# Mixing 2D electron and atomic hydrogen on the liquid helium surface

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**Abstract**

Two-dimensional (2D) electrons on the liquid $^4$He surface are mixed with atomic hydrogen. The density of 2D electrons decays as a result of the reaction with hydrogen atoms. The measured reaction rates indicates that two H atoms participate in the reaction to form a negative hydrogen ion, namely, $H + H + e^- \rightarrow H^- + H$. Then, $H^-$ submerges into the liquid. It is argued that the reaction can be the dissociative attachment of electrons to excited $H_2(14,4)$ molecules, which are produced by the surface recombination of hydrogen atoms.

*Key words:* Atomic hydrogen; Helium surface; 2D electrons; Dissociative attachment

## 1. Introduction

We find that the two-dimensional (2D) mixture of surface state electrons (SSE) and hydrogen atoms on the surface of liquid $^4$He is suitable for exploring phenomena of slow electron impact, which plays an important role in interstellar chemical reactions, for example [1]. These phenomena are still difficult to study in the laboratory. The properties of both electrons and hydrogen atoms on liquid $^4$He are well understood [2,3]. The motion of the adsorbed particles perpendicular to the surface is strongly restricted, whereas the motion along the surface is nearly free. Since the temperature can be less than 1 K, the thermal kinetic energy of electrons and hydrogen atoms is less than 0.1 meV. By varying temperature, the electron energy is tunable. Our preliminary measurements showed that a chemical reaction of SSE with atomic hydrogen takes place on the surface and gives rise to the reduction of SSE density at temperature-dependent rates [4,5]. In this paper, we show that the reaction involves two H atoms and one electron, namely, $H + H + e^- \rightarrow H^- + H$. On the basis of this result, we propose a possible reaction mechanism of dissociative attachment (DA) of electrons to rovibrationally excited $H_2$ molecules, which are created in the early stage of the hydrogen surface-recombination process.

## 2. Experimental

Liquid $^4$He level in a sample cell is set midway between a pair (upper and lower) of parallel disk electrodes 25 mm in diameter and 3 mm apart. A positive DC potential, $V_{\rm DC}$, is applied to the lower electrode, while the upper electrode and a guard ring are connected to the ground potential. A tungsten filament is briefly heated to produce SSE. The SSE density is measured using a vibrating capacitor electrometer (VCE), which consists of the upper electrode and a piezo actuator. The details of the setup are described elsewhere [5]. The resolution is $2 \times 10^5$ electrons/cm$^2$, which is approximately 0.2% of the saturated density for $V_{\rm DC} = 90$ V .

Hydrogen atoms are created in an $H_2$ dissociator mounted on the still of a dilution refrigerator, and are guided to the cell through a capillary tube of which the inner diameter is 0.7 mm. A helical resonator in the dissociator is excited by a 430 MHz rf pulse to ignite glow discharge, which dissociates $H_2$ molecules.

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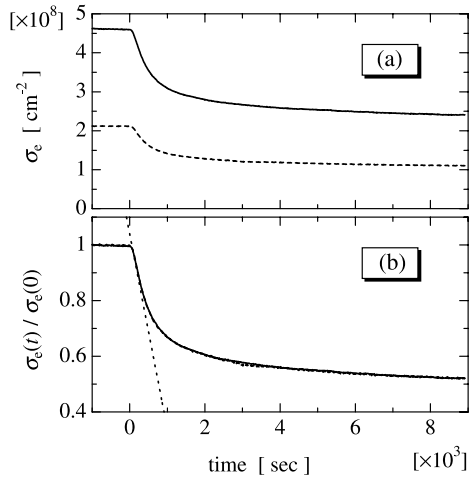


Fig. 1. (a) Density decay curves of SSE ($T = 0.275$ K, $V_{\rm DC} = 90$ V). Hydrogen atoms are fed at $t = 0$. These curves are measured under the same conditions except that the initial SSE densities are different. (b) Two curves in (a) are normalized by the value at $t = 0$. Perfect scaling behavior is observed. (There are actually two lines overlapping each other.) The dotted line is the tangent at $t = 0$, which defines the initial slope, $v_0$. See text.

