STABILITY OF SPIN-POLARIZED ATOMIC HYDROGEN AGAINST RECOMBINATION REACTIONS

J. Yuan, T. Lim

STABILITY OF SPIN-POLARIZED ATOMIC HYDROGEN AGAINST RECOMBINATION REACTIONS

J.M. Yuan and T.K. Lim

Drexel University, Philadelphia, Pa. 19104, USA.

Résumé.- Nous passons brièvement en revue les études sur la stabilité de l'hydrogène atomique polarisé par rapport aux collisions de "quenching". Des travaux antérieurs révèlent l'importance des réactions de recombinaison à trois corps en tant que mécanismes de destruction. Une estimation antérieure de l'ordre de grandeur de ce taux de réaction à trois corps conduit à prédire que la densité d'un gaz stable de H↑ ne peut dépasser 10^{17} atomes par cm^3 sur une durée de un jour. Une discussion des approximations faites suggère que la densité réelle pourrait être de deux ordres de grandeur supérieure à cette estimation.

Abstract.- Studies on the stability of spin-polarized atomic hydrogen against collisional quenching are briefly reviewed. Previous work reveals the importance of the three-body recombination reaction as a destructive mechanism. An order-of-magnitude estimate of this three-body reaction rate made previously leads to a maximal stable density equal to 10^{17} atoms/cm^3 for a duration of a day. A discussion of approximations used suggests that the real density could be a couple of orders of magnitude higher.

INTRODUCTION.- Hydrogen atoms with electronic spin polarized by an intense magnetic field constitute a Bose gas which should exhibit quantum properties more pronounced than ^{4}He. /1,2/ This arises from the fact that spin-polarized hydrogen atoms (H↑) have small masses and interact mainly via weakly attractive $b\,^3\Sigma_u^+$ interaction. A major current issue in this area of research is the stability of H↑ at a workable density for a sufficiently long time. Various destructive mechanisms /3-8/ have been considered and it appears at the present time all but the three-body collisional quenching reaction can be effectively suppressed by proper experimental conditions.

Quenching of H↑ via two-body and three-body collisions was studied by Jones et al /8/. This work, done about twenty years ago has stimulated research activity that has contributed to our understanding of H↑. However several of their conclusions are incorrect. The lifetime of H↑, τ, against 2-body collisions they obtained is about 10^{-5} to 10^{-7} sec for a density of 10^{22} atoms/cm^3. τ is far too small as was pointed out by Stwalley /9/. Using quantum considerations he argued that the spin-flip mechanism due to nonadiabatic transition is not important and suggested that H↑ is stable against 2-body collisions for $B/T \gtrsim 10^6$ Gauss/K. This reveals the importance of the three-body recombination reaction in determining the stability of H↑. The lifetime $\tau \sim 4\times10^{16} T^{-9/2}$ sec estimated by Jones et al. based on barrier penetration is again incorrect and this time far too large. This arises from their assumption that hydrogen molecules are always formed in the ground

vibrational state /10/. This is not true according to the Franck-Condon principle and this point becomes clear in a simple calculation /11/ we made.

An accurate calculation of the three-body recombination reaction rate presents a new challenge to molecular reaction dynamicists. The difficulties involve the representation of the initial state of three free particles, treatment of non-adiabatic transition between the states involved, existence of many open final states and unavailability of an accurate upper electronic potential energy surface. Because of these difficulties, in our recent work /11/ we aimed at an order-of-magnitude calculation based on physical arguments. Results of this work will be reported here. We begin with a brief review of the treatment of Jones et al. about 2-body collisions and Stwalley's argument against it. Comments on the fact that the actual density could be higher than our estimate and an intense magnetic field could reduce the three body recombination rate of H↑ considerably conclude the report.

CALCULATION.- The strategy we took is to calculate the three-body recombination reaction rate k_3 as a product of two factors. The first factor $k_3(GK)$ describes the rate that three H↑ atoms come into the interaction region at the same time. The second factor P estimates the probability that an electronic spin flips each time three H↑ atoms are close together. $k_3(GK)$ can be obtained in two ways. Based on purely geometric arguments $k_3(GK)$ is proportional to the product of the average thermal velocity and the fifth power of the average interatomic distance, as given by Smith's formula /12/. $k_3(GK)$ obtained this way is 1×10^{-31} $cm^6/atom^2$ sec , if the crossing distance of 8 bohr in a magnetic field of 100 kG is used. This value is reasonably close to $K_3(H) \simeq 1 \times 10^{-32}$ $cm^6/atom^2$ sec, the experimental value for the termolecular recombination rate of hydrogen atoms at 77°K. The latter value will be used.

