Adsorption and Two-Body Recombination of Atomic Hydrogen on ^{3}He-^{4}He Mixture Films

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We present the first systematic measurement of the binding energy E_a of hydrogen atoms to the surface of saturated ^{3}He-^{4}He mixture films at temperatures 70–400 mK. E_a is found to decrease almost linearly from 1.14(1) K down to 0.39(1) K, when the population of the ground surface state of ^{3}He grows from zero to 6×10^{14} cm^{-2}, yielding the value $1.2(1) \times 10^{-15}$ K cm^2 for the mean-field parameter of H-^{3}He interaction in 2D. Measuring by ESR the rate constants K_{aa} and K_{ab} for second-order recombination of hydrogen atoms in hyperfine states a and b, we find the ratio K_{ab}/K_{aa} to be independent of the ^{3}He content and to grow with temperature.

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Two-dimensional (2D) Bose systems acquire growing interest since the observation of local coherence in the weakly interacting gas of hydrogen atoms adsorbed on a liquid ^{4}He surface [1]. We found that at high quantum degeneracy the probability of three-body surface recombination of H atoms is suppressed at least by a factor of 11(2). The phenomenon was attributed to the formation of a 2D quasicondensate (QC), a condensate with fluctuating phase. However, for an ideal gas three-body recombination in the condensate would be a factor of 3! less probable than in the noncondensate [2], and H-H interactions are expected to make the effect of QC on the local correlations even smaller [3]. Delocalization of the bound state wave function in the surface-normal direction [4] or many-body effects [5] may offer explanations for the observed suppression being larger than 3!. The addition of ^{3}He to ^{4}He is known [6,7] to weaken the binding of H atoms to the surface and thus to increase their delocalization. In order to elucidate the role of the delocalization we plan experiments with 2D H on ^{3}He-^{4}He mixtures. For that goal we need to know the binding strength as a function of the ^{3}He content.

In this paper we report on experiments where the binding of hydrogen to liquid helium is found to be tunable, as the adsorption energy E_a is observed to decrease almost linearly from 1.14(1) to 0.39(1) K when the ^{3}He coverage grows from zero to about one atomic layer. We have also studied two-body recombination of H atoms in their two lower hyperfine states a and b, since the probability of this process does not change upon the appearance of QC and thus serves as a reference for three-body recombination [1]. Our data unambiguously corroborate the prediction [8] that the recombination rate constant ratio K_{ab}/K_{aa} increases with temperature.

In our experiments ESR operating at 128 GHz (field $B = 4.57$ T) and NMR at 910 MHz have been employed, respectively, to measure and control the a and b state populations. The versatile combination of ESR and NMR provides well-defined conditions for studying different recombination processes. Moreover, the data analysis is simple and reliable. The ESR spectrometer has been calibrated calorimetrically with an estimated absolute accuracy of 10% and long-term stability of 2%. The minimum detectable density is about 2×10^{12} cm^{-3}.

The sample cell is a thick-walled cylinder made of high-purity OFHC copper with the ESR and NMR cavities annexed, respectively, to the side and top walls. The volume of H gas in the cell is $V = 4.5$ cm^3 and the area of the inner cell walls coated with helium film is $A = 22$ cm^2. The cell temperature T is measured with a RuO$_2$ thick-film resistor attached to the outer cell wall and calibrated against the ^{3}He melting curve with an absolute accuracy of 1 mK.

