Photoproduction of Spin-Polarized Hydrogen Atoms and Electrons in Mixtures of Cesium Vapor and Hydrogen Gas

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First observations of the photogeneration of spin-polarized hydrogen atoms and electrons are reported. A mixture of cesium vapor and helium and hydrogen buffer gases is optically pumped with a circularly polarized tunable—dye-laser beam (4593 Å). The paramagnetic species (H atoms, e^-) generated by the laser-induced processes are detected with use of spin-exchange—magnetic-resonance spectroscopy.

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In 1975 Tam, Moe, and Happer[1] reported that the blue lines of an argon-ion laser at 4545 and 4579 Å would produce micron-sized particulates in glass cells containing cesium vapor and traces of hydrogen or deuterium gas. They suggested that the particulates, often called "laser snow," were crystals of cesium hydride salt produced by the following sequence of reactions:

$$h\nu + \mathrm{Cs}(6S) \to \mathrm{Cs}^*(7P); \tag{1}$$

$$\mathrm{Cs}^*(7P) + \mathrm{H}_2 \to \mathrm{CsH} + \mathrm{H} \tag{2a}$$

or

$$\begin{aligned} &\mathrm{Cs}^*(7P) + \mathrm{H}_2 \to \mathrm{Cs}(6S) + \mathrm{H}_2{}^\dagger, \\ &\mathrm{Cs}(6S) + \mathrm{H}_2{}^\dagger \to \mathrm{CsH} + \mathrm{H}; \end{aligned} \tag{2b}$$

$$\mathrm{CsH(gas)} \to \mathrm{CsH(crystal)}, \tag{3}$$

where $\mathrm{H}_2{}^\dagger$ denotes vibrationally excited hydrogen.

Tam, Moe, and Happer[1] were able to demonstrate that substantial numbers of CsH diatomic molecules were produced in their experiments. However, neither the original[1] nor any subsequent studies[2-5] of "laser snow" have provided any proof that free hydrogen atoms are generated, as required by the postulated reaction (2). In this paper we report on magnetic resonance experiments which show for the first time that substantial numbers of free hydrogen atoms are indeed produced, and surprisingly, that the blue second resonance pumping light always produces free electrons in cesium cells, whether hydrogen is in the cells or not.

We have used spin-exchange—magnetic-resonance spectroscopy to detect any paramagnetic species produced in "laser snow" cells.[6-8] The apparatus used in our work is illustrated in Fig. 1. A circularly polarized, tunable blue dye-laser beam[9] (4593 Å, $6^2S_{1/2}$-$7^2P_{1/2}$) was used to optically pump a mixture of cesium vapor and various amounts of buffer gas. As indicated in Fig. 1, some of the cells were made with internal parallel-plate electrodes to unambiguously identify any charged paramagnetic species like e^- or $\mathrm{Cs}_2{}^+$. The cells were heated in a transparent glass oven. A uniform magnetic field could be swept slowly from 0 to 20 G along the direction of the laser beam. A transverse 3 MHz radio frequency field with an oscillating amplitude of up to 0.5 G was also applied to the cells. To avoid instrumental scattering of the blue pumping light we monitored the intensity of the first resonance fluorescent light at 8521 Å ($6^2P_{3/2}$-$6^2S_{1/2}$) at right angles to the laser beam with a photomultiplier tube. The upper state of the 8521 Å transition ($6^2P_{3/2}$) is populated with a branching ratio of about 70% by cascade transitions after

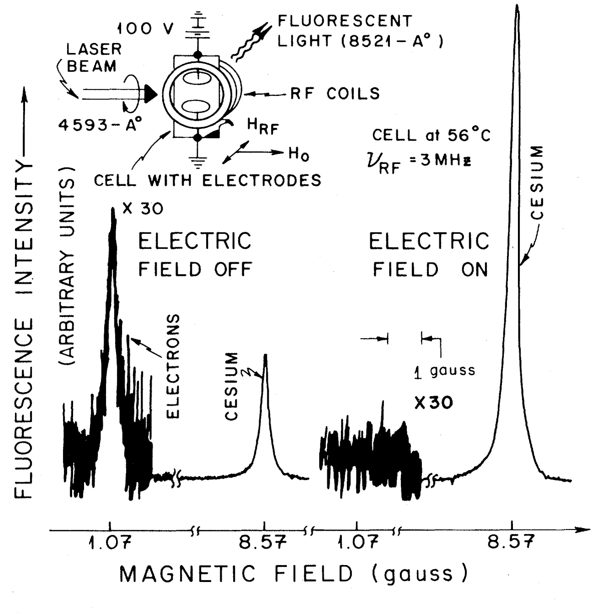

FIG. 1. Experimental arrangement and representative magnetic-resonance signals.

the cesium atoms absorb a blue 4593-Å photon. Depolarization of the cesium atoms or of any other paramagnetic species coupled to the cesium atoms by spin-exchange collisions leads to an increase in the 8521-Å fluorescence, which is a measure of the rate of absorption of the blue 4593-Å light.