Discharge conditions, such as rf power, pulse width, number of pulses and temperature of the dissociator, are carefully maintained so as to regulate the amount of H atoms fed to the cell.

### 3. Results and Discussion

As a fixed amount of H atoms are fed into the cell in a few seconds, the VCE output starts to vary, signaling the decay of the SSE density. The influence of the H atoms is to diminish SSE from the surface. We confirmed that without $H_2$ in the dissociator, the discharge had no influence on the SSE density. This means that atomic hydrogen does influence the SSE density. Typical traces of the VCE output are shown in Fig. 1(a). Here, the vertical axis is the SSE density ($\sigma_{\rm e}$) which is converted from the VCE output. At $t = 0$, hydrogen atoms are fed into the cell. The data were taken at $T = 0.275$ K and $V_{\rm DC} = 90$ V. Between the two curves only the initial SSE density $\sigma_{\rm e}(0)$ is different.

We attribute the decrease of the SSE density to the attachment of electrons to hydrogen atoms to form negative hydrogen ions. Then, the ions penetrate into liquid helium, because the electrostatic energy gain dominates over the loss due to the zero-point motion of the ion inside liquid He, which is essential for the electron bubble formation. It is less probable for charges to escape from the surface into the free volume, because there is a potential barrier comparable to $eV_{\rm DC}$ that needs to be overcome.

In general, one electron can react with $n$ H atoms to form negative hydrogen, for which the chemical reaction is written as $e^- + nH \rightarrow H^- + (n-1)H$. This reaction occurs only on the $^4$He surface of area $A_{\rm e}$, where SSE are confined. Another relevant reaction that should be taken into account is the recombination of H atoms to form the $H_2$ molecule: $H + H \rightarrow H_2$. H atoms exist on the entire surface area $A$ of the cell with surface density $\sigma_{\rm H}$ as well as in the free volume $V$ with volume density $n_{\rm H}$ [6]. The recombination occurs both on the surface and in the volume.

The rate equations for the total number of SSE, $N_{\rm e} = A_{\rm e}\sigma_{\rm e}$, and of hydrogen atoms, $N_{\rm H} = A\sigma_{\rm H} + Vn_{\rm H}$, may be written as

$$\frac{dN_{\rm e}}{dt} = -K_{\rm e}N_{\rm e}(\alpha N_{\rm H})^n, \tag{1}$$

$$\frac{dN_{\rm H}}{dt} = -K_{\rm e}N_{\rm e}(\alpha N_{\rm H})^n - K_{\rm s}^{\rm eff}(\alpha N_{\rm H})^2, \tag{2}$$

$$\alpha = \left[A + (V/\lambda_{\rm th})\, e^{-E_{\rm a}/k_{\rm B}T}\right]^{-1}. \tag{3}$$

Here, $K_{\rm e}$ and $K_{\rm s}^{\rm eff}$ are the rate coefficients for electron–H reaction and H–H recombination, respectively. We assumed the adsorption isotherm of H, $\sigma_{\rm H} = n_{\rm H}\lambda_{\rm th}\exp(E_{\rm a}/k_{\rm B}T)$, with the surface binding energy $E_{\rm a}$ of atomic hydrogen to liquid $^4$He and the thermal de Broglie wavelength $\lambda_{\rm th} = (2\pi\hbar^2/m_{\rm H}k_{\rm B}T)^{1/2}$, where $m_{\rm H}$ is the atomic hydrogen mass. We used the most reliable experimental value of $E_{\rm a}$, $1.0k_{\rm B}$ [7], in the analysis. The coefficient $\alpha$ relates $\sigma_{\rm H}$ and $N_{\rm H}$ as $\sigma_{\rm H} = \alpha N_{\rm H}$. The effective recombination rate coefficient $K_{\rm s}^{\rm eff}$ is expressed in terms of surface and volume recombination rate coefficients, $K_{\rm s}$ and $K_{\rm v}$, as $K_{\rm s}^{\rm eff} = AK_{\rm s} + VK_{\rm v}\lambda_{\rm th}^{-2}\exp(-2E_{\rm a}/k_{\rm B}T)$ [6].

