flip processes.

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The stabilization of spin-polarized hydrogen ($H_\uparrow$) has been of considerable interest for some time.[1] Recently densities of ~ 10^{14}/cm^3 were reported[2] and very recently new results at ~ 10^{16}/cm^3 (Refs. 3 and 4) and at ~ 10^{14}/cm^3 (Ref. 5) have been obtained. There is great interest in extending these to higher density where, e.g., Bose condensation should occur. The $H_\uparrow$ atoms undergo various collision processes in the gas phase predicted[6] (e.g., at $T = 0.1$ °K, $B = 10^5$ G). Several of these give rise to possible destruction mechanisms.[1] One of us[1] has predicted a destructive effect for $D_\uparrow$ impurities in $H_\uparrow$ because of field-dependent scattering resonances, corresponding to weakly bound singlet molecular vibration-rotation levels (long-range molecules).[7] For example,

the $v=17$, $J=0$ level of the HD $X^1\Sigma_g^+$ state lies ~4.96 °K below dissociation. The Feshbach scattering resonance associated with this level gives long time delays with appreciable singlet character and implies a small but significant destructive process at high density if $D_\uparrow$ impurities are present. The very slight degree of adiabaticity in the avoided crossing between singlet and triplet hyperfine potential curves is important in estimation of the field/temperature conditions needed for stability of $H_\uparrow$. In other words, spin-exchange arises from adiabatic collisions via the hyperfine interaction between two atoms.[8] Our purpose here is to give a preliminary but quantitative report of various cross sections (elastic and inelastic) in H-D scattering to verify these predictions. The results given here are all at $B=10^5$ G, since experimental programs to produce $H_\uparrow$ (including the one at our laboratory) are using such fields, although we have other results (e.g., at 10^n G, $n=0$–4).

The close-coupling formalism has been adopted in our numerical calculations. This presents a reasonable representation for the low-energy scattering process. Use of the Landau-Zener-Stueckelberg (LZS)[9] model seems inadequate under our conditions. While LZS approximation does treat electronic degrees of freedom quantum mechanically, translational degrees of freedom are treated classically or semiclassically. This is inappropriate here since de Broglie wavelengths are tens or hundreds of angstroms. It is interesting to note that estimates with the LZS model are usually 2 to 3 orders of magnitude larger than the accurate inelastic cross sections reported below.

In the general theory of inelastic collisions, the full wave function expanded in terms of the unperturbed (diabatic) orthonormal eigenstates gives the close-coupled equations. Following the work (and notation) of Mies,[10] one has the coupled equation

$$\underline{G}'' + (2\mu/\hbar^2)(E\underline{1} - \underline{U})\underline{G} = 0,$$

where the potential-energy matrix element $U_{ij}(R) = \langle i|\hat{H}_0|j\rangle$ is expanded in terms of the basis set (diabatic states) consisting of the two atomic product states $|i\rangle$ and $|j\rangle$ ($\equiv|\xi_H,\xi_D\rangle$).[8] The effective Hamiltonian, $\hat{H}_0$, is written explicitly (neglecting a small relativistic effect)[11] as

$$\hat{H}_0 = E_c(R) - E_x(R)(\tfrac{1}{2} + 2\hat{\vec{S}}_1\cdot\hat{\vec{S}}_2) + g_e\mu_B(\hat{\vec{S}}_1+\hat{\vec{S}}_2)\cdot\vec{B} - \mu_N(g_H\hat{\vec{I}}_H + g_D\hat{\vec{I}}_D)\cdot\vec{B} + A_H\hat{\vec{S}}_1\cdot\hat{\vec{I}}_H + A_D\hat{\vec{S}}_2\cdot\hat{\vec{I}}_D,$$

where $E_c = \frac{1}{2}[E(^1\Sigma_g^+) + E(^3\Sigma_u^+)]$ and $E_x = \frac{1}{2}[E(^1\Sigma_g^+) - E(^3\Sigma_u^+)]$; $E(^1\Sigma_g^+)$ and $E(^3\Sigma_u^+)$ are the precisely known potential curves of H_2 by Kolos and Wolniewicz [$(0.4-12)a_0$].[12] The C_6, C_8, and C_{10} long-range coefficients are given by Hirschfelder and Meath.[13] Because the total spin angular-momentum projection $M[=m(S_1)+m(S_2)+m(I_H)+m(I_D)]$ along the B-field direction remains a good quantum number, one can block diagonalize the HD 24×24 matrix into two one-dimensional, two four-dimensional, and two seven-dimensional submatrices.[8,11] For example, one of the sets of coupled equations involving the collision of H+D (which we present here) is the case of $M=-\frac{1}{2}$, a 7×7 matrix. In considering only S-wave scattering (which, of course, dominates at very low T), it is a seven-channel problem. In this particular case, the diabatic basis set $|\xi_H,\xi_D\rangle$ which is expanded in terms of spin basis functions $|m(S_1), m(I_H);m(S_2),m(I_D)\rangle$ is given in Table I. It is easily recognized that channels 1 and 2, channels 3–6, and channel 7 correspond to the $M_S=-1$, 0, and 1 asymptotes (Fig. 1 in Ref. 1), respectively.

