

## Cold Collision Frequency Shift in Two-Dimensional Atomic Hydrogen

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(Received 2 October 2006; published 24 January 2007)

We report a measurement of the cold collision frequency shift in atomic hydrogen gas adsorbed on the surface of superfluid  $^4\text{He}$  at  $T \lesssim 90$  mK. Using two-photon electron and nuclear magnetic resonance in 4.6 T field we separate the resonance line shifts due to the dipolar and exchange interactions, both proportional to surface density  $\sigma$ . We find the clock shift  $\Delta\nu_c = -1.0(1) \times 10^{-7} \text{ Hz cm}^{-2} \times \sigma$ , which is about 100 times smaller than the value predicted by the mean field theory and known scattering lengths in the three-dimensional case.

DOI: [10.1103/PhysRevLett.98.043004](https://doi.org/10.1103/PhysRevLett.98.043004)

PACS numbers: 32.70.Jz, 32.30.Dx, 32.80.Cy, 67.65.+z

Elastic collisions between atoms play an important role in the physics of quantum gases. At low enough temperatures, when the thermal de Broglie wavelength  $\Lambda_{\text{th}} = (2\pi\hbar^2/mk_B T)^{-1/2}$  exceeds the range of the interaction potential, one enters the cold collision regime. In this case the effect of collisions can be easily interpreted and leads to a shift of the resonance lines known as cold collision or clock shift. This phenomenon puts severe limitations on the precision of atomic clocks [1]. The cold collision frequency shift of the  $1S$ - $2S$  transition in three-dimensional (3D) atomic hydrogen gas [2] has been used to detect the formation of the Bose-Einstein condensate [3]. Recently, the studies of collisions in quantum degenerate gases of reduced dimensionality [4,5] attracted considerable interest, and novel phenomena like modified interaction properties have been predicted [6].

The interaction potentials between two hydrogen atoms are well described by theory and allow accurate calculations of collisional cross sections [7,8]. However, serious discrepancies between the theory and experimental studies of collisions of hydrogen atoms in the ground electronic state remain to date [8,9]. Mainly due to their application to a hydrogen maser, the experiments were performed in nearly zero field. In this case the frequency shifts depend in a complicated way on the occupations of the hyperfine states of the colliding atoms which are nearly equal in thermal equilibrium even at the lowest temperatures of 0.5 K. This complication will be eliminated in a strong magnetic field when one can easily realize a situation of electron and nuclear polarized gas ( $\text{H}\downarrow\downarrow$ ), with >99% of atoms being in a single hyperfine state [10]. In this case broadening of the resonance lines due to field inhomogeneities makes precise spectroscopic measurements difficult and it requires much higher densities of the gas to discern collisional shifts. The problem can be solved in atomic hydrogen gas adsorbed on the surface of helium film. The surface binding potential effectively compresses atoms, strongly increasing the collision rate and the interaction energy.

Relatively large (up to 5 G) shifts of the electron spin resonance (ESR) lines of the adsorbed atoms from that of

the 3D gas have been observed [11,12]. The shifts are proportional to the surface density  $\sigma$  and anisotropic with respect to the orientation of the surface in the polarizing magnetic field, in fair agreement with calculations of the internal dipolar fields in the 2D gas [11]. A possibility of the clock shift was not considered, as it was believed that the shift may not appear due to a coherent interaction of the atoms with the rf excitation so that the interaction in collisions always occurs via triplet potential. Later the influence of coherence has been clarified in experiments with cold bosonic and fermionic alkali vapors [13,14]. It has been proved [14] that the interaction of rf excitation with an atomic system is always coherent and the clock shift does not depend on the level of coherence between the internal states.

Here we present the first measurement of the exchange and dipolar contributions to the interaction energy in  $\text{H}\downarrow\downarrow$  gas adsorbed on the surface of superfluid helium. In addition to the ESR method used previously [15], we employed nuclear magnetic resonance (NMR), for which there is no clock shift because atoms in the initial and final states interact via the same triplet potential. We carried out a coherent two-photon study of the resonances as well as a separate measurement of ESR and NMR transitions in the sample of the same surface density. Results of the measurements agree well with each other.