At the relatively low densities considered here the H gas both in 2D and in 3D is well described by Boltzmann statistics. The recombination of hydrogen atoms takes place in the adsorbed phase, whereas the large majority of atoms is in the bulk. Then the effective rate constant of the second-order decay of the bulk density is related to the intrinsic rate constant of two-body surface recombination by the relation [9]

$$K_{ij}^{\text{eff}} = \frac{A}{V} \lambda^2 \exp\left(\frac{2E_a}{kT}\right) K_{ij}, \tag{1}$$

where $\lambda = \sqrt{2\pi\hbar^2/mkT}$ is the thermal de Broglie wavelength, m is the hydrogen atomic mass, and subscripts i and j denote the hyperfine states. Therefore, by measuring the temperature dependence of K_{ij}^{eff} one can determine both E_a and K_{ij} as has been done for H on ^{4}He in many previous experiments [9]. In case of equally populated states a and b one has

$$\frac{dn_b}{dt} = \frac{dn_a}{dt} = -(K_{aa}^{\text{eff}} + K_{ab}^{\text{eff}}) n_b^2. \tag{2}$$

We apply rf power to the sample saturating the $b \leftrightarrow a$ NMR transition to continuously equalize the two populations. Being to a high accuracy linear in time, the measured $1/n_b$ gives $K^{\text{eff}} \equiv K_{aa}^{\text{eff}} + K_{ab}^{\text{eff}}$. Evolution of

$1/n_a$ observed in a separate experiment yields exactly the same values of $K^{\rm eff}$. In an experiment of another type short rf pulses resonant with the $b \rightarrow a$ transition are used to convert a small fraction of the otherwise b-state sample to the a state. From the lifetime $\tau = 1/K_{ab}^{\rm eff} n_b$ of a atoms we obtain $K_{ab}^{\rm eff}$ [10]. We believe that this procedure to determine $K_{aa}^{\rm eff}$ and $K_{ab}^{\rm eff}$ is more reliable than extraction of the rate constants from multiparameter nonlinear fits of the density decays to coupled rate equations.

The experiments are carried out at $T = 70$–400 mK for overall ^{3}He concentrations $c_3 = 0.1$, 1, 10, and 100 ppm, 0.1%, 1%, and 5% as well as for isotopically purified ^{4}He ($\lesssim 1$ ppb of ^{3}He) and commercial helium. The total amount of liquid helium in the cell, including the bellows system used to open and close the inlet, is 11 cm^3. The bellows are thermally pinned to the cell body only and are therefore at the same temperature. The middle section of the inlet tube coming from the dissociator ($\sim$0.6 K) is, similar to the cell, anchored to the mixing chamber (60–300 mK) of the dilution refrigerator. Also the tube is lined with a saturated helium film, but during the measurements its free surface area of 35 cm^2 accessible to ^{3}He is separated from the film in the cell. Unlike in many earlier experiments with ^{3}He-^{4}He mixture films, the area-to-volume ratio of liquid helium in our cell is relatively low, about 5 cm^{-1}, and thus for $c_3 \geqslant 0.1$ ppm the majority of ^{3}He atoms stays in the bulk at all temperatures of the measurements. Then the chemical potential of ^{3}He is mainly determined by the 3D fraction and neither the temperature inhomogeneity along the inlet tube nor the exact value of the area of the tube plays a significant role.

Figure 1 shows the temperature dependence of the ratio $K_{ab}^{\rm eff}/K_{aa}^{\rm eff}$ obtained in this work together with the results of Statt *et al.* [11]. In agreement with the theory of Greben *et al.* [8], but in contradiction with some earlier experimental results [9], the rate constant ratio grows with T. In fact, ab recombination produces only ortho-H$_2$ with odd angular momentum and consequently the atoms must overcome a centrifugal barrier [8]. The probability of such a process vanishes at $T = 0$. We also emphasize that, within experimental scatter, $K_{ab}^{\rm eff}/K_{aa}^{\rm eff}$ shows no systematic change upon addition of ^{3}He and is therefore averaged over all concentrations. The error bars in Fig. 1 represent standard deviation of the data.