We have summarized our numerical results for various cross sections in Fig. 1 for energies ranging from 0 to 100 °K with respect to the asymptote of channel 1. The two vertical lines indicate the approximate threshold energies for the channel opening at 100 kG corresponding to a single electronic spin flip [$M(S)=-1$ to 0] and a double electronic spin flip [$M(S)=-1$ to 1]. Both elastic and inelastic collision cross sections involving channel 1 are given. The detailed behaviors of the channel opening and resonance regions are also separately shown in insets a, b, c, and d (labeled on the main figure).

(i) Q_{11}: The elastic cross section of channel 1. There are two Ramsauer-Townsend zeros[14] (one of which is shown in detail in inset b) reflecting the character of the H_2 ($^3\Sigma_u^+$) potential having a largely repulsive core and a weak attractive tail. This has been implicitly shown by Buckingham, Fox, and Gal[15] (with less-accurate potentials) for the H-H collision. As predicted, the Feshbach-scattering resonance is found at $E_R=8.5169$ °K (inset a). An independent check with an eigenvalue program gives the $v=17$, $J=0$ vibration-rotation level at 8.49 °K.[16] We obtain a resonance width of 0.000 144 °K (time delay $\simeq 3.3\times10^{-7}$ sec) compared with 10^{-6} sec estimated previously.[1] At the zero-kinetic-energy limit in inset b, Q_{11}

TABLE I. The eigenenergies (at $R=\infty$, $B=100$ kG) of the seven hyperfine potential-energy curves with projection quantum number $M=-\frac{1}{2}$. The channel number increases from the lowest-energy state with the dominant expanded spin basis function shown. The type of transition from channel 1 is also given.

Channel number j	Asymptotic energy E_j (°K)	Dominant spin basis function[a] $\lvert m(S_1), m(I_H); m(S_2), m(I_D)\rangle$	Transition from channel 1: Electronic Spin flip	Transition from channel 1: Nuclear Spin flip
7	26.916 41	$\lvert 1/2, -1/2; 1/2, -1\rangle$	double	double
6	13.504 87	$\lvert -1/2, -1/2; 1/2, 0\rangle$	single	single
5	13.495 42	$\lvert 1/2, 1/2; -1/2, -1\rangle$	single	single
4	13.470 86	$\lvert 1/2, -1/2; -1/2, 0\rangle$	single	single
3	13.445 55	$\lvert -1/2, 1/2; 1/2, -1\rangle$	single	single
2	0.043 61	$\lvert -1/2, -1/2; -1/2, 1\rangle$	none	double
1	0.0	$\lvert -1/2, 1/2; -1/2, 0\rangle$	elastic	

[a]The complete expansion for channel 1, for example, is $\lvert 1\rangle$ $= 0.999\,996\,457\,3\ \lvert -1/2, 1/2; -1/2, 0\rangle - 0.000\,826\,330\,5\ \lvert -1/2, 1/2; 1/2, -1\rangle$ $- 0.002\,530\,331\,4\ \lvert 1/2, -1/2; -1/2, 0\rangle + 0.000\,000\,209\,1\ \lvert 1/2, -1/2; 1/2, -1\rangle$.

converges to a finite value $\sim 2.54a_0^2$. This allows the estimation of the scattering length A for $H_\uparrow$-$D_\uparrow$ scattering via ${}^3\Sigma_u^+$ potential based on the effective-range theory,[17] i.e.,

$$Q_{11} \underset{k_1 \to 0}{\longrightarrow} 4\pi A^2,$$

$$A \simeq -(2.54/4\pi)^{1/2} a_0 = -0.45 a_0 = -0.24 \text{ Å}.$$

(ii) Q_{12}: The inelastic cross section of channel 1 to 2. This is a double nuclear spin-flip process; $[m(I_H) = \frac{1}{2} \to -\frac{1}{2}]$ and $[m(I_D) = 0 \to 1]$. It has a small magnitude except in the resonance region shown in inset *a*. Note also the zero-energy limit shown in inset *d*. A careful examination of inset *d* gives

$$Q_{12} \propto (E - E_2)^{1/2} \propto k_2 \text{ as } k_2 \to 0.$$

Detailed balancing implies that

$$Q_{21} = (k_1^2/k_2^2) Q_{12} \propto k_2^{-1} \text{ as } k_2 \to 0,$$

i.e.,

$$Q_{12} \to 0, \quad Q_{21} \to \infty \text{ as } k_2 \to 0,$$

where k_1 and k_2 are the wave numbers corresponding to asymptotic channels 1 and 2.

(iii) Q_{13}, Q_{15}: The electronic single-spin-flip cross sections of channel 1 to 3 and channel 1 to 5. Q_{13} and Q_{15} agree within the width of the curve. Since the respective dominant spin basis functions of channels 3 and 5 have the same nuclear-spin states, Q_{13} and Q_{15} are expected to be close except near threshold (inset *c*).