There is a single bound state for  $\text{H}\downarrow\downarrow$  on a helium surface with the adsorption energy of  $E_a = 1.14(1)$  K. Because of the low mass  $m$  and low  $E_a$  delocalization of  $\text{H}\downarrow$  in the out-of-plane direction,  $l = \hbar/\sqrt{2E_a m} \approx 0.5$  nm largely exceeds the three-dimensional  $s$ -wave scattering length  $a_l \approx 72$  pm. Therefore, in terms of collisions the gas may be considered as three-dimensional. In the limit  $l \gg a_l$  the interaction energy per particle of such a quasi-2D gas can be evaluated using a scaling approach with the effective bulk density  $n \approx \sigma/l$  [6,16]:

$$E_i \approx \frac{4\pi\hbar^2 g a_l \sigma}{ml}, \quad (1)$$

where  $g$  is the two body correlator equal to 2 in the thermal, noncondensed gas of bosons [13,14]. Densities exceeding

$\sigma = 10^{12} \text{ cm}^{-2}$  are easily accessible by the thermal compression method [15]. Then, the mean field interaction energy is of the same order as in the bulk gas of density  $n \sim \sigma/l \approx 2 \times 10^{19} \text{ cm}^{-3}$ , 10 orders of magnitude larger than in a typical hydrogen maser.

As described in Ref. [15], two-dimensional samples of atomic hydrogen gas are created on a cold spot (CS) of the sample cell (SC) [Fig. 1(a)]. In this work we keep the hydrogen dissociator continuously filling the SC. To reduce the flux of atoms in the highly reactive state  $a$  [Fig. 1(b)] we feed the atoms into the SC through a beam polarizer. It is a separate chamber with a surface area of  $\sim 10 \text{ cm}^2$ , located in a reduced magnetic field ( $\approx 3.0 \text{ T}$ ) at a temperature of 100–130 mK, optimized for preferential recombination of the  $a$  state. Varying the temperatures of the SC and CS and the dissociator power we get a steady state with bulk  $\text{H}\downarrow\downarrow$  density  $n \leq 10^{13} \text{ cm}^{-3}$  in the SC and surface density  $\sigma = 10^{11} - 3.5 \times 10^{12} \text{ cm}^{-2}$  on the CS. The main advantage of this method is a long term stability of the surface density and temperature, required for accurate spectroscopic studies. In addition to the 128 GHz Fabry-Perot ESR resonator, we have an NMR resonator in the vicinity of the CS [Fig. 1(a)]. It is a helix (HR) resonant at 909 MHz, close to the  $a$ - $b$  nuclear spin transition [Fig. 1(b)] in the field of  $B_0 \approx 4.6 \text{ T}$ .

We performed continuous wave ESR on bulk and surface  $\text{H}\downarrow\downarrow$  sweeping the magnetic field across the  $b$ - $c$  transition at a fixed frequency  $\nu_{bc}$ . Both absorption and dispersion components of the signal are detected simultaneously by a cryogenic millimeter-wave receiver [17]. The ESR excitation power is always kept low enough to avoid distortions of the resonance lines [12]. A typical  $b$ - $c$  spectrum shown in Fig. 2(a) contains two peaks. One originates from free atoms in the bulk gas, and the other from adsorbed atoms. The distance between the peaks has been found to be proportional to the surface density [11,18]. The much weaker  $a$ - $b$  transition was studied calorimetrically with a miniature bolometer utilizing the

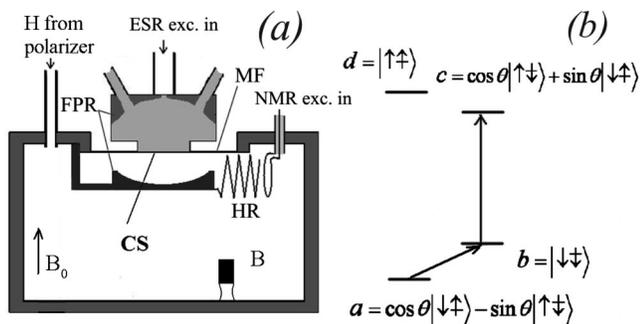


FIG. 1. (a) Schematic drawing of the sample cell: FPR, Fabry-Perot ESR resonator; HR, helical NMR resonator; MF, Mylar foil; B, bolometer; CS, cold spot. (b) Hyperfine level diagram for a hydrogen atom in a strong magnetic field. Arrows denote electron and nuclear spin projections.

large recombination energy released after the transfer of  $\text{H}\downarrow\downarrow$  atoms to the reactive  $a$  state [19].

We employed the electron-nuclear double resonance (ENDOR) method to study adsorbed  $\text{H}\downarrow\downarrow$  gas. The sweep field  $h$  of the ESR spectrometer was stopped in the center of the  $b$ - $c$  transition for the surface atoms [dashed line in Fig. 2(a)], and then rf excitation was applied to the NMR helix. By sweeping the rf frequency we detect the  $a$ - $b$  transition through a change in the ESR signal [Fig. 2(b)], which can be caused by two effects: (i) destruction of the  $b$ -state population on the CS due to the transfer of atoms to the state  $a$  with subsequent recombination; (ii) coherent two-photon excitation of three level system.