During the course of this work we were surprised to find that free electrons were always produced by the blue pumping light, whether hydrogen was mixed with the cesium vapor or not. These free electrons seriously degraded the cesium spin polarization. A particularly clear example of the effect of free electrons is illustrated in Fig. 1. A cell with internal electrodes was filled with 650 Torr of He and 100 Torr of D_2 at room temperature. As shown in Fig. 1, we observed clear signals at 2800 kHz/G, the magnetic resonance frequency of free electrons, in addition to a strong cesium-atom signal at 350 kHz/G. When an electric field of 100 V/cm is applied to the cell, the signal at 2800 kHz/G vanishes while the atomic-cesium signal amplitude is increased by a factor of 4. The destruction of the signal at 2800 kHz/G by the application of an electric field supports the interpretation of this peak as that of free electrons. The enhancement of the magnetic-resonance peak of the cesium atoms by the application of the electric field suggests that the free electrons and possibly other charged species (e.g., Cs_2^+) are destroying the cesium spin polarization at a substantial rate.

Strong, unpolarized blue fluorescence at 4593 Å ($6^2S_{1/2}$-$7^2P_{1/2}$) and 4555 Å ($6^2S_{1/2}$-$7^2P_{3/2}$) from atomic cesium could be seen along the path of the laser beam within the cell of Fig. 1 and in most other cells. Examination of the fluorescent beam through a red-transmitting filter showed that a large amount of red fluorescence was also produced by the laser beam as was previously reported by Picqué, Vergès and Vetter.[4] At higher temperatures, say 200 °C, the red fluorescence was much stronger than the blue second resonance line and examination of the fluorescence with a spectrometer revealed numerous cesium emission lines originating from *S*, *D*, and *F* states with principal quantum numbers as large as 10. Such states lie more than 1 eV higher than the $7P$ state which was excited by the laser. The emission spectrum is consistent with what one would expect from a recombining plasma of Cs^+, Cs_2^+, and e^-. Possible formation mechanisms for the highly excited atoms are discussed in the literature.[10] When an electric field was applied to the cell of Fig. 1 the red fluorescence from the laser beam decreased so much that it was barely visible when observed through a red-transmitting filter. The fact that the red fluorescence is always diminished by the application of an electric field gives further weight to the idea that much of the red fluorescence is generated in a recombining plasma. The red fluorescence is present in all cesium cells, even in those that contain no hydrogen or deuterium.

Although the electrode cell of Fig. 1 was filled with 100 Torr of D_2, no trace of an atomic-deuterium magnetic-resonance signal was seen. This can be understood on the basis of the equilibrium thermodynamics of alkali hydride systems. Hydrogen and deuterium gas react very slowly with alkali metals to form alkali hydride salts. The reaction takes many weeks to come to equilibrium at room temperature and several hours at 100 °C. As the reaction proceeds, a frostlike coating of white crystals forms on the inner walls of the cell. In full thermal equilibrium the partial pressures of gas over a salt-metal mixture are[11, 12]

$$\log_{10} p(H_2) = 11.27 - 5419/T, \quad (4)$$

$$\log_{10} p(D_2) = 11.89 - 5956/T, \quad (5)$$

where T is the absolute temperature in degrees Kelvin and p is the partial pressure of H_2 or D_2 in Torr. The equilibrium deuterium pressure at 56 °C, the temperature of the cell in Fig. 1, is 10^{-7} Torr, a negligibly small value, which has no influence on the formation of free electrons. Cells with a few Torr of nitrogen and a few hundred Torr of helium gas also exhibit free-electron resonance.

For a cell in chemical equilibrium, Eqs. (4) and (5) imply that temperatures well above 200 °C are needed to obtain a partial pressure of a few Torr of H_2 or D_2 gas. We were unable to detect any spin polarization in hydrogen cells at temperatures above 200 °C, perhaps because of the copious production of "snow," radiation trapping, depolarization by free electrons, etc. This dilemma can be overcome by using cells which are *not* in chemical equilibrium.

Magnetic-resonance spectra from cells without internal electrodes are shown in Fig. 2. These cells were operated at 78 °C. The cells had been heated to 250 °C to decompose the frosty coating of salt on the walls prior to taking data, and as we shall discuss below, the reestablishment of chemical equilibrium is so slow that the H_2 and

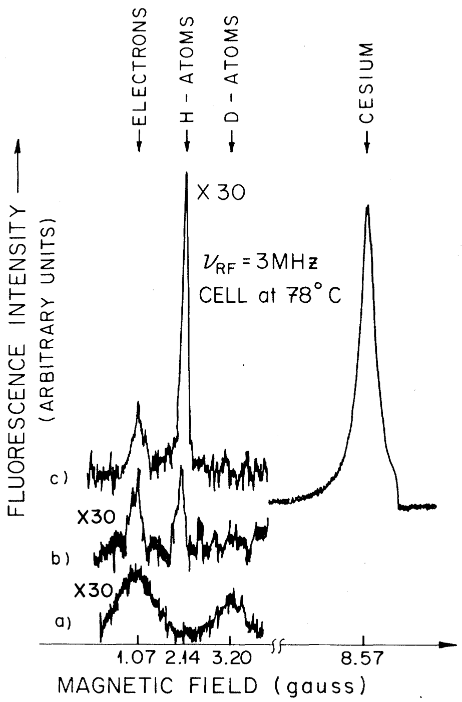

FIG. 2. (a) Magnetic-resonance signals in a cell containing Cs + D_2 (100 Torr) + He (600 Torr). The peak at 3.20 G is identified as due to D atoms. (b) and (c) Similar signals obtained in a cell containing Cs + H_2 (100 Torr) + He (600 Torr), with focused and unfocused incident laser beam, respectively. A typical strong signal due to Cs atoms (seen in all the cells) is also shown for comparison.

