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. $E_a$ 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 $6 \times 10^{14}$ 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. The experiments were carried out with overall $^3$He concentrations ranging from 0.1 ppm to 5 % as well as with commercial and isotopically purified $^4$He at temperatures 70...400 mK. 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 liquid helium 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), 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 [3] and H-H interactions are expected to make the effect of QC on local correlations even smaller [4]. The difference between the experimental and theoretical suppression factors has been accounted for on the basis of increasing delocalization of the bound state wave function in surface-normal direction with increasing density of the 2D hydrogen [5, 6]. Thus it seems desirable to experimentally separate the roles of local coherence and delocalization. Experiments with 2D hydrogen on $^3$He-$^4$He mixtures are anticipated to give such an opportunity by virtue of weaker [7, 8].

In this paper we report on experiments where the binding energy $E_a$ of hydrogen to liquid helium has been measured as a function of $^3$He surface coverage. $E_a$ is found to decrease almost linearly from 1.14(1) K 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 reference for three-body recombination [4]. Our data unambiguously corroborates the prediction [9] 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 $2 \times 10^{12}$ cm$^{-3}$.

The volume of H gas in the sample cell, including the annexed ESR and NMR cavities, is $V = 4.5$ cm$^3$. The area of 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 [10]

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

where $\lambda = \sqrt{2\hbar^2/m_kT}$ 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 $K_{ij}^{\text{eff}}$ one can determine both $E_a$ and $K_{ij}$ as has been done for H on $^4$He in...
that, within experimental scatter, \( K_{ab}/K_{aa} \) (left scale) and the ab recombination crosslength \( l_{ab} \) (right scale) obtained in this work (●) and by Statt et al. [10] (∇).

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 [9], the measured \( 1/n_b \) gives \( K_{aa}^{\text{eff}} + K_{ab}^{\text{eff}} \). Evolution of \( 1/n_a \) observed in a separate experiment yields exactly the same values of \( K_{ab}^{\text{eff}} \). 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 \( \tau = 1/K_{ab}^{\text{eff}}n_b \) of a-atoms we obtain \( K_{ab}^{\text{eff}} \). We believe that this procedure to determine \( K_{aa}^{\text{eff}} \) and \( K_{ab}^{\text{eff}} \) is more reliable than extraction of the rate constants from multi-parameter non-linear fits of the density decays to coupled rate equations.

The experiments are carried out at \( T = 70...400 \text{ mK} \) for overall \(^3\text{He} \) concentrations \( c_3 = 0.1, 1, 10, \) and 100 ppm, 0.1, 1, and 5% as well as for isotopically purified \(^3\text{He} \) (\( \lesssim 1 \text{ ppb of } ^3\text{He} \)) and commercial helium. The total amount of liquid helium in the cell is about 11 cm\(^3\). The free surface area accessible to \(^3\text{He} \) is 57 cm\(^2\) including the film-covered low-temperature part of the H inlet tube coming from a dissociator.

Fig. 1 shows the temperature dependence of the ratio \( K_{ab}^{\text{eff}}/K_{aa}^{\text{eff}} \) obtained in this work together with the results of Statt et al. [10]. In agreement with the theory of Greben et al. [9], but in contradiction with some earlier experimental results [1], 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 [1]. The probability of such a process vanishes at \( T = 0 \). We also emphasize that, within experimental scatter, \( K_{ab}^{\text{eff}}/K_{aa}^{\text{eff}} \) shows no systematic change upon addition of \(^3\text{He} \) and is therefore averaged over all concentrations. The error bars in Fig. 1 represent standard deviation of the data.

In Fig. 2 the temperature dependence of \( K_{aa}^{\text{eff}} \) is presented for various \(^4\text{He} \) concentrations and for commercial as well as isotopically pure \(^4\text{He} \). Following Ref. 7, we assume the crosslength \( l_{aa} \) for aa surface recombination to be temperature independent. Then \( K_{aa} = \eta_{aa} \varepsilon^2 \propto \sqrt{T} \) where \( \varepsilon \approx 2.53 \times 10^{-2} \text{T}/B \) is the hyperfine mixing parameter and \( \eta = \sqrt{\pi kT/m} \) the relative thermal velocity in 2D. For \( ^4\text{He} \) \( E_a \) does not vary with \( T \). Then half of the slope of the ln \( (\frac{4}{3} K_{aa}^{\text{eff}}/\lambda^2 \sqrt{T}) \) versus \( 1/T \) line is \( E_a = 1.14(1) \text{ K} \) and the intercept gives \( l_{aa} = 0.40(10) \text{Å} \). For \( T \)-independent \( l_{aa} \) Fig. 2 may also be regarded as the temperature variation of the crosslength \( l_{ab} \).