Both types of the double resonance were observed in the experiments. At high enough temperatures ( $\geq 100 \text{ mK}$ ) a rapid exchange with the bulk gas destroys the coherence of the adsorbed atoms with the rf excitation and case (i) is realized. Absorption and dispersion components of the ESR signal are decreased due to the pulling of the ESR surface line to the left caused by the  $b$ -state destruction. This leads to a broad ( $\approx 600 \text{ Hz}$ ) width of the ENDOR line defined by the magnetic field inhomogeneity over the CS. At lower temperatures the surface residence time becomes long enough to maintain coherence and a second narrow (120 Hz) feature appears in the middle of the ENDOR spectrum, which we attribute to case (ii). The incoherent line becomes weaker at lower surface temperatures and disappears completely at  $\approx 80 \text{ mK}$ , leaving the two-photon line only [Fig. 2(b)]. The two-photon absorption component has a “dispersive” line shape. The absorption change is driven by the rf field and depends on the detuning, the effect known in quantum optics as electromagnetically induced transparency [20]. We verified by changing the rf power that the two-photon resonances are not influenced by the nonlinear effects caused by too strong excitation. The bolometer does not detect any extra recombination heat, implying that all atoms remain in the  $b$  state, as in the effect of the coherent population trapping [20]. These quantum optics effects are for the first time observed in magnetic resonance and require further studies. We used

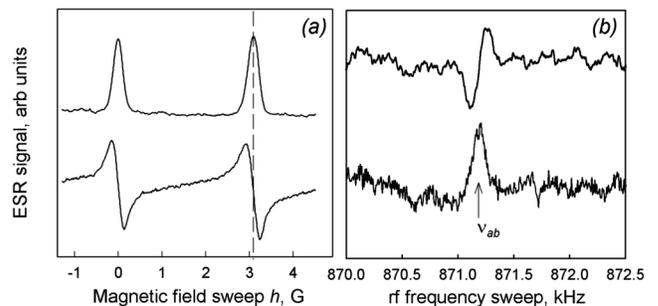


FIG. 2. Observed ESR and two-photon spectra. Upper traces, absorption; lower traces, dispersion. (a) Bulk gas (left peak) and surface (right peak) ESR lines; (b) two-photon resonances observed at lowest surface temperature of  $\approx 70 \text{ mK}$ .

the two-photon resonance to measure the  $a$ - $b$  transition frequency as a function of surface density on the CS.

There are two reasons for the density dependent shift of the resonance lines. First is the average dipolar field  $B_d$  in the plane of the adsorbed atoms, which has negative sign for the surface perpendicular to the polarizing field. Second is the clock shift, following from Eq. (1)

$$\Delta\nu_c = \frac{2\hbar g}{ml}(a_s - a_t)\sigma \equiv \kappa\sigma, \quad (2)$$

where  $a_t$  and  $a_s$  are the triplet and singlet  $s$ -wave scattering lengths. In addition, there is also a density independent frequency shift due to the change  $\Delta A_w$  of the hyperfine constant  $A$  caused by the interaction of the adsorbed atoms with the substrate, known as the wall shift [21]. Taking the above mentioned shifts into account, the resonance condition for the  $b$ - $c$  transition of atoms adsorbed on the surface can be written in the strong field approximation as

$$\nu_{bc} = \frac{\gamma_e}{2\pi}(B_0 + h + B_d) - \frac{A + \Delta A_w}{2} + \Delta\nu_c, \quad (3)$$

where  $h$  is the sweep field and  $B_0$  is the main polarizing field. We adjust the latter so that the resonance line of the bulk gas is observed at  $h = 0$ , i.e.,  $\nu_{bc} = \gamma_e B_0/2\pi - A/2$ . According to Eq. (3) the position of the surface ESR line  $h_e = \alpha\sigma$  depends on the internal dipolar field  $B_d$  and the clock shift  $\Delta\nu_c$ , both proportional to  $\sigma$ . The clock shift for the  $a$ - $b$  transition is absent and the resonance equation is

$$\nu_{ab} = \frac{\gamma_n}{2\pi}(B_0 + h + B_d) + \frac{A + \Delta A_w}{2}. \quad (4)$$