One of the most prominent properties of the observed decay curves $\sigma_{\rm e}(t)$ is that when the decay curves are normalized by the initial SSE density $\sigma_{\rm e}(0)$, all the curves with different $\sigma_{\rm e}(0)$ fall on a single curve (Fig.1(b)). This property implies that $d\log N_{\rm e}/dt$ must be independent of $N_{\rm e}$, and accordingly the evolution of $N_{\rm H}(t)$ should be independent of $N_{\rm e}$ (it can be seen from Eq. (1)). This condition is satisfied if the first term in the right hand side (RHS) of Eq. (2) is negligible in comparison with the second term.

The characteristic measure of the SSE-density decay rate is given by

$$v_0 = \frac{1}{N_{\rm e}(0)}\left.\frac{dN_{\rm e}}{dt}\right|_{t=0}. \tag{4}$$

This is the initial slope of $N_{\rm e}(t)/N_{\rm e}(0)$ and indicated in Fig. 1(b) by a dotted line. We refer to $v_0$ as the initial rate, hereafter. The initial rate was measured as a function of temperature. Fig. 2 is the Arrhenius plot of $v_0$. The difference between the circles and the squares

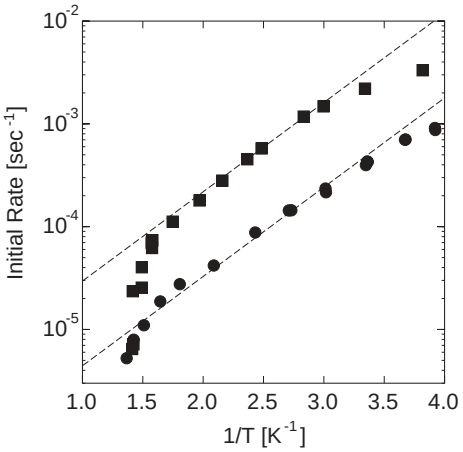


Fig. 2. The Arrhenius plot of the initial rate $v_0$. Circles and squares denote the data for 30 and 50 discharge pulses, respectively. The dashed lines are proportional to $\exp(2E_{\rm a}/k_{\rm B}T)$.

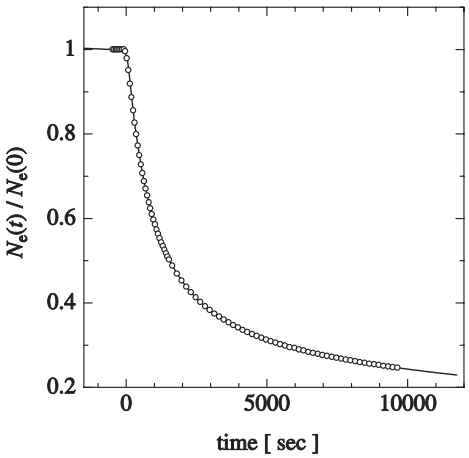


Fig. 3. Measured SSE density decay at $T = 0.398$ K (circles) and its fit to the solution Eq.(6) of the rate equation (solid line).

is the amount of H atoms fed at $t = 0$. In the temperature range, $1/T \leq 3\ {\rm K}^{-1}$, the initial rate shows exponential dependence on $1/T$. This is the indication that adsorbed H atoms play an important role. As the temperature is lowered, $\sigma_{\rm H}$ increases according to the adsorption isotherm and the electrons on the surface collide with hydrogen more frequently. The dashed lines in Fig. 2 are proportional to $\exp(2E_{\rm a}/k_{\rm B}T)$, which agree well with the data in $1.5 < 1/T < 3\ {\rm K}^{-1}$.

