Collisions between Metastable Hydrogen Atoms at Thermal Energies

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The complex interaction potentials arising in the approach of two metastable hydrogen $2s$ atoms are calculated and the cross sections for ionization, excitation transfer, and elastic scattering are predicted. The measured cross section for associative ionization at $E = 4.1$ meV equals 2×10^{-15} cm^2. We calculate a total ionization cross section of 2×10^{-13} cm^2, varying as $E^{-2/3}$ at higher energies. Thus it appears that dissociative ionization is the major ionization channel. We find also that double excitation transfer into two excited H($2p$) atoms is still more probable with the large cross section of 9×10^{-12} cm^2 at $E = 4.1$ meV varying as $E^{-1/2}$ at higher energies. The detection of the resulting Lyman alpha photons would provide a diagnostic test of our predictions.

Several experiments involving interactions of metastable hydrogen atoms with various targets have been performed [1–8]. The theoretical simplicity of atomic hydrogen makes it an ideal system for studying fundamental physics. Because of the near degeneracy of the $2s$ and $2p$ states, metastable hydrogen offers the possibility for the development of an intense source of Lyman alpha radiation. Its intensity would be limited by the density of metastable atoms that could be produced and maintained. The metastable density that could be achieved depends on the efficiencies of the collision processes that lead to loss of metastable atoms. The same collision processes restrict the densities of Bose-Einstein condensates that can be measured by determining the frequency shifts of the two-photon $2s$-$1s$ transition [9]. The Stark chirped rapid-adiabatic-passage (SCRAP) technique has recently been proposed as a means to achieve complete population transfer from the ground $1s$ state to the metastable $2s$ state [10]. The time scale for sustaining the population inversion, however, depends inversely on the atom density which is limited again by the collision processes that control the quenching of the metastable atoms. Measurements have been reported [6] of the cross sections for associative ionization

$$\text{H}(2s) + \text{H}(2s) \rightarrow \text{H}_2^+ + e\,. \qquad (1)$$
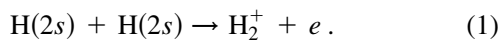
Associative ionization is not the only loss channel. We calculate here the total cross section for ionization including the dissociative Penning ionization channels,

$$\text{H}(2s) + \text{H}(2s) \rightarrow \text{H} + \text{H}^+ + e\,. \qquad (2)$$
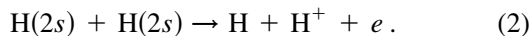
We find that double excitation transfer to two excited H($2p$) atoms

$$\text{H}(2s) + \text{H}(2s) \rightarrow \text{H}(2p) + \text{H}(2p) \qquad (3)$$
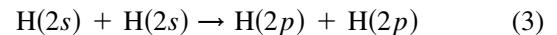
is a more probable event than ionization, and we present estimates of the cross sections.

At energies of 4 meV and above, we may ignore the energy differences between the $2s_{1/2}$, $2p_{1/2}$, and $2p_{3/2}$ levels of hydrogen and treat the $2s$ and $2p$ states as degenerate. We calculate the interaction potentials of the pairs of excited atoms in the Born-Oppenheimer approximation using an extension of the methods of Kolos and Wolniewicz [11] that incorporates a complex scaling of the electronic coordinates [12] to take into account the existence of energetically open ionization channels. The method yields the R-dependent potential energy $V(R)$ and the autoionization width $\Gamma(R)$ of the molecular state formed in the approach of the two H($2s$) atoms. The nuclear Schrödinger equation is then solved in the corresponding complex interaction potential $V(R) - \frac{1}{2}i\Gamma(R)$. The molecular eigenfunctions are singlets or triplets and they separate at large distances into combinations of products $|n_1 l_1 m_1\rangle_a |n_2 l_2 m_2\rangle_b$ of pairs of hydrogen atom eigenfunctions $|nlm\rangle$ on nuclei a and b with $n_1 = n_2 = 2$.