In the two-photon experiment we measure  $\nu_{ab}$  with the sweep field being fixed to the surface resonance, i.e.,  $h = h_e$ . Then, denoting the resonance frequency of the  $a$ - $b$  transition for the bulk gas as  $\nu_{ab}^0 \equiv \gamma_n B_0/2\pi + A/2$  and neglecting  $\gamma_n/\gamma_e$  with respect to unity, we obtain from Eqs. (2)–(4)

$$\nu_{ab} - \nu_{ab}^0 = \frac{\Delta A_w}{2} - \frac{\gamma_n}{\gamma_e} \Delta\nu_c = \frac{\Delta A_w}{2} - \frac{\gamma_n}{\gamma_e} \frac{\kappa}{\alpha} h_e. \quad (5)$$

In Fig. 3 we plot the frequency difference  $\nu_{ab} - \nu_{ab}^0$  as a function of the ESR line shift  $h_e$ . Fitting the data to a straight line we obtain the wall shift  $\Delta A_w = -45.58(4)$  kHz and the clock shift  $\Delta\nu_c = -1.0(1) \times 10^{-6}$  Hz cm<sup>2</sup>  $\times$   $\sigma$ , where we used known relation  $h_e = \alpha\sigma$  with  $\alpha = 1.1(1) \times 10^{-12}$  G cm<sup>2</sup> [18]. The latter is the main reason for the 10% systematic error of the clock shift which is much larger than the other errors marked with bars in Fig. 3. The contribution of the clock shift is  $\Delta B_c = 2\pi\Delta\nu_c/\gamma_e = 3.6(4) \times 10^{-13}$  G cm<sup>2</sup>  $\times$   $\sigma$ , which comprises approximately one-third of the total observed ESR line shift  $\Delta B$ , the rest being due to the internal dipolar field  $B_d = 7.4(7) \times 10^{-13}$  G cm<sup>2</sup>  $\times$   $\sigma$ .

The clock shift can be measured by a somewhat different method. We apply both ESR and NMR excitations simul-

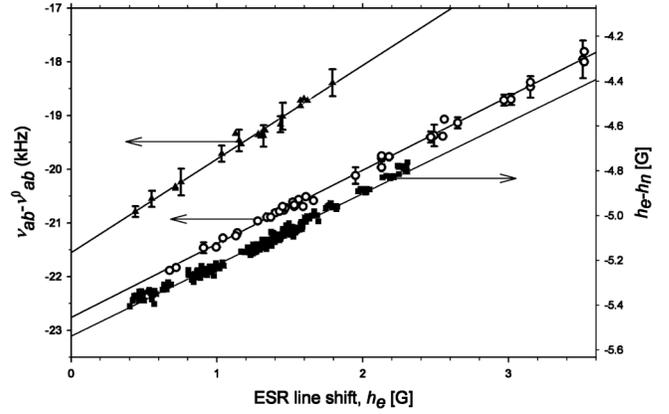


FIG. 3. Frequency shift of the  $a$ - $b$  transition as a function of the ESR line shift obtained by the two-photon method: (○) pure  $^4\text{He}$  film, (▲)  $^3\text{He}$ - $^4\text{He}$  mixture, (■) difference of the ESR and NMR resonance line positions measured at fixed frequencies  $\nu_{bc}$  and  $\nu_{ab}$ . Solid lines are linear fits to the data.

taneously, with the latter tuned to the resonance value of the free atoms in the field  $B_0$ ; i.e., we set  $\nu_{ab} = \nu_{ab}^0$ . Sweeping the magnetic field we detect both  $b$ - $c$  and  $a$ - $b$  transitions by the bolometer and study their positions  $h_e$  and  $h_n$  as functions of the surface density, or the ESR line shift  $h_e$ . If the density is uniform over the CS, the difference of the surface line positions is proportional to the clock shift. For these experimental conditions we get from Eqs. (3) and (4)

$$\frac{\gamma_n}{2\pi}(h_n - h_e) = \frac{\Delta A_w}{2} - \frac{\gamma_n}{\gamma_e} \Delta\nu_c = \frac{\Delta A_w}{2} - \frac{\gamma_n}{\gamma_e} \frac{\kappa}{\alpha} h_e. \quad (6)$$

Data for such an experiment are also plotted in Fig. 3. The points follow a straight line with the same (within  $\approx 3\%$ ) slope as the two-photon data and shifted down by  $\approx 0.1$  G, which can be explained by the magnetic field difference between the edge and the center of the CS. The ESR transition is effectively excited in the  $\sim 1$  mm diam field maximum in the CS center. The rf field is larger near the CS edge, which is closer to the HR. Therefore, the NMR and ESR probe the adsorbed gas in slightly different positions. This makes a major difference with the two-photon measurement where ESR and NMR photons are absorbed *simultaneously* by the atoms located in the CS center. Good agreement with the two-photon data can be considered as a confirmation of the uniform density over the cold spot and of the reliability of the clock shift measurement.