According to Eq. (1), $v_0$ should be given by

$$v_0 = -K_{\rm e}(\alpha N_{\rm H}(0))^n. \tag{5}$$

Since the temperature dependence of $K_{\rm e}$ is weak (this will be verified later), the temperature dependence of $v_0$ should be dominated by $\alpha^n$. At high temperatures where the second term in the bracket of Eq. (3) dominates, $\alpha \simeq (\lambda_{\rm th}/V)\, e^{E_{\rm a}/k_{\rm B}T}$. Ignoring the $T^{-1/2}$ dependence of $\lambda_{\rm th}$, $v_0$ should be proportional to $e^{nE_{\rm a}/k_{\rm B}T}$. Therefore, we conclude that $n = 2$. This means that two H atoms participate in the electron attachment to form negative hydrogen, that is, the reaction ${\rm H} + {\rm H} + {\rm e}^- \rightarrow {\rm H}^- + {\rm H}$ is occurring in our system.

The negative hydrogen is known to have only one electron bound state of which the binding energy is about 0.75 eV. The cross section of radiative attachment ${\rm H} + {\rm e}^- \rightarrow {\rm H}^- + h\nu$ for slow electron impact is small [8,9]. The absence of one hydrogen process should be understood in this context. No theoretical analysis of the process has been done in the presence of the liquid He surface.

In the following discussion, we focus our attention on the temperature range of $1.5 < 1/T < 3.0\ {\rm K}^{-1}$, where $v_0 \propto e^{2E_{\rm a}/k_{\rm B}T}$. Putting $n = 2$ in Eq. (1) and neglecting the first term of Eq. (2), we can solve Eqs. (1)-(3) analytically to obtain

$$\frac{N_{\rm e}\,(t)}{N_{\rm e}\,(0)} = \exp\left[-\frac{K_{\rm e}\alpha^2 N_{\rm H}^2\,(0)\,t}{K_{\rm s}^{\rm eff}\alpha^2 N_{\rm H}\,(0)\,t+1}\right]. \tag{6}$$

By fitting the measured decay curves to Eq.(6), we obtain two fitting parameters, $N_{\rm H}(0)$ and $K_{\rm e}$. We obtained the value of $K_{\rm s}^{\rm eff}$ from Arai *et al.* [10]. As shown in Fig. 3, Eq. (6) fits the data well. The parameters thus obtained are $N_{\rm H}\,(0) = (3.5 \pm 0.5) \times 10^{12}$ atoms and $(8 \pm 1) \times 10^{12}$ atoms for the circles and the squares in Fig. 2, respectively, and $K_{\rm e} = (5 \pm 3) \times 10^{-16}$ cm$^4$/sec for both circles and squares. No significant temperature dependence is found for $N_{\rm H}\,(0)$ or $K_{\rm e}$ with our resolution.

As for the direct three-body collision ${\rm H} + {\rm H} + {\rm e}^-$, the rate coefficient, $K_{\rm e}$, may be estimated roughly as $K_{\rm e} \sim a^3\overline{v_{\rm H}}$ from a simple consideration of collision frequency [11], where $a$ is the scattering cross length and $\overline{v_{\rm H}}$ is the thermal velocity of H atoms. Considering that $a$ should be on the order of atomic scale ($10^{-8}$ cm), we reach the conclusion that the upper limit of $K_{\rm e}$ is $10^{-18}$ cm$^4$/sec. This is still two orders of magnitude smaller than the measured value. Another candidate is the following two-step mechanism. (i) ${\rm H} + {\rm H} \rightarrow {\rm H}_2(v, J)$, (ii) ${\rm H}_2(v, J) + {\rm e}^- \rightarrow {\rm H} + {\rm H}^-$. The first step is the surface H recombination to the rovibrational state of ${\rm H}_2(v, J)$, where $v$ and $J$ are vibrational and rotational quantum numbers, respectively. The second step is the DA of an electron to ${\rm H}_2(v, J)$.