A pair of $2s$ hydrogen atoms may approach in either a $^1\Sigma_g^+$ or a $^3\Sigma_u^+$ molecular state. There are three asymptotically coupled states and one uncoupled state for each of these symmetries. These asymptotic states are defined by

$$\chi_i = \frac{1}{\sqrt{2}} (1 \pm P_{ab})\phi_i\,, \qquad (4)$$

where the upper (lower) sign applies to $^1\Sigma_g^+$ ($^3\Sigma_u^+$) symmetry, P_{ab} permutes the electrons between the two atoms, and

$$\phi_I = |2,0,0\rangle_a |2,0,0\rangle_b,$$

$$\phi_{II} = |2,1,0\rangle_a |2,1,0\rangle_b,$$

$$\phi_{III} = \frac{1}{\sqrt{2}} \{|2,0,0\rangle_a |2,1,0\rangle_b - |2,1,0\rangle_a |2,0,0\rangle_b\}, \tag{5}$$

$$\phi_{IV} = \frac{1}{\sqrt{2}} \{|2,1,1\rangle_a |2,1,-1\rangle_b + |2,1,-1\rangle_a |2,1,1\rangle_b\}.$$

The coupling matrix is given to first order in perturbation theory by

$$V_{ij} = \frac{C_{ij}^{(3)}}{R^3} + \frac{C_{ij}^{(5)}}{R^5} + O(R^{-6}), \tag{6}$$

where the $C_{ij}^{(3)}$ and $C_{ij}^{(5)}$ coefficients are obtained using the asymptotic theory of Dalgarno and Davison [13]. The only nonzero $C_{ij}^{(3)}$ coefficients are $C_{I,II}^{(3)} = C_{II,I}^{(3)} = -18$ a.u. and $C_{I,IV}^{(3)} = C_{IV,I}^{(3)} = -9\sqrt{2}$ a.u. The only nonzero $C_{ij}^{(5)}$ coefficients are $C_{II,II}^{(5)} = 864$ a.u., $C_{IV,IV}^{(5)} = 432$ a.u., and $C_{II,IV}^{(5)} = C_{IV,II}^{(5)} = 432\sqrt{2}$ a.u. We diagonalize the coupling matrix to obtain the asymptotic molecular eigenfunctions (ordered by increasing energy)

$$\psi_1 = \frac{1}{\sqrt{6}} (\sqrt{3}\, \phi_I + \sqrt{2}\, \phi_{II} + \phi_{IV}),$$

$$\psi_2 = \frac{1}{\sqrt{6}} (2\, \phi_{IV} + \sqrt{2}\, \phi_{II}),$$

$$\psi_3 = \phi_{III}, \tag{7}$$

$$\psi_4 = \frac{1}{\sqrt{6}} (\sqrt{3}\, \phi_I - \sqrt{2}\, \phi_{II} - \phi_{IV}),$$

and the corresponding eigenvalues (in a.u.)

$$V_1 = -9\sqrt{6}/R^3 + 648/R^5 + O(R^{-6}),$$

$$V_2 = O(R^{-6}),$$

$$V_3 = 18/R^3 + O(R^{-6}), \tag{8}$$

$$V_4 = 9\sqrt{6}/R^3 + 648/R^5 + O(R^{-6}).$$

The state $\psi_3 = \phi_{III}$ does not couple asymptotically to the other molecular states of the same symmetry. The electronic structure calculations were computed to distances of 20 a.u., which was sufficient to obtain satisfactory agreement with the asymptotic values given in (8). A suitable matching procedure was then applied to obtain smooth potentials that could be used for the scattering calculations.

The amplitude $f_m(\theta)$ for scattering through an angle θ by a complex interaction potential that correlates asymptotically to $V_m(R)$ may be written in terms of the complex phase shift $\delta_l^{(m)}$ corresponding to orbital angular momentum l in the form

$$f_m(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1)(e^{2i\delta_l^{(m)}} - 1)P_l(\cos\theta), \tag{9}$$

where k is the wave number. To describe the approach of two H(2s) atoms, the wave function must contain the incident plane wave

$$e^{i\vec{k}\cdot\vec{R}}\phi_I = e^{i\vec{k}\cdot\vec{R}} \frac{1}{\sqrt{2}} (\psi_1 + \psi_4), \tag{10}$$

which from Eq. (7) evolves into

$$e^{i\vec{k}\cdot\vec{R}}\phi_I + R^{-1}\exp(ikR)$$
$$\times \left\{ \frac{1}{2}(f_1 + f_4)\phi_I \right.$$
$$\left. + \frac{1}{2\sqrt{3}}(f_1 - f_4)(\sqrt{2}\,\phi_{II} + \phi_{IV}) \right\}. \tag{11}$$