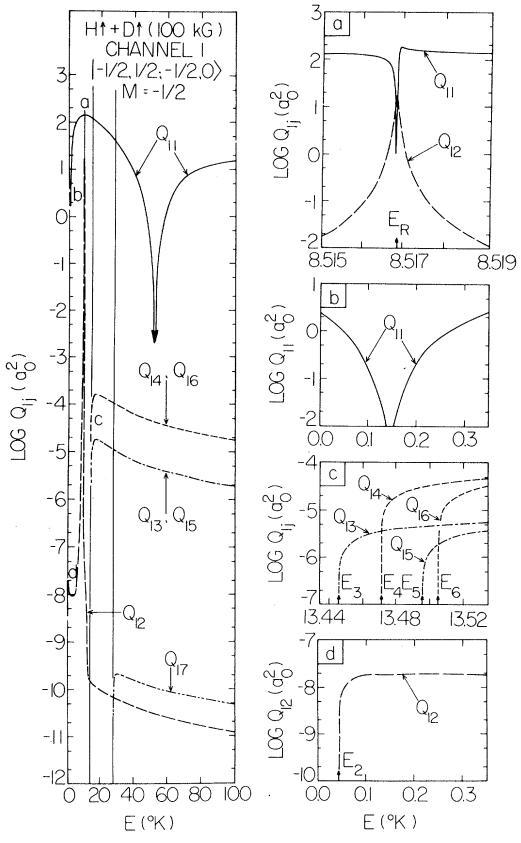

FIG. 1. Elastic and inelastic collision cross sections Q_{1j} for H-D collisions with $M=-\frac{1}{2}$ at 100 kG (for details, see text).

(iv) Q_{14}, Q_{16}: The electronic single–spin-flip cross sections of channel 1 to 4 and channel 1 to 6. Q_{14} and Q_{16} agree within the width of the curve. Again, Q_{14} and Q_{16} are expected to be close except near threshold (inset c) because the dominant spin basis functions of channels 4 and 6 have the same nuclear-spin states.

(v) Q_{17}: The electronic double–spin-flip cross section of channel 1 to 7.

We note that the electronic spin-flip cross sections at 100 kG [$(\sim 10^{-4}-10^{-5})a_0^2$] are much smaller than those at 0 G ($\sim 10a_0^2$). The order of magnitude of the H-D spin-flip cross sections agree with those of H-H collisions given by Allison.[18] Detailed study of H-H collision spin-exchange cross sections including hyperfine interaction at nonzero fields is currently being completed. Generally speaking it is the large electronic Zeeman splitting which results in several orders of magnitude smaller cross sections for electron-spin flip. This excludes the resonance and the zero-energy limit where the inelastic effect may become stronger than the elastic one. Qualitatively, the larger the magnetic field strength, the smaller the spin-flip cross section one expects.

The above spin-exchange cross sections can be used to estimate the destruction rate of the $H_\uparrow$ system for a given kinetic temperature and a given density. The rate constant k_{HD} is defined by[19]

$$k_{HD}(T) = c\int_{E_T}^{\infty} dE Q_{HD}(E) E e^{-E/kT},$$

where E_T is the threshold energy.

We have seen the threshold divergence of $Q_{21} \propto (E-E_2)^{-1/2}$. However, the factor EQ will not be significant until E is close to the resonance region where Q_{12} (or Q_{21}) has a relatively large contribution. At 100 kG, HD has a threshold energy at 8.517 °K. k_{HD} is expected to be reduced by the small width [full width at half maximum (FWHM)] of sharp peak, $\Delta_{HD} = 0.000\,144$ °K; and by the Boltzmann factor $\exp(-E_R/kT)$ at very low temperatures. Nevertheless, it still is large compared to the rate constant for H-H spin-flip collision, k_{HH}, whose spin-flip threshold energy is about 13.4 °K. The width (FWHM) of H-H spin-flip collision, Δ_{HH}, can be estimated through the following equation:

$$\exp[-(13.4+\Delta_{HH}/T]/\exp(-13.4/T) = \tfrac{1}{2}.$$

At $T = 0.1$ °K, for instance,

$$\Delta_{HH} = \tfrac{1}{10}\ln 2 = 0.0693\ \text{°K}.$$

Therefore,

$$\frac{k_{HD}}{k_{HH}} = \frac{e^{-8.5/0.1\Delta_{HD}}}{e^{-13.4/0.1\Delta_{HH}}} = e^{49}\frac{0.000\,144}{0.0693} = 4.0\times 10^{18}.$$

This large number confirms the importance of the destructive process $HD^{\infty}+H_\uparrow \rightarrow HD(v \leq 17) + H_\uparrow + \text{heat}$, even if there is a very small fraction of D impurity, which thus should be avoided in the preparation of bulk $H_\uparrow$ system.

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