Observation of nonstatistical ortho–para ratio in hydrogen recombination at low temperatures

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As one of the simplest chemical reactions and one that is well suited for rigorous calculations, hydrogen recombination has generated wide interest both theoretically and experimentally. Typically, theoretical calculations provide both recombination rates and ortho–para compositions of resultant molecules. One unique prediction, shared by most of quantum theories, is that at low temperatures (below 300 K) the recombination is predominantly determined by a small discrete set of resonance or weakly bound states of molecular hydrogen. Consequently, it is predicted[1–3] that the resultant molecular hydrogen has a nonstatistic ortho–para composition at low temperatures. The calculated values of the ortho–para ratio are found to be sensitively dependent on the actual model and approximation being used, therefore, it is suggested that measurements of the ortho–para ratio could provide much needed information to improve our understanding of the recombination process.[4,5] Although the importance of measuring the ortho–para composition was recognized more than twenty years ago and many experimental studies of hydrogen recombination have been reported since then,[5–11] a convincing measurement is yet to be reported. One of the obstacles towards measuring the composition is that the recombination produces molecules in vibrationally excited states and the analysis of the ortho–para composition is typically carried out after the molecules have relaxed back to the vibrational ground states.[7,8] So far, little is known about these vibrational states. Since both experiments at 77 K[7] and at 300 K[8] fail to observe the expected nonstatistical ortho–para ratio, it is suggested[8] that the exchange reaction between molecules in vibrationally excited states could cause rapid ortho–para conversion during the vibrational relaxation period.

In this communication, we report, for the first time, observations of nonstatistical ortho–para compositions for hydrogen recombined at low temperatures. By selecting atoms in nuclear spin polarized states, we obtained pure ortho hydrogen through a two-body surface recombination process. Although a specific recombination theory is yet to be developed, the experimental results can be understood based on the orbiting resonance model for the recombination of physisorbed atoms.[3] The pure ortho hydrogen obtained in the experiments clearly demonstrated that if the rapid exchange process discussed by Mitchell and LeRoy[8] does exist, if has been successfully quenched in our experimental conditions. Our work suggests that it is possible to carry out detailed comparison between calculations and measurements at conditions similar to our experiments. It is likely that such a comparison will significantly improve our understanding of the atomic recombination process.

Taking advantage of the technical progress of recent years, the experiments are carried out at temperatures from 0.1 K to 0.5 K. At the experimental temperatures, hydrogen atoms are in the gaseous phase; and hydrogen molecules are in the solid phase; the statistical value of the ortho–para ratio for molecular hydrogen is virtually zero (the energy difference between the ortho state and the para state is 171 K,[12] much less than the experimental temperatures). Depending on the gas density and the nature of the cell surface, the required third body in the recombination process can be either an atom or the cell surface. The data presented in this communication is obtained at 0.3 K, and the cell is coated with superfluid helium-4 and placed in a magnet field of 6.7 tesla. The typical gas density is 1.6×10^{16}/cc. Previous experiments[10] have demonstrated that the two-body surface recombination process is the dominant recombination process under these conditions.

Figure 1 shows a schematic diagram of the experimental cell. The cell is placed in a 6.7 tesla magnetic field. At the center of the cell is an NMR chamber, a cylindrical can of inside diam 1.8 cm and inside length 2.0 cm. Atoms are excluded from a region along the axis of the chamber by a sapphire coil form. The accessible volume of the NMR chamber is 3.7 cm^3 and it has surface area of 25.7 cm^2. The NMR chamber is positioned inside a concentric cylindrical cavity 3.18 cm in diam and 3.81 cm long. The polarization chamber consists of the space between the cylindrical cavity and the NMR chamber, plus the region of the filling tube which is located in the high field. The volume of the polarization chamber is 13.4 cm^3 and it has a surface area of 180 cm^2. The two chambers are connected by a 1.0 cm length, 0.11 cm inner diam tube. By changing the helium level in the cell the chambers can be isolated from each other. We refer to this system as the helium level valve. In a magnetic field, atomic hydrogen has four hyperfine states, commonly referred as states: **a**, **b**, **c**, **d**, according to the energy levels. As is discussed in our previous work,[10] when filling the cell with an atomic beam, a doubly polarized atomic gas (**b**-state atoms, both the electron spin and the nuclear spin are polarized) will accumulate in the cell. The atomic beam is produced at 77 K, and the atom flux reaching the cell is about 1.0×10^{15}/s. A pressure transducer is attached to the polarization chamber for monitoring the gas density. The polarization of the gas is derived from the decay rate of the gas after the atomic beam has been turned off, as is done in our previous work.[10] Ortho