Thus the differential cross section for elastic scattering is given by

$$d\sigma_{I\to I} = \frac{1}{4} |f_1 + f_4|^2 \tag{12}$$

and for elastic double excitation transfer by

$$d\sigma_{I\to II} + d\sigma_{I\to IV} = \frac{1}{4} |f_1 - f_4|^2. \tag{13}$$

The cross section σ_{ion} for inelastic scattering into the ionization channel can be obtained by calculating the loss of flux using the asymptotic form (11). The cross terms involving f_1 and f_4 cancel with the result that

$$\sigma_{ion} = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1)\{1 - \tfrac{1}{2}[A_l^{(1)}]^2 - \tfrac{1}{2}[A_l^{(4)}]^2\}, \tag{14}$$

where the complex phase shifts $\delta_l^{(m)}$ corresponding to scattering in channel m are written as $\exp(2i\delta_l^{(m)}) = A_l^{(m)} \exp(2i\eta_l^{(m)})$, $A_l^{(m)}$ and $\eta_l^{(m)}$ being real quantities.

An approximate expression for the ionization cross section can be derived by recognizing the dominating influence of the long range R^{-3} term in the interaction potentials and the rapidly increasing probability of auto-ionization as the atoms approach. In channel 4 the potential is repulsive and the particles do not enter the region where autoionization is probable. In channel 1 the potential is attractive and we may assume that once the centrifugal barrier is surmounted, the probability of ionization is unity. If l_0 is the critical value of the angular momentum, then $A_l^{(4)} = 1$ for all l and $A_l^{(1)}$ equals unity for $l > l_0$ and zero for $l < l_0$. The corresponding value of the critical angular momentum may be found from the effective potential

$$V_{eff}(R) = \frac{l(l+1)}{2\mu R^2} - \frac{C_3}{R^3}, \tag{15}$$

where μ is the reduced mass and C_3 is $9\sqrt{6}$ in atomic units. Differentiating V_{eff} with respect to R and setting it equal to zero gives $l_0 = (54\mu^3 C_3^2 E)^{1/6}$ and the ionization cross section is approximately

$$\sigma_{\text{ion}} \sim \frac{3\pi}{2}\left(\frac{C_3}{2E}\right)^{2/3} = 23E^{-2/3} \text{ a.u.} \qquad (16)$$

The cross section for double excitation transfer is given by

$$\sigma_{\text{I}\to\text{II}} + \sigma_{\text{I}\to\text{IV}} = \frac{\pi}{4k^2}\sum_{l=0}^{\infty}(2l+1)$$
$$\times |A_l^{(4)}\exp(2i\eta_l^{(4)})$$
$$- A_l^{(1)}\exp(2i\eta_l^{(1)})|^2. \qquad (17)$$

Expression (17) can be simplified. Making the same assumptions about the opacities $A_l^{(1)}$ and $A_l^{(4)}$, we find

$$\sigma_{\text{I}\to\text{II}} + \sigma_{\text{I}\to\text{IV}} \sim \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2[\eta_l^{(4)} - \eta_l^{(1)}]. \qquad (18)$$