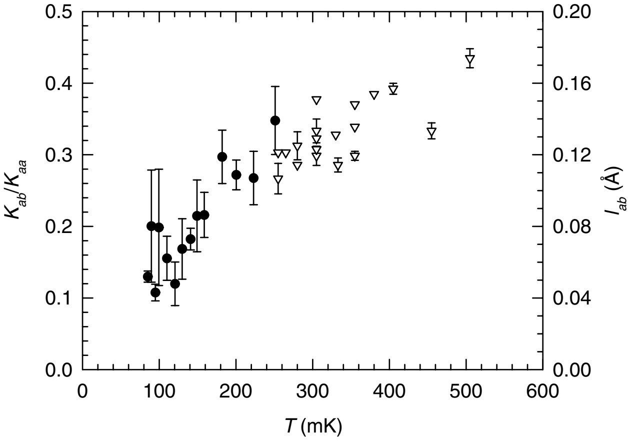

FIG. 1. Temperature dependence of the rate constant ratio K_{ab}/K_{aa} (left scale) and the ab recombination cross length l_{ab} (right scale) obtained in this work (•) and by Statt *et al.* [11] (▽).

In Fig. 2 the temperature dependence of $K_{aa}^{\rm eff}$ is presented for various ^{3}He concentrations and for commercial as well as isotopically pure ^{4}He. Following Ref. [8], we assume the cross length l_{aa} for aa surface recombination to be temperature independent. Then $K_{aa} = \overline{v} l_{aa} \varepsilon^2 \propto \sqrt{T}$, where $\varepsilon \simeq 2.53 \times 10^{-2}$ T$/B$ is the hyperfine mixing parameter and $\overline{v} = \sqrt{\pi k T/m}$ the relative thermal velocity in 2D. For H on pure ^{4}He, E_a does not vary with T. Then half of the slope of the $\ln(\frac{V}{A} K_{aa}^{\rm eff}/\lambda^2 \sqrt{T})$ versus $1/T$ line is $E_a = 1.14(1)$ K and the intercept gives $l_{aa} = 0.40(10)$ Å. For T-independent l_{aa} Fig. 1 may also be regarded as the temperature variation of the cross length l_{ab}.

In Fig. 2 the data also for $c_3 = 5\%$ fall on a straight line. Yet the ^{3}He surface coverage changes [12] and we cannot take E_a to be constant. Instead we assume, to the first approximation, that the cross length l_{aa} does not depend on ^{3}He content either. Then we determine E_a for each concentration and temperature from the measured $K_{aa}^{\rm eff}$ using Eq. (1) with l_{aa} fixed to its pure-^{4}He value. The results are shown in Fig. 3, from which one notices that the behavior of E_a resembles that of the surface tension

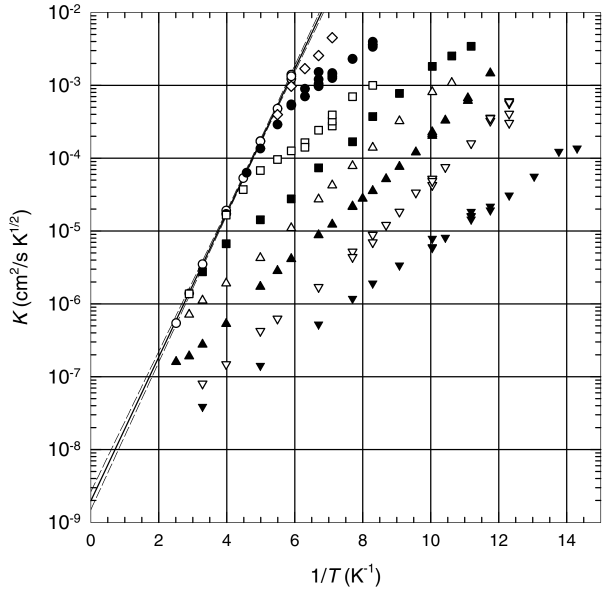

FIG. 2. The effective rate constant plotted as $K = \frac{V}{A} K_{aa}^{\rm eff}/\lambda^2 \sqrt{T}$ versus $1/T$ for H on isotopically pure (∘) and commercial (◇) ^{4}He, 0.1 (•), 1 (□), 10 (■), and 100 (△) ppm; 0.1% (▲), 1% (▽), and 5% (▼) of ^{3}He. Solid and dashed lines represent linear regression and its 99% confidence intervals, respectively, for pure ^{4}He.

of ^{3}He-^{4}He solutions [12]. It is well known that the latter originates from 2D ^{3}He bound to the surface of the liquid.