To explain how we estimated P, let us briefly review the treatment by Jones et al. for two H↑ atoms. In the Born-Oppenheimer approximation one first solves the electronic part of the Schroedinger equation of the field-free Hamiltonian for fixed nuclear configurations. This gives us the $X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ potential curves of concern here. In a magnetic field the $b\,^3\Sigma_u^+$ level is split into three curves. The $M_s = -1$ component crosses with the $X\,^1\Sigma_g^+$ curve. Now this crossing becomes an avoided one when the hyperfine coupling term is included. This means that in a low energy collision between 2H↑ atoms the atoms can follow the adiabatic potential curve and come close to each other to form a $H_2(X\,^1\Sigma_g^+)$. Based on this semiclassical argument, it seems that H_2 molecules should be formed with appreciable rate as predicted by Jones et al. Fortunately, as was first pointed out by Stwalley, this process will not take place for there are no vibrationally excited states of hydrogen molecule ($H_2^\dagger$) within the thermal energy range considered (0.1°K). But this spin-flip mechanism has to be considered in three-body collisions. This is because the final states of two-body collisions of H↑ are discrete and those of three H↑ collisions are in the continuum. In other words, the third atom in the three-body collision case can carry away the excess energy of dissociation and permit the first two atoms to combine into a bound H_2 molecule. Of course, the reaction probability of some final states can be extremely small. The probability of electronic transition from the quartet state of three H↑ atoms to the $M_s = -\frac{1}{2}$ component of the doublet ground state where H_2^+ is formed in a

specific vibrational state n_2 can be estimated. The generalized Landau-Zener Model /13, 14/ yields

$$P(n_2) \simeq 2\pi |H_{12}|^2 |\langle \varepsilon_1 | n_2 \rangle|^2 / \hbar v |s_1 - s_2| \qquad (1)$$

where H_{12} is the hyperfine coupling matrix element between the initial and final electronic states; ε_1 is the initial translational energy between the two H↑ atoms which recombine into $H_2^\dagger$. v is the velocity of the third atom relative to the center of mass of the other two at the crossing point and s_i is the slope of the i th potential surface along a direction perpendicular to the crossing seam. The overlapping factor, $\langle \varepsilon_1 | n_2 \rangle$, in Eq. (1) predicts that most of the hydrogen molecules formed are in highly vibrationally excited states. Further collisions of $H_2^\dagger$ with H↑ can bring $H_2^\dagger$ down the vibrational ladder and release its internal energy. From Eq. (1) it is also clear that the assumption of Jones et al. that H_2 are formed solely in the ground state will give an extremely small spin-flip probability. Summing $P(n_2)$ over n_2 and assuming that a complete set of states is summed over, we obtained $P \simeq 5 \times 10^{-8}$, so that $k_3 \simeq 5 \times 10^{-40}$ $cm^6/atom^2$ sec , which yields a density $\rho \sim 10^{17}$ atoms/cm^3 for a duration of about a day. Because of the approximations introduced, for example, the semi-classical method of calculating the electronic transition probability, our estimate of the density could be several orders of magnitude too low. One direct consequence of this model is that an intense magnetic field (e.g., above 440 kG) could be extremely effective in inhibiting collisional quenching processes, because the potential at the crossing seam is then much higher than the thermal energies of H↑.

Acknowledgement.- In the early stages of this work we had the counsel of Dr. L.H. Nosanow who was at Drexel on leave from the NSF.

References and Comments

/1/ R.D. Etters, J.V. Dugan and R.W. Palmer, J. Chem. Phys. 62, 313 (1975).

/2/ W.C. Stwalley and L.H. Nosanow, Phys. Rev. Letters 36, 910 (1976).

/3/ A.J. Berlinsky, R.D. Etters, V. Goldman and I.F. Silvera, Phys. Rev. Letters 39, 356 (1977); A.J. Berlinsky, Phys. Rev. Letters 39, 359 (1977).

/4/ L.J. Lantto and R.M. Nieminen, J. Low Temp. Phys. 37, 1 (1979).

/5/ R.A. Guyer and M.D. Miller, Phys. Rev. Letters 42, 1754 (1979).

/6/ S.B. Cramptom, T.J. Greytak, D. Klepper, W.D. Phillips, D.A. Smith and A. Weinrib, Phys. Rev. Letters 42, 1039 (1979).

/7/ I.F. Silvera and J.T.M. Walraven, Phys. Rev. Letters 44, 164 (1980); J.T.M. Walraven and I.F. Silvera, Phys. Rev. Letters 44, 168 (1980).

/8/ J.T. Jones, M.H. Johnson, H.L. Mayer, S. Katz and R.S. Wright, Aeronutronics Systems, Inc. Publication No. U-216, 1958 (unpubl.)

/9/ W.C. Stwalley, Phys. Rev. Letters 37, 1628 (1976).

/10/ Jones et al.[8] had doubt about this assumption themselves, but their results presented are within this assumption.

/11/ J.M. Yuan, T.K. Lim and L.H. Nosanow, submitted for publication.

/12/ F.T. Smith in "Kinetic Processes in Gases and Plasmas," ed. by A.R. Hochstim, Academic Press, New York (1969).

/13/ E. Bauer, E.R. Fisher and F.R. Gilmore, J. Chem. Phys. 51, 4173 (1969).

/14/ J.M. Yuan and T.F. George, J. Chem. Phys. 68, 3040 (1978).