Cold electron attachment to atomic hydrogen on liquid helium surface

Toshikazu Arai [a,1], Toshiyuki Shiino [a], Kimitoshi Kono [a]

[a] *Low Temperature Physics Lab., RIKEN, Hirosawa 2-1, Wako-shi, Saitama 351-0198, Japan*

Abstract

Surface state electrons (SSE) on liquid helium is applied to cold electron-atom/molecule collision experiment. In a two-dimensional mixture of SSE and adsorbed atomic hydrogen below 1 K, we found a chemical reaction reduces the SSE density. From the SSE density decay kinetics measurement, we found that the reaction is expressed as H + H + e^- → H^- + H. As a possible explanation, we propose a dissociative attachment mechanism to a highly rovibrationally excited hydrogen molecule which is an early product of atomic hydrogen recombination.

Key words: atomic hydrogen; surface state electrons; dissociative attachment

In the previous experiments we found that surface state electrons (SSE) density decreases when it is mixed with atomic hydrogen (H). [1,2] As the measured density reduction rates were faster at lower temperatures, we attributed the process to electron attachment to H on the surface since more H atoms are adsorbed as the temperature is decreased. If the negatively charged chemical product, most likely it is negative hydrogen H^-, stays on the surface, the total surface charge is not influenced even the reaction proceeds. But we measured the surface charge reduction [2]. That means the product penetrates into the bulk liquid.

In this work we employ an identical sample cell with that of ref. [2], which contains a vibrating capacitor electrometer to measure the surface charge. H atoms are produced in the H_2 dissociator on the still of a dilution refrigerator by pulsed rf glow discharge and are guided to the sample cell attached on the mixing chamber. SSE is prepared before filling H and fixed number of H atoms are introduced to the cell at $t = 0$. The evolutions of SSE density by the influence of H are recorded.

In general an electron reacts with n H atoms and we write down the rate equations the total numbers of SSE (N_e) and H (N_H) as

$$\frac{dN_e}{dt} = -K_e N_e (\alpha N_H)^n, \tag{1}$$

$$\frac{dN_H}{dt} = -K_e N_e (\alpha N_H)^n - K_s^{eff} (\alpha N_H)^2, \tag{2}$$

$$\alpha = \left[A + (V/\lambda_{th})\, e^{-E_a/k_B T} \right]^{-1}. \tag{3}$$

Here, K_e and K_s^{eff} are the rate coefficients for electron–H reaction and H–H recombination, respectively. We assumed the