According to Pavloff and Treiner [13] there are at least two surface states of ^{3}He on bulk ^{4}He. The binding energies relative to the bulk liquid and the effective masses in zero coverage limit are $e_{s0} = 2.64$ K and $M_0 = 1.29m_3$ for the ground state and $e_{s1} = 0.81$ K and $M_1 = 1.6m_3$ for the excited state. Here m_3 denotes the bare mass of ^{3}He. The variations of these quantities with ^{3}He coverage are also given in Ref. [13]. In good agreement with Ref. [13] the occupation of the excited surface state at $n_{3s} \geq 3.5 \times 10^{14}$ cm^{-2} has been recently observed in an experiment [14]. Therefore, using the above values we may calculate the populations n_{3s0} and n_{3s1} of both ^{3}He surface states for all concentrations c_3 and temperatures.

Figure 4 presents the hydrogen adsorption energy E_a as a function of n_{3s0}. The population of the excited state is also shown for reference. The decrease of E_a is obviously due to interaction of adsorbed H atoms with the surface states of ^{3}He. The slope of the E_a vs n_{3s0} line is the effective mean-field parameter $U_{30} = 1.2(1) \times 10^{-15}$ K cm^2. It does not seem to change at $n_{3s0} = 3.5 \times 10^{14}$ cm^{-2}, where the occupation of the excited state begins. This points to the interaction of H with the excited state of ^{3}He being weak, $U_{31} \ll U_{30}$.

Despite the above assumption we can consider two reasons why the cross length l_{aa} might change upon addition of ^{3}He. First, helium atoms play the role of the third body in hydrogen recombination. Clearly, the probability of collisions with helium increases in the presence of 2D ^{3}He due to a larger overlap of the wave functions. On the other hand, the surface-normal delocalization length $d = \hbar/\sqrt{2E_a m}$ of the hydrogen wave function grows with n_{3s0}. The latter reason causes the H-H recombination cross length $l_{aa} \propto 1/d \propto \sqrt{E_a}$ [2] to decrease with growing n_{3s0}. Even if the two effects do not completely cancel each other, our results for E_a remain practically unchanged because the variation of l_{aa} is important when both T and n_{3s0} are high, i.e., for very few data points only (cf. Figs. 2 and 4).

Confiding in our techniques to monitor and manipulate the hyperfine level populations in our H samples we believe that the present work sheds new light on the long-standing discrepancies between numerous previous determinations of E_a. Unknown hyperfine polarization is one of several possible sources of systematic error in the determination of E_a listed by Godfried *et al.* [15]. Another source is ^{3}He impurity and from Fig. 2 it is obvious that even a very small amount of ^{3}He can considerably change the average slope typically taken as $2E_a$. This would also affect the value of the recombination cross length l_{aa} extracted from the T dependence of the effective rate constants under the assumption of constant E_a. It is likely that in several earlier studies "pure" ^{4}He was, if not explicitly stated otherwise, just nonpurified commercial helium with unknown ^{3}He contamination. This is not a problem at $T \gtrsim 200$ mK (cf. Fig. 3) or if there is no bulk helium in the sample cell but a saturated film only. In the latter case the area-to-volume ratio is so large, about 10^5 cm^{-1}, that the ^{3}He surface coverage is at most 10^{-4} monolayers even for $c_3 =$ 1 ppm which is at least an order of magnitude larger than the natural abundance.

