

attenuation, roughness, etc., in the solid surface make, at most, secondary contributions. The experimental situation is similar for metals [J. D. N. Cheeke, B. Hébral, and J. Richard, *J. Low Temp. Phys.* **12**, 359 (1973)].

¹¹We use for layer 2, $\rho = 0.258 \text{ g/cm}^3$, $C_l = 0.96 \text{ km sec}^{-1}$, and $C_t = 0.48 \text{ km sec}^{-1}$; for layer 1, $\rho = 0.195 \text{ g/cm}^3$, $C_l = 0.5 \text{ km sec}^{-1}$, $C_t = 0.25 \text{ km sec}^{-1}$. The results are not critically dependent upon the choice of these values, which has been made as realistically as possible; full details of the determination of such constants and of their relative importance is given in Ref. 9. The model used here corresponds to the currently accepted value of *about* 1.6 statistical atomic layers of solid helium.

¹²A. F. G. Wyatt, N. A. Lockerbie, N. G. Mills, and R. A. Sherlock, *Solid State Commun.* **11**, 1089 (1972).

¹³It has been shown quite conclusively [J. G. Dash, in *Critical Reviews in Solid State Sciences* (Chemical Rubber Company, Cleveland, Oh., 1976), p. 209] absorbed helium can be described surprisingly well as an elastic two-dimensional Debye continuum insofar as its low-temperature acoustic and thermal properties are concerned.

¹⁴C. H. Anderson and E. S. Sabisky, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1971), Vol. 8.

¹⁵Even supposing the simple k dependence of the absorption term assumed here, ν will generally be a temperature- and thickness-dependent parameter, which could of course be included in more sophisticated versions of the present model.

¹⁶Previous workers [W. Dietsche and H. Kinder, *J. Low Temp. Phys.* **23**, 27 (1976)] have discussed the possibility of a similar model to explain phonon reflection experiments. However these authors ruled out an explanation based upon the use of acoustic mismatch. In the present work we show that the classic Kapitza problem can be explained by such a model using acoustic mismatch alone.

¹⁷L. J. Challis and R. A. Sherlock, *J. Phys. C* **3**, 1193 (1970).

¹⁸For the copper-⁴He interface, the numerical values and methods stated in the text lead to $r_1 = 0.6$, $t_1 = 0.4$, $r_2 \sim 1$, and $t_2 = 1.5 \times 10^{-3}$.

¹⁹J. T. Folinsee and A. C. Anderson, *Phys. Rev. Lett.* **31**, 1580 (1973), and *J. Low Temp. Phys.* **17**, 409 (1974).

²⁰N. S. Snyder, *J. Low Temp. Phys.* **22**, 257 (1976). These measurements were made on what were probably the most carefully controlled R_K surfaces ever studied.

²¹R. C. Johnson and W. A. Little, *Phys. Rev.* **130**, 596 (1963).

Stability of Spin-Aligned Hydrogen at Low Temperatures and High Magnetic Fields: New Field-Dependent Scattering Resonances and Predissociations*

William C. Stwalley

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

(Received 12 October 1976)

Spin-aligned hydrogen ($\text{H}\uparrow$) and deuterium ($\text{D}\uparrow$) are generally predicted to be stable for $\mathcal{H}/T \gtrsim 10^6 \text{ G/K}$. Magnetic-field-dependent resonances (inverse to field-induced predissociations of high vibrational-rotational levels of HD and D_2) provide exceptions to this general rule. Their existence suggests 50 kG ($\text{H}\uparrow + \text{D}\uparrow$) and 19 kG ($\text{D}\uparrow + \text{D}\uparrow$) should be avoided for stable $\text{H}\uparrow$ and $\text{D}\uparrow$. Induced predissociation observations should yield ultra-precise resonance information and dissociation limits.

Spin-aligned hydrogen ($\text{H}\uparrow$) and deuterium ($\text{D}\uparrow$) are extremely interesting but heretofore hypothetical substances with all electronic spin projections (M_s) parallel. Here only the lowest energy M_s is considered (e.g., $M_s = -\frac{1}{2}$ for $\text{H}\uparrow$). $\text{H}\uparrow$ and $\text{D}\uparrow$ are especially simple, and complete understanding of all phenomena should be possible. For example, $\text{H}\uparrow$ is predicted¹⁻³ to remain a gas down to absolute zero temperature (for pressures $\leq 50 \text{ atm}$ where it should solidify²) and to show strong quantum behavior² characteristic of a nearly ideal Bose gas (including Bose-Einstein condensation and superfluidity). $\text{D}\uparrow$ is predicted² to be on the verge of liquidity at absolute zero temperature and low pressures (compared to a solidification pressure of $\sim 8 \text{ atm}$), and unique liquid-

gas equilibria of this highly quantal Fermi fluid should occur. $\text{T}\uparrow$ is predicted² to be very similar to that of ^4He . The solid phases^{4,5} and magnetic properties of these ferromagnetic substances should also be of major interest. The energy content per gram of $\text{H}\uparrow$ is higher than any known substance; hence, it is possibly of interest for rocket propulsion^{1,6-10} (which is the original motivation^{6,7}).