In the absence of magnetic field, H recombination proceeds via van der Waals recombination mechanism [6]. In order that DA follows H recombination, ${\rm H}_2(v, J)$ stays necessarily on the surface. However, most of the recombination products are expected to leave the surface immediately since their recombination energies exceed the surface binding energy of a molecule. ${\rm H}_2(14, 4)$, whose bound state energy is 0.7 K below H + H dissociation limit, is the only product

which may stay on the surface after the recombination. Greben *et al*. [12] calculated that 6% of the van der Waals recombination product in the volume is $H_2(14,4)$ at 1 K. Similar amount of $H_2(14,4)$ can be expected for the surface recombination.

Employing the DA model, we rewrite the rate equation for $N_e$ as

$$\frac{dN_e}{dt} = -\frac{K_{DA}}{A_e} N_* N_e, \tag{7}$$

where $K_{DA}$ is the surface DA rate coefficient and $N_*$ is the number of $H_2\,(14,4)$ in area $A_e$. The coefficient $K_{DA}$ may be expressed as $K_{DA} = \sigma_{DA}\overline{v_e}/d$, where $\sigma_{DA}$ is the three-dimensional DA cross section, $\overline{v_e}$ is the thermal velocity of electrons, and $d$ is the thickness of the SSE layer, $\sim 76$ Å [13]. The rate equation for $N_*$ is

$$\frac{dN_*}{dt} = \frac{1}{2}\beta K_s A_e (\alpha N_H)^2 - \frac{1}{\tau} N_* - \frac{K_{DA}}{A_e} N_* N_e. \tag{8}$$

The first term on RHS is the production term of $H_2(14,4)$, where the fraction $\beta$ of the recombination products is $H_2(14,4)$. The second term is the relaxation term of $H_2(14,4)$ on the surface with the life time $\tau$. According to the same argument as before, we may neglect the last term on the RHS of Eq. (8). In order to retrieve the form of Eq. (1), $dN_*/dt$ should be zero, implying that the steady state is achieved. Accordingly, we obtain the following equation.

$$\frac{dN_e}{dt} = -\frac{1}{2}\beta K_s K_{DA} \tau N_e (\alpha N_H)^2. \tag{9}$$

Comparing Eq.(9) with Eq.(1), we find the relation

$$K_e = \frac{1}{2}\beta K_s K_{DA} \tau. \tag{10}$$

Using Eq.(10) with the measured $K_e$, $\beta = 0.06$ and a calculated maximum value of three-dimensional endothermic DA cross section $\sigma_{DA} \approx 10^{-15}$ cm$^2$ for $H_2\,(9,0)$ [14], we obtain $\tau \approx 10^{-6}$ sec. A theoretical calculation is needed for the lifetime of the highly excited rovibrational states of $H_2(v,J)$ on the surface of liquid $^4$He, in order to make a comparison with our present estimation. Except for the quantitative argument, this model is one of the most probable candidates for the explanation.

## 4. Conclusion

In this work, we studied the surface charge reduction in the 2D mixture of electrons and atomic hydrogen. The reduction is due to the formation of negative hydrogen via the reaction, $H + H + e^- \rightarrow H^- + H$. The direct three-body collision process, $H + H + e^-$, is too small to explain the observed reaction rate. The reaction may be the exothermic dissociative attachment of electrons to highly excited $H_2$ molecules at very low electron energy. This energy region of slow electron impact has been investigated for the first time. We believe that the cryogenic electron-hydrogen system will cast a new light on the study of slow electron impact on atoms and molecules.


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