Although we cannot directly measure the surface gas temperature, its upper limit of 70–90 mK can be estimated from the adsorption isotherm assuming dynamic equilibrium between the bulk and surface gases [18]. The lower bound is set by the temperature of the  $^3\text{He}$ - $^4\text{He}$  mixture cooling the CS, which was varied in the range 50–90 mK. We have not observed any influence of the surface temperature on  $\nu_{ab}$  in this temperature range.

We compare our data for the wall shift with the result  $\Delta A_w = -44.8(10)$  kHz of Ref. [22] measured for the surface parallel to the magnetic field,  $-43.2(1)$  kHz for the surface having no preferential orientation [23] and  $\Delta A_w = -49$  kHz in zero field [24]. The agreement is good, especially taking into account the very different methods used in these measurements.

Using our data for the clock shift and Eq. (3) we obtain the difference of the scattering lengths  $a_t - a_s = 0.42(4)$  pm. The theoretical values of  $a_t = 72$  pm and  $a_s = 17$  pm [25] give a much larger difference  $a_t - a_s = 55$  pm. Our result may be interpreted as the singlet scattering length being nearly equal to the triplet one, i.e., 4 times larger than predicted. The authors of Ref. [25] pointed out that their calculation for  $a_s$  is sensitive to nonadiabatic corrections. But the  $\sim 5\%$  difference they obtained completely neglecting these corrections cannot explain the value of  $a_s$  extracted from our data.

The very small value of the clock shift found in this work can be due to the change of the collision properties in the adsorbed phase. To verify such possibility we attempted to modify the interaction of the adsorbed atoms with the film by admixing some small amount of  $^3\text{He}$ . The presence of  $^3\text{He}$  on the surface reduces the adsorption energy and increases delocalization  $l$  of the adsorbed atoms [26]. This should lead to a  $\sim l^{-3}$  reduction of the wall shift [21] and to a  $\sim l^{-1}$  reduction of the clock shift [Eq. (2)]. We condensed  $1.5(5) \times 10^{16}$  of  $^3\text{He}$  atoms into the SC, which would provide a maximum surface coverage of  $1.5 \times 10^{14} \text{ cm}^{-2}$ , assuming that all the  $^3\text{He}$  atoms are evenly distributed on the surface. With this coverage the adsorption energy decreases to  $\approx 0.9$  K [26] and the corresponding increase of  $l$  is  $\leq 10\%$ . The actual concentration of  $^3\text{He}$  on the CS is difficult to estimate since it strongly depends on the temperature profile inside the SC. However, we believe that the concentration did not change in the experiment, since we observed no difference of  $\nu_{ab}$  at different SC temperatures (70–90 mK) and same  $h_e$ . In the measurements (Fig. 3) we found an  $\approx 6\%$  decrease of the wall shift implying a larger  $l$ , i.e., in qualitative agreement with the expectation. The change of the data slope, on the contrary to the prediction of Eq. (1), corresponds to a 25% increase of the clock shift. Unfortunately, we were not able to increase  $l$  further. Adding more  $^3\text{He}$  created instabilities of the helium level in the SC and no reliable data could be taken.

The observed increase of the clock shift at larger  $l$  is in line with our previous measurements of the surface three-body recombination rate constant [18]. The rate constant found in that work has also revealed serious discrepancy with the estimate based on the scaling approach.

In conclusion, we have measured the clock shift of atomic hydrogen gas adsorbed on the surface of helium film. The observed value is  $\sim 100$  times smaller than

evaluated on the basis of the mean field theory applied to a quasi-2D gas and existing data on the scattering lengths in the 3D case. A small increase of the delocalization length of adsorbed atoms leads to a substantial increase in the clock shift. This may indicate that the strong reduction of the clock shift is a feature of the reduced dimensionality. A measurement of the clock shift in the 3D case at high magnetic field would help one to understand the nature of the discrepancy. The two-photon magnetic resonance method realized in this work opens up new possibilities for studying the coherent interaction of the rf excitation with the quantum degenerate gas of H.

This work was supported by the Academy of Finland Grant No. 206109 and the Wihuri Foundation. We also wish to thank K.-A. Suominen, S. Jaakkola, and M. Hayden for valuable discussions.

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