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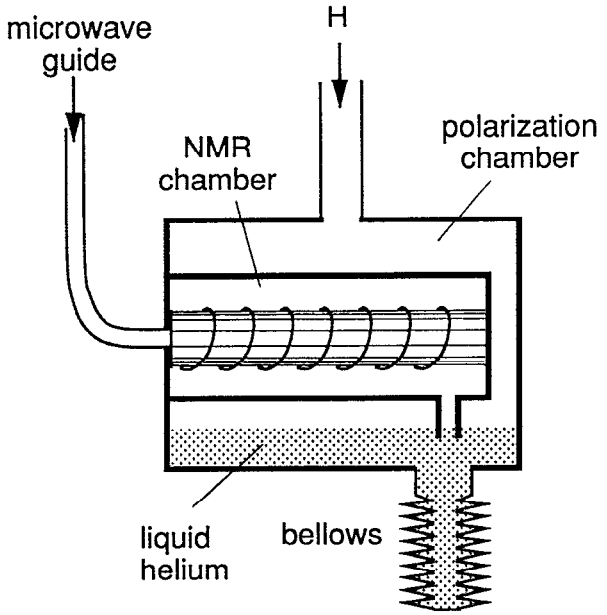

FIG. 1. A schematic diagram of the double chamber cell. The cell is placed inside a magnet. The liquid helium level in the cell is variable.

molecules inside the NMR chamber are detected by a pulse NMR spectrometer. The sensitivity of the spectrometer is 10^{14} fully polarized protons, limited by the background protons.[13] The waveguide on the side of the NMR chamber allows the illumination of the NMR chamber with 187 GHz microwaves, which is the electron spin resonance (ESR) frequency at 6.7 tesla. The ESR is used in one of the two experiments described below to control the recombination channel and rate.

Experiment A. In this experiment, a qualitative observation of the nonstatistical ortho–para composition is obtained by keeping the helium level valve open and filling the cell with the atomic beam continuously for about six hours. In the six hour period, about 2×10^{19} atoms are recombined in the cell. Comparing the NMR signal amplitudes before and after the filling, an increase equivalent to 5×10^{17} ortho molecules are detected. Assuming that 12% (surface ratio of the two chambers) of the recombination occurs in the NMR chamber, the ortho–para ratio of the newly formed molecules is about 20%. This relatively simple experiment confirms that hydrogen produced by recombination at low temperatures has nonstatistical ortho–para composition.

Experiment B. In this experiment, the following procedure is adopted: (1) raise the cell temperature to 77 K to bake out the hydrogen molecules accumulated in the cell in previous experiments; (2) fill the cell with the atom beam with the helium level valve closed; (3) turn off the beam allowing the gas to self-polarize[14] in the polarization chamber. Typically, a gas with density of 1.6×10^{16}/cc and polarization close to 100% is accumulated in the polarization chamber; (4) open the helium level value; (5) turn on the ESR radiation which is preadjusted to drive the transition of **b** state to **c** state at an average rate of 10^{16} atoms/s; (6)

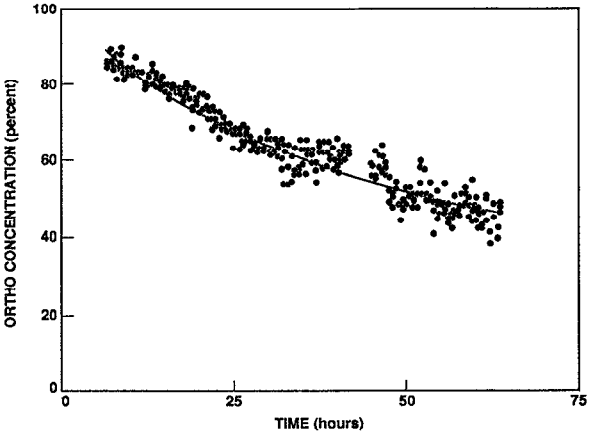

FIG. 2. Ortho concentration via time curve. The solid line is fitting of the data to $X=X_0/kX_0t+1$, with $X_0=0.99(2)$ and $K=0.019(1)$ (per hour).

collect NMR data. The above procedure ensures that molecules detected by the NMR spectrometer are newly formed and the recombination occurs dominantly between atoms with the same nuclear spin polarization (the **c** state is a mixing state). In the experimental field of 6.7 tesla, the mixing angle is 3.8×10^{-3}. Neglecting the small admixture, the **c** state has the same nuclear spin as the **b** state. In addition, since the recombination rate for the polarized gas is very low[10] and the ESR radiation is confined in the NMR chamber, most of the polarized atoms (2×10^{17}) recombine in the NMR chamber. The NMR data are used to derive the ortho–para ratio of the newly formed molecular hydrogen in the following three methods.