In Fig. 2 the data also for \( c_3 = 5 \% \) fall on a straight line. Yet the \(^3\text{He} \) surface coverage changes [11] and we cannot take \( E_a \) to be constant. Instead we assume, to the first approximation, that the crosslength \( l_{aa} \) does not depend on \(^3\text{He} \) content either. Then we determine \( E_a \) for each concentration and temperature from the measured \( K_{aa}^{\text{eff}} \) using Eq. (1) with \( l_{aa} \) fixed to its pure-\(^4\text{He} \) value. The results are shown in Fig. 3, from which one notices that the behavior of \( E_a \) resembles that of the surface tension of \(^3\text{He} \)-\(^4\text{He} \) solutions [11]. Both have their origin in 2D \(^3\text{He} \) bound to the surface of the liquid. Since the chemical potential of H atom inside liquid helium is large positive, even a small overlap of the wavefunctions.

![Fig. 1: Temperature dependence of the rate constant ratio](image1)

![Fig. 2: The effective rate constant plotted as](image2)
of adsorbed H and \(^3\)He repels hydrogen atoms from the surface, i.e., raises the energy level of the single bound state of the H atom.

According to Pavloff and Treiner \cite{12} 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 \(e_{a0} = 2.64 \text{ K} \) and \(M_0 = 1.29m_3\) for the ground state and \(e_{a1} = 0.81 \text{ K} \) 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. \cite{13}. In good agreement with Ref. \cite{12} the occupation of the excited surface state at \(n_{3a} \geq 3.5 \times 10^{14} \text{ cm}^{-2}\) has been recently observed in an experiment \cite{13}. Therefore, using the above values we may calculate the populations \(n_{3a0}\) and \(n_{3a1}\) of the both \(^3\)He surface states for all concentrations \(c_3\) and temperatures.

Fig. \ref{fig3} presents the hydrogen adsorption energy \(E_a\) as a function of \(n_{3a0}\). 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. \(n_{3a0}\) line is the effective mean-field parameter \(U_{30} = 1.2(1) \times 10^{-15} \text{ K cm}^2\). It does not seem to change at \(n_{3a0} = 3.5 \times 10^{14} \text{ cm}^{-2}\), 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 of the above assumption we can consider two reasons why the crosslength \(l_{aa}\) 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 presence of 2D \(^3\)He due to a larger overlap of the wave functions. On the other hand, the surface-normal delocalization length \(d = \hbar/\sqrt{2E_{am}}\) of the hydrogen wavefunction grows with \(n_{3a0}\). The latter reason causes the H-H recombination crosslength \(l_{aa} \propto 1/d \propto \sqrt{E_a}\) to decrease with growing \(n_{3a0}\). 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 \(n_{3a0}\) are high, i.e., for very few data points only (cp. Figs. \ref{fig2} and \ref{fig3}).

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 the several possible sources of systematic error in the determination of \(E_a\) listed by Godfried et al. \cite{14}. Another source is \(^3\)He impurity and from Fig. \ref{fig3} 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 crosslength \(l_{aa}\) 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 \(^3\)He was, if not explicitly stated otherwise, just non-purified commercial helium with unknown \(^3\)He contamination. This is not a problem at \(T \geq 200 \text{ mK}\) (cp. Fig. \ref{fig2}) 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 \(10^8 \text{ cm}^{-1}\), that the \(^3\)He surface coverage is at most \(10^{-4}\) monolayers even for \(c_3 = 1 \text{ ppm}\) which is at least an order of magnitude larger than the natural abundance.

The ESR results of Statt et al. \cite{10} for \(K_{aa}^{\text{eff}}\) and \(K_{ab}^{\text{eff}}\) at \(T = 250\ldots500 \text{ mK}\) agree quite well with ours scaled to the same magnetic field and \(A/V\) ratio. Morrow et al. \cite{15} measured the zero field NMR frequency shift for H above 200 mK and found, as coupled fitting parameters, the binding energy \(E_a = 1.15(5) \text{ K}\) and the wall shift \(\Delta_s = -49(2) \text{ kHz}\). Later Pollack et al. \cite{17} observed simultaneously surface and bulk H atoms by NMR and directly found \(\Delta_s = 43.2(10) \text{ kHz}\), as extrapolated to \(B = 0\). Shinkoda and Hardy \cite{17} used ESR for a direct detection of H atoms at the surface of \(^3\)He. They had several
cm$^3$ of liquid helium in the sample cell and measured the apparent $E_a$ to increase from 0.75 K 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. 10, 15, 16, 17 our value $E_a = 1.14(1)$ K for H on isotopically pure $^3$He and the theoretical prediction [7] with each other we gather strong support for the assumption of a temperature independent crosslength $l_{aa}$. 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 0.39(1) K for pure $^4$He [8] and 0.34(3) K for the mixture of two parts of $^3$He and one part of $^4$He [9].

The linear decrease of $E_a$ with $n_3$, 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, $e_{0F} = \pi \hbar^2 n_{3a0}/2M_0 \gg kT$. 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 $n_{3a0}T/e_F = 2M_0T/\pi \hbar^2$, is independent of $n_{3a0}$. On the other hand, the Fermi level rises with $n_{3a0}$, the corresponding wave function expands in surface-normal direction [12] 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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