It has been suggested^{1,2,6,9} that $\text{H}\uparrow$ and $\text{D}\uparrow$ would be stable under low-temperature ($T \leq 1 \text{ K}$), high-magnetic-field ($\mathcal{H} \gtrsim 50 \text{ kG}$) conditions. Experiments under roughly these conditions on D/D_2 mixtures⁸ and H/H_2 mixtures⁹ suggest marginal stability for partial electronic spin alignment. The primary purpose here is to argue that long-

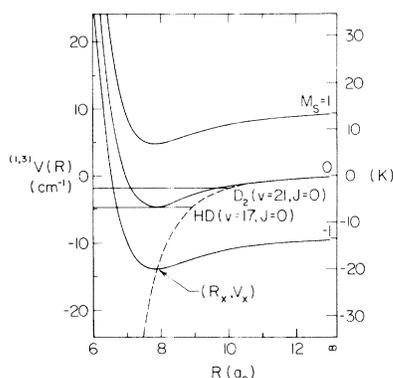


FIG. 1. Potential energy curves for $X^1\Sigma_g^+$ (---) and $b^3\Sigma_u^+$ (—) states of isotopic H_2 . The three triplet components (the lowest being $H\uparrow + H\uparrow$) are shown for $\mathcal{H} = 100$ kG. Note the crossing at (R_x, V_x) and the "long-range" levels of singlet HD ($v=17, J=0$) and D_2 ($v=21, J=0$) which correspond to low-energy scattering resonances.

term stability (even at high densities) of pure $H\uparrow$ and $D\uparrow$ should occur for $\mathcal{H}/T > 10^6$ G/K (e.g., feasible combinations such as 100 mK and 100 kG).

In connection with these arguments, a new resonance mechanism for destruction of $H\uparrow$ and $D\uparrow$ at specific magnetic fields is presented. Resonance occurs when the lowest-energy asymptote of the $b^3\Sigma_u^+$ potential curve (proportional to \mathcal{H}) matches the (\mathcal{H} -independent) energy of the highest vibrational-rotational states of the $X^1\Sigma_g^+$ ground-state potential curve (Fig. 1). These high-lying levels ("long-range molecules") are of interest in their own right^{11,12} since their properties are different and nonintuitive, but related to the long-range potential (e.g., $-C_6/R^6$). The inverse of the above resonant collisions, namely

the magnetic-field-induced predissociation of long-range molecules is also discussed, with specific regard to isotopic H_2 . Such predissociations should allow accurate determination of resonance parameters and dissociation limits.

Stability involves the rate of processes which destroy $H\uparrow$ (and produce recombination to H_2 and destructive heating). Consider low-density gaseous $H\uparrow$, in which three kinds of collisions are of concern: $H\uparrow-H\uparrow$, $H\uparrow$ -wall, and $H\uparrow$ -impurity. For higher densities, three-atom (and, ultimately, multi-atom) collisions become important.

The $H\uparrow-H\uparrow$ collisions are governed by precisely known^{13,14} potential curves (Fig. 1). (Accurate close-coupled calculations¹⁵ of these collisions are planned.) Recall that H has four hyperfine states (using Brown's notation¹⁶):

$$|1\rangle = \alpha a \quad - \quad H\uparrow \quad - \quad |2\rangle = (1-\theta)^{1/2}\alpha b + \theta^{1/2}\beta a,$$

$$|3\rangle = \beta b \quad - \quad H\uparrow \quad - \quad |4\rangle = (1-\theta)^{1/2}\beta a - \theta^{1/2}\alpha b.$$

Hence the collision of two H atoms involves 16 hyperfine "molecular" states.^{16,17} For $H\uparrow-H\uparrow$, the possibilities are listed in Table I. Only relative angular momentum $J=0$ and $J=1$ collisions should be important at these low energies. Because $M = M_s + M_I$, J , and P_{AB} (the atomic permutation eigenvalue) are good quantum number, during collision (spin-rotation coupling is negligible), for energies below threshold only nondestructive scattering and $|3\rangle/|4\rangle$ exchange occur. For energies above threshold, destructive processes begin, but are dramatically suppressed by the small collision fraction with sufficient energy, i.e., by a factor $\exp[-E_T(K)/T(K)]$. [Bose statistics for $H\uparrow$ do not modify this as $\exp(-E_T/T) \ll 1$.] Even

TABLE I. Low-energy $H\uparrow + H\uparrow$ collisions in hyperfine states $|3\rangle$ or $|4\rangle$ conserve $M = M_s + M_I$, P_{AB} (the atomic permutation eigenvalue), and J (relative angular momentum). Threshold energies E_T for channel openings at 100 kG, as well as approximate probabilities P [from Ref. 16, with $\gamma = \exp(-E_T/T)$], are given.