The ESR results of Statt *et al.* [11] for K_{aa}^{eff} and K_{ab}^{eff} at $T = 250$–500 mK agree quite well with ours scaled to the same magnetic field and A/V ratio. Morrow *et al.* [16] measured the zero field NMR frequency shift for H above 200 mK and found, as coupled fitting parameters, the binding energy $E_a = 1.15(5)$ K and the wall shift $\Delta_s = -49(2)$ kHz. Later Pollack *et al.* [17] observed simultaneously surface and bulk H atoms by NMR and directly found $\Delta_s = 43.2(10)$ kHz, as extrapolated to $B = 0$. Shinkoda and Hardy [18] used ESR for a direct

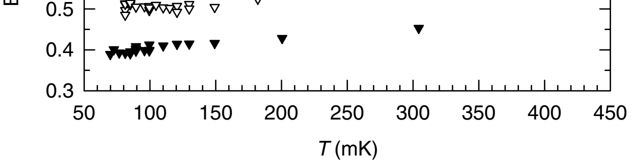

FIG. 3. Temperature dependence of E_a for the same ^{3}He concentrations as in Fig. 2. The lines are the average value and confidence intervals for E_a of H on pure ^{4}He.

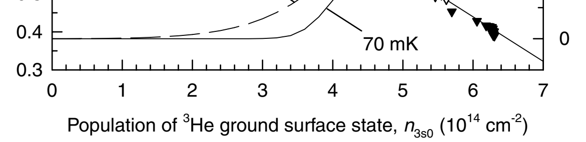

FIG. 4. Dependence of H binding energy on ^{3}He surface density for the same concentrations as in Figs. 2 and 3. Curved lines are populations of the excited surface state of ^{3}He calculated for $T = 70$ and 300 mK.

detection of H atoms at the surface of ^{4}He. They had several cm^3 of liquid helium in the sample cell and measured the apparent E_a to increase from 0.75 to 1.03 K when T increased from 70 to 140 mK. This observation is just an extrapolation of our results for commercial helium (open diamonds in Fig. 3) to lower temperatures. Associating the results of Refs. [11,16–18], our value $E_a = 1.14(1)$ K for H on isotopically pure ^{4}He and from the theoretical prediction [8] with each other we gather strong support for the assumption of a temperature independent cross length l_{aa}. It should also be added that another potential pitfall in the E_a determination was avoided in this work by extending the measurements over a wide enough temperature range.

It is worth comparing the lowest value of the binding energy, $E_a = 0.39(1)$ K, measured in our experiment for $c_3 = 5\%$ with earlier results extracted from pressure measurements of density decays. The latter are 0.34(3) K for ^{3}He and ^{4}He mixed in proportions from 2:1 to 6:1 [6] and 0.39(1) K for pure ^{3}He [7].

The linear decrease of E_a with n_{3s} shows that H-^{3}He interaction is well described by the mean-field approximation. This is an important observation as such, but it seems to disagree with the following arguments. Typically the Fermi energy of 2D ^{3}He gas is much higher than temperature, $e_{0F} = \pi\hbar^2 n_{3s0}/2M_0 \gg kT$. Then elastic H-^{3}He collisions in 2D responsible for decreasing E_a involve ^{3}He quasiparticles from the Fermi level only. Their density, of order $n_{3s0}T/e_F = 2M_0T/\pi\hbar^2$, is independent of n_{3s0}. On the other hand, the Fermi level rises with n_{3s0}, the corresponding wave function expands in the surface-normal direction [13], and overlaps more with adsorbed hydrogen.

The present measurements of hydrogen adsorption energy E_a as a function of ^{3}He surface density offer a unique opportunity to perform experiments on a degenerate 2D Bose gas with tunable interaction strength which scales as $\sqrt{E_a}$. As such, the quantum system of a degenerate 2D Bose gas (H) coupled with a degenerate 2D Fermi gas (^{3}He) would also be an interesting object to study. The mean-field parameter U_{30} obtained here should play a key role in the behavior of that system.

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