The phase shifts increase rapidly with l and for l less than some value l^*, $\sin^2[\eta_l^{(4)} - \eta_l^{(1)}]$ may be replaced by its mean value of $\frac{1}{2}$. When $l > l^*$ we may use the semiclassical formula for the phase shifts for a potential decreasing as R^{-3},

$$\eta_l^{(1)} = -\eta_l^{(4)} = \frac{kC_3\mu}{l^2}. \qquad (19)$$

We choose l^* such that $\eta_{l^*}^{(4)} - \eta_{l^*}^{(1)} = \frac{\pi}{4}$ which gives $l^* = \sqrt{8C_3k\mu/\pi}$. At high energies, l^* is much greater than l_0 and $\sigma_{\text{I}\to\text{II}} + \sigma_{\text{I}\to\text{IV}}$ reduces to

$$\sigma_{\text{I}\to\text{II}} + \sigma_{\text{I}\to\text{IV}} \sim 2\sqrt{2\mu}\left(1 + \frac{\pi^2}{8}\right)C_3 E^{-1/2}$$
$$= 4195E^{-1/2} \text{ a.u.} \qquad (20)$$

The total collision cross section is given by

$$\sigma_T = \sigma_{\text{I}\to\text{I}} + \sigma_{\text{I}\to\text{II}} + \sigma_{\text{I}\to\text{IV}}$$
$$= \frac{\pi}{2k^2}\sum_{l=0}^{\infty}(2l+1)|A_l^{(4)}\exp[2i\eta_l^{(4)}] - 1|^2 \qquad (21)$$
$$+ \frac{\pi}{2k^2}\sum_{l=0}^{\infty}(2l+1)|A_l^{(1)}\exp[2i\eta_l^{(1)}] - 1|^2.$$

With the same approximate opacities and the use of the random phase approximation for the low angular momentum phase shifts, expression (21) may be replaced by the simple formula

$$\sigma_T \sim 2\sqrt{2\mu}\left(4 + \frac{\pi^2}{8}\right)C_3 E^{-1/2} = 9832E^{-1/2} \text{ a.u.}, \qquad (22)$$

and by subtraction we obtain

$$\sigma_{\text{I}\to\text{I}} \sim 6\sqrt{2\mu}\,C_3 E^{-1/2} = 5636E^{-1/2} \text{ a.u.} \qquad (23)$$

We have evaluated the quantum mechanical cross sections (14), (17), and (21) by numerical integration of the coupled partial wave equations that describe scattering by a complex potential [14] for the singlet molecular symmetry. The ionization cross section was found to be in excellent agreement with the semiclassical expression (16) and is equal to 2×10^{-13} cm^2 at $E = 4.1$ meV. The cross section for associative ionization has been measured [6] to have the much smaller value of 2×10^{-15} cm^2. The difference suggests that most ionization is Penning ionization into the dissociative continuum $H^+ + H$ of H_2^+.

The calculated quantal cross sections for elastic scattering and double excitation transfer were found to be closely approximated by $4500E^{-1/2}$ a.u. and $4000E^{-1/2}$ a.u., respectively, which agree satisfactorily with the approximate semiclassical results given by Eqs. (20) and (23). Thus, we expect to obtain similar results for scattering in the triplet molecular state. The cross section for double excitation transfer is larger than the total ionization cross section. The excitation transfer cross section at 4.1 meV is 9×10^{-12} cm^2. Thus we predict that in the collision of two metastable hydrogen atoms at thermal energies, excitation transfer is the dominant quenching mode, resulting in the emission of two Lyman alpha photons.

The rate coefficients for ionization and excitation transfer are $5.6 \times 10^{-8}T^{-1/6}$ cm^3 s^{-1} K$^{1/6}$ and 1.2×10^{-6} cm^3 s^{-1}, respectively. The excitation transfer rate coefficient is constant, whereas the ionization rate coefficient decreases with temperature. Therefore, the excitation transfer quenching mode will become increasingly more dominant with temperature. These results indicate that thermal sources of metastable $H(2s)$ atoms such as those produced by the SCRAP technique [10] could sustain population inversions lasting 1 μs with an atomic density of 10^{12} cm^{-3}.

At low energies it will be necessary to take account of the energy level splittings of the $2s_{1/2}$, $2p_{1/2}$, and $2p_{3/2}$ states. The removal of the degeneracy of the $2s$ and $2p$ states will change the long range interaction from an R^{-3} to an R^{-6} variation with R in the vicinity of 300 a.u. The potentials computed for the present study represent an important first step in understanding the competition between the exothermic ionization and excitation transfer channels that takes place at the ultracold temperatures reached in BEC experiments.

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