M	P_{AB}	J	Initial	Final	E_T (K)	P
-2	1	0	$ 3,3\rangle$	$\rightarrow 3,3\rangle$	0	1
-1	1	0	$\left\{ \begin{array}{l} 3,4\rangle \\ 4,3\rangle \end{array} \right\}$	$\rightarrow \left\{ \begin{array}{l} 3,4\rangle \\ 4,3\rangle \end{array} \right\}$	0	$1 - 2\theta\Delta\gamma$
	-1	1		$\rightarrow 3,2\rangle, 2,3\rangle$	13.4	$2\theta\Delta\gamma$
0	1	0	$ 4,4\rangle$	$\rightarrow 4,4\rangle$	0	$1 - 4\theta\Delta\gamma - 4\theta^2\Delta\gamma^2$
			$\left\{ \begin{array}{l} 3,1\rangle, 1,3\rangle \\ 2,4\rangle, 4,2\rangle \end{array} \right\}$	$\rightarrow \left\{ \begin{array}{l} 3,1\rangle, 1,3\rangle \\ 2,4\rangle, 4,2\rangle \end{array} \right\}$	13.4	$4\theta\Delta\gamma$
				$\rightarrow 2,2\rangle$	26.9	$4\theta^2\Delta\gamma^2$

for a very high density such as 10^{22} H \uparrow /cm 3 (\sim solid H \uparrow), one estimates a rough upper bound to the H \uparrow -H \uparrow destruction rate (Ref. 16 with $\Delta = \frac{1}{2}$) at $E_T = 10$ K ($\mathcal{H} = 74.4$ kG) to be $\sim 10^{24}$ atoms/cm 3 sec at 1 K (explosive!?), $\sim 10^{-14}$ at 100 mK (geologically stable), and $\sim 10^{-404}$ at 10 mK (infinitely stable). Indeed, this exponential energy factor is the key to stable H \uparrow . Even if the selection rules ($\Delta M = 0$, $\Delta P_{AB} = 0$, $\Delta J = 0$, and $\Delta M_J = 0$) broke down slightly, the *destructive* collisions ($\Delta M_s = 1$) would still be negligible for small $\exp(-E_T/T)$ ($\mathcal{H}/T \gtrsim 10^3$ kG/K). Jones *et al.*⁶ made much of the singlet-triplet crossing at (R_x, V_x) in Fig. 1. However, there are no energetically accessible states of the singlet curve below the $M_s = 0$ asymptote. For impractically high $\mathcal{H} > 520$ kG, this crossing point becomes energetically inaccessible.¹⁸ Tri- (or poly-) atomic collisions should similarly be limited by the $\exp(-E_T/T)$ factor. Collisions with diamagnetic impurities (e.g., ^4He) and (e.g., Ne-coated, though perhaps H \uparrow -covered) walls should be unimportant because no spins are present as well.

The only destruction mechanism found thus far involves D \uparrow impurities. As shown in Fig. 1 and Table II, the "long-range" $v = 17$, $J = 0$ level of $X^1\Sigma_g^+ \text{HD}$ (symbolized HD $^\infty$) lies only 4.71 ($\pm \sim 0.5$) cm $^{-1}$ below dissociation. At 50.4 ($\pm \sim 5$) kG, HD $^\infty$ becomes degenerate with the $M_s = -1$ asymptote, and hence mixing via the hyperfine interaction of previously bound HD $^\infty$ and the H \uparrow -D \uparrow continuum occurs. [For H $_2$, the highest levels ($v = 14$, $J = 0$ and 1) do not become degenerate except for impractical fields of 1525 and 1365 kG.] This mixing has negligible effects on the potentials except near the crossing point (R_x, V_x) , where most hyperfine states show avoided crossings ($M = -\frac{5}{2}$ does not). Landau-Zener-type treatments¹⁹ indicate triplet-singlet transition probabilities of $\sim 10^{-6}$, predissociative lifetimes for HD $^\infty$ of $\sim 10^{-6}$

sec, and field-dependent scattering resonance widths of $\sim 10^{-5}$ K. The precise determination of such widths (and also energy shifts of $\sim 10^{-5}$ K) particularly in the zero-energy limit (where modified effective-range theory²⁰ is appropriate) is a major motivation for the above-mentioned close-coupled calculations.