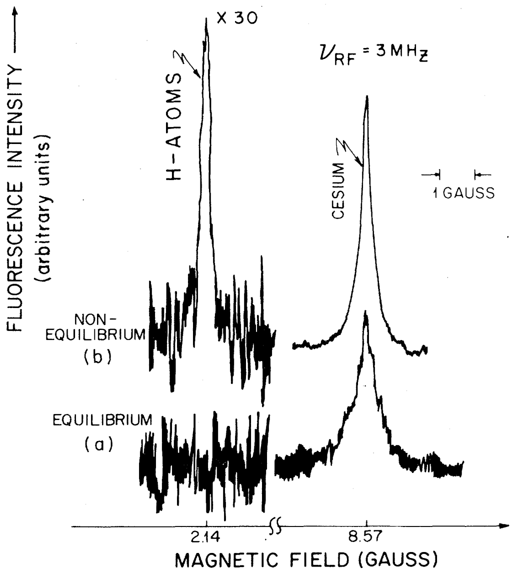

FIG. 3. Magnetic-resonance signals in a cell containing Cs + H_2 (1 Torr) + He (600 Torr) for equilibrium and nonequilibrium conditions in the cell.

D_2 pressures almost certainly remained well above the values predicted by (4) and (5) for the duration of the experiments.

In Fig. 2(a) we show the spectrum of a cell containing 100 Torr D_2 and about 600 Torr He. A clear magnetic-resonance peak is observed at 933 kHz/G, the magnetic-resonance frequency of D atoms, in addition to the free-electron and atomic-cesium signals. In Fig. 2(b) we show the spectrum of a similar cell with 100 Torr H_2 instead of D_2. A signal at 1400 kHz/G, the magnetic-resonance frequency of H atoms, was observed in addition to free-electron and cesium-atom signals. The spectrum of Fig. 2(b) was taken with the laser beam focused in the cell with a lens of 28 cm focal length. When the lens is removed the magnetic-resonance spectrum of Fig. 2(c) is obtained. The signal from the H atoms becomes much stronger relative to the signal from the electrons. This shows that more photons are required to form an electron than to form a free H atom. Photoionization of an excited Cs atom or the ionizing collision of two excited Cs atoms could produce electrons, and both mechanisms require two photons. According to the postulated reactions (1) and (2), only one photon is needed to form a free H atom.

The importance of the sluggish approach to chemical equilibrium in the sample cells is illustrated in Fig. 3. The cell contained 1 Torr H_2 and 600 Torr He and was operated at 125 °C. The magnetic-resonance spectrum of Fig. 3(a) was obtained after the cell had been maintained at 125 °C for 8 h. No trace of a free–hydrogen-atom signal was observed, and bright blue and red fluorescence of the type described earlier was observed. In Fig. 3(b) we show the magnetic-resonance spectrum of the same cell after it had been heated to 250 °C, maintained at that temperature for about 1 h, and rapidly cooled again to 125 °C. A clear magnetic-resonance signal from atomic hydrogen was observed, and in addition very little fluorescence could be seen from the cell. These observations indicate that the hydrogen gas released from the decomposed salt at 250 °C where $p(H_2) = 8$ Torr according to (4) has remained in the gaseous state where it can participate in reaction (2) to produce hydrogen atoms for detection by magnetic resonance. The H_2 gas can also nonradiatively deexcite the excited cesium atoms by reaction (2) or by nonchemical quenching and thereby eliminate much of the fluorescence. The H signal of Fig. 3(b) disappears after several hours, but it can be regenerated by heating the cell to 250 °C and rapidly cooling again.

These experiments constitute the first use of spin-exchange spectroscopy to detect a chemical reaction, the simple photochemical reaction (2). The same laser beam drives the chemical reaction, spin polarizes the atoms, and monitors the spin polarization. It may well be that an improved version of this experiment can lead to much higher spin polarizations and to the control of the photochemistry by magnetic-resonance techniques. For example, both the primary photoabsorption of circularly polarized light (1) and the parasitic reaction

$$\mathrm{Cs} + \mathrm{H} + \mathrm{He} \rightarrow \mathrm{CsH} + \mathrm{He} \tag{6}$$

are forbidden if the Cs and H are spin polarized along the magnetic field. One could therefore turn on the laser-snow production for a specific alkali isotope by selectively depolarizing the isotope with a resonant radio frequency field. This would transfer isotopically selective control of a chemical reaction from the optical region where isotope shifts are small to a region of the spectrum where isotope shifts are enormous, the radio frequency and microwave magnetic resonance spectrum.

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