Method A. Measurement of the spin relaxation time constant. Previous work on solid hydrogen[15] has demonstrated that the spin relaxation time constant, T_1, is sensitively dependent on the ortho–para ratio. In fact, for high ortho concentration solid, $X>0.56$, it can be described by,

$$T_1=AX^4T^{-1}e^{B/T}, \tag{1}$$

where $A=1.0(3)$ minute, $B=0.4(1.8X-1)$. The measured T_1 is 11(1) minutes at 0.3 K. Assuming that the molecules are in regular solid phase the derived ortho concentration is near 100%.

Method B. Measurement of the ortho–para conversion rate. The ortho–para conversion rate of solid hydrogen can be described by,[15]

$$X(t)=\frac{X(0)}{kX(0)t+1}, \tag{2}$$

where $X(t)$ is the ortho concentration, k is a constant, and $t=0$ corresponds to the time of the recombination. Note that the recombination is completed in less than 10 s, a much shorter time scale than the conversion process, allowing us to neglect the duration of the recombination process. Figure 2 shows a direct fitting of the amplitudes of the NMR free induction decay to Eq. (2), with k and $X(0)$ as the fitting parameters. The conversion rate constant obtained is 0.019(1) per hour, in good agreement

with previous work of 0.0190(5) per hour,[12] and the initial ortho concentration obtained is 99 (+ 1/ − 2) percent.

Method C. Absolute calibration of the signal amplitude. Since the amplitude of the NMR free induction decay is proportional to the total amount of ortho hydrogen in the NMR chamber, the ortho–para ratio can be directly obtained from the signal amplitude and the determination of the total amount of hydrogen in the NMR chamber. This method requires a good calibration of the NMR spectrometer. The calibration is performed at 77 K with molecular hydrogen gas. The largest uncertainty of this method is the uncertainty of the filling factor for the solid hydrogen. Assuming that the solid hydrogen uniformly covers the chamber surface, we estimate that the filling factor is about 4 ± 1 times higher for the solid than for the calibration gas. This results in an ortho concentration of the recombined hydrogen of 85 (+ 15/ − 21) percent, consistent with methods A and B.

Note that there are about 10^{17} molecules produced in each fill. The molecules distribute on the surface of the NMR chamber, each fill producing a sample about five monolayers thick if the distribution were completely uniform. Since no surface effects are observed,[13] we use a bulk sample approximation for the analysis. The good agreement of the three independent methods also justifies using Eq. (1) and Eq. (2) to derive the ortho–para ratio for the samples.

We are not aware of any theory of two body recombination on a liquid helium surface. Assuming that the model proposed by Schwartz and Le Roy[3] for recombination of physisorbed atoms on Xe crystals can be extended for a liquid helium surface, one would expect that nuclear spin polarized atoms only recombine into ortho hydrogen, as we observed in experiment B. Furthermore, any ortho–para conversion process would reduce the ortho concentration in experiment B. The very high ortho concentration observed suggests that there is no ortho–para conversion until the molecules freeze into solid. In other words, we finally have a system which is suitable for detailed comparison between experimental results and theoretical calculations.

In conclusion, we have observed nonstatistical ortho–para ratio in hydrogen recombination at temperature below 1 K and demonstrated that there is no ortho–para conversion during the vibrational relaxation process. Although no specific theory has been developed for the recombination process of the described experiments, the experimental results can be understood based on the orbiting resonance model for recombination of physisorbed atoms. We suggest that rigid tests of various recombination theories could be carried out under similar experimental conditions. It is interesting to notice that hydrogen recombination is probably the simplest chemical reaction, yet many interesting questions remain unanswered. We hope that knowledge accumulated in recent years, especially techniques of manipulating large amount polarized hydrogen atoms at low temperatures, can help to improve our understanding of atomic recombination process.

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