A direct study of the field-induced predissociation would be valuable, although the predissociation linewidth itself is too sharp. Several schemes for producing long-range levels are now contemplated in this laboratory. Since available magnetic fields are homogeneous and stable to $\lesssim 10^{-3}$ G (corresponding to $\sim 10^{-7}$ cm $^{-1}$), the magnetic-field onset of predissociation should provide exceedingly accurate binding energies of long-range levels (e.g., determined as frequencies relative to proton NMR).

These Feshbach scattering resonances are harmless themselves (i.e., at very low densities) since they dissociate to H \uparrow + D \uparrow . However, they involve long time delays^{12a} ($\sim 10^{-6}$ sec) with appreciable singlet character, as opposed to ordinary nonresonant collisions with $\sim 10^{-13}$ -sec time delays and negligible singlet character. Thus, at higher densities destructive processes such as HD $^\infty$ + H \uparrow \rightarrow [HD($v < 17$) + H \uparrow + heat] or (H $_2$ + D \uparrow + heat), etc. will occur with small but significant rates *without input energy*. However, for $\mathcal{H} \gg \mathcal{H}_T$, the formation of HD $^\infty$ can be suppressed by $\exp(-E_R/T)$, where $E_R(K)$ is the resonance energy with respect to the field-dependent $M_s = -1$ asymptote.

In principle, paramagnetic impurities such as O $_2$ (in its lowest M_s state) also yield resonant destruction processes similar to (but more complex than) those outlined above. An additional complication for these species is the formation of clusters such as (H \uparrow) $_n$ (O $_2$ \uparrow) [species such as (H \uparrow) $_n$ or (H \uparrow) $_n$ (D \uparrow) should not be bound¹⁻³]. Fortunately, the vapor pressure of O $_2$ is negligible (e.g., at 1 K $P_{\text{O}_2} \approx 10^{-78}$ Torr), but air leaks should be avoided!

While it might be possible to prepare H \uparrow only in the hyperfine state $|3\rangle$, and thereby seemingly avoid worrying about $\Delta M_s = 1, 2$ processes (Table I), in practice $\Delta M_I = 1$ processes should occur unless the nuclear Zeeman energy is much greater than kT (i.e., $\mathcal{H}/T > 10^9$ G/K). Thus no advantage is expected, except possibly at low density.

Spontaneous emission was considered and rejected by Jones *et al.*⁶ (giving an estimated lower bound to lifetime of 3.4×10^{22} sec). Magnetic inhomogeneities (and instabilities) at boundaries

TABLE II. Binding energies $\epsilon_{v,J}$ of vibration-rotation levels near dissociation in HD [from I. Dabrowski and G. Herzberg, Can. J. Phys. 54, 525 (1976)] and D $_2$ (from Ref. 12b) and corresponding threshold magnetic fields \mathcal{H}_T for field-induced predissociation.

Species	v	J	$\epsilon_{v,J}$ (cm $^{-1}$)	\mathcal{H}_T (kG)
HD $^\infty$	17	0	4.7 $_1$	50.4
	17	1	0.0	0.0
D $_2$ $^\infty$	21	0	1.80 $_3$	19.3 $_1$
	21	1	-0.08 $_7$...

could cause electronic Majorana transitions but should be avoidable.²¹

High-density and, ultimately, solid $H\uparrow$ should not involve new destruction mechanisms. Moreover, local fields from adjacent atoms are still small [for a high density interatomic distance of $\sim 10a_0$, $\mathcal{H}_{\text{local}} \sim \mu_B/(10a_0)^3 \sim 1$ G]. Destructive spin waves (magnons) should be unimportant for large \mathcal{H}/T .

Stability conditions for $D\uparrow$ are like those for $H\uparrow$. There are six hyperfine states for D (three for $D\uparrow$) and 36 hyperfine molecular states.^{17b} Again, only $J=0$ and $J=1$ collisions are important (except perhaps $J=2$ at ~ 1 K); and similar selection rules should be valid; in any case, the $\exp(-E_T/T)$ factor insures negligible spin-flip rate for $\mathcal{H}/T \geq 10^3$ kG/K. In addition to HD^∞ (50.4 kG), there is a D_2^∞ resonant level only $1.80_3 \pm 0.20$ cm^{-1} below singlet dissociation,^{12b} corresponding to a 19.3 ± 2.0 kG threshold field to be avoided.

Stability predictions for other spin-aligned systems [e.g., $N\uparrow$ or $(Li\uparrow)(H\uparrow)$] are hampered by lack of information on potentials and long-range levels and by anticipated clustering. Nevertheless, it is expected that additional stable spin-aligned systems can be prepared for large \mathcal{H}/T .

Helpful discussions with Dr. D. Kleppner, Dr. R. E. Packard, Dr. W. M. Fairbank, Dr. J. O. Hirschfelder, Dr. T. A. Miller, Dr. F. H. Mies, Dr. A. Pines, Dr. D. E. Ramaker, Dr. S. C. Yang, Dr. D. C. Lee, and especially Dr. L. H. Nosanow are acknowledged.

*Work supported by the Petroleum Research Fund, administered by the American Chemical Society.

¹J. V. Dugan and R. D. Etters, *J. Chem. Phys.* **59**, 6171 (1973); R. D. Etters, J. V. Dugan, and R. W. Palmer, *J. Chem. Phys.* **62**, 313 (1975); R. D. Etters, *Phys. Lett.* **42A**, 429 (1973); R. L. Danilowicz, J. V. Dugan, and R. D. Etters, *J. Chem. Phys.* **65**, 499 (1976).

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

³L. W. Bruch, *Phys. Rev. B* **13**, 2873 (1976).

⁴T. R. Proctor and W. C. Stwalley, unpublished.

⁵D. E. Ramaker, private communication.

⁶J. T. Jones, M. H. Johnson, H. L. Mayer, S. Katz, and R. S. Wright, Aeronutronics Systems, Inc. Publication No. U-216, 1958 (unpublished).

⁷M. W. Windsor, in *Formation and Trapping of Free Radicals*, edited by A. M. Bass and H. P. Broida (Academic, New York, 1960), p. 400f.

⁸R. Hess, *Adv. Cryog. Eng.* **18**, 427 (1973); R. Hess, doctoral dissertation, University of Stuttgart, 1971 (unpublished); and *Deutsche Luft- und Raumfahrt, Forschungsbericht 73-74: Atomärer Wasserstoff* (Institut für Energie Wandlung und Elektrische Antriebe, Stuttgart/Braunschweig, 1973); W. Peschka, private communication.

⁹R. W. H. Webeler, *J. Chem. Phys.* **64**, 2253 (1976); see also G. Rosen, *J. Chem. Phys.* **65**, 1795 (1976).

¹⁰M. L. Yaffee, *Aviat. Week Space Technol.* **101**, 47 (1974).

¹¹For reviews see W. C. Stwalley, in *Energy, Structure, and Reactivity*, edited by D. W. Smith and W. B. McRae (Wiley, New York, 1973), p. 259f; R. J. Le Roy, in *Specialist Periodical Report on Electronic Spectroscopy*, edited by R. F. Barrow, D. A. Lang, and D. J. Millen (Chemical Society, London, 1974), p. 113.

^{12a}For treatments of H_2 see R. J. Le Roy and R. B. Bernstein, *J. Chem. Phys.* **54**, 5114 (1971).

^{12b}For treatment of H_2 see R. J. Le Roy and M. G. Barwell, *Can. J. Phys.* **53**, 1983 (1975).

¹³W. Kołos and L. Wolniewicz, *Chem. Phys. Lett.* **24**, 457 (1974), and *J. Mol. Spectrosc.* **54**, 303 (1975).

¹⁴D. M. Bishop and K. Shih, *J. Chem. Phys.* **64**, 162 (1976).

¹⁵See, e.g., F. H. Mies, *Phys. Rev. A* **7**, 942, 957 (1973).

¹⁶R. L. Brown, *J. Res. Natl. Bur. Stand.* **76A**, 103 (1972); see also A. E. Glassgold and J. F. Walker, *Phys. Rev.* **160**, 11 (1967).

^{17a}J. E. Harriman, M. Twerdochlib, M. B. Milleur, and J. O. Hirschfelder, *Proc. Natl. Acad. Sci. U. S. A.* **57**, 1558 (1967).

^{17b}M. B. Milleur, L. A. Curtiss, M. Twerdochlib, and J. O. Hirschfelder, *J. Chem. Phys.* **48**, 4261 (1968).

¹⁸S. C. Yang, private communication.

¹⁹See, e.g., M. S. Child, *Can. J. Phys.* **53**, 1838 (1975).

²⁰O. Hinckelmann and L. Spruch, *Phys. Rev. A* **3**, 642 (1971).

²¹N. F. Ramsey, *Molecular Beams* (Oxford Univ. Press, London, 1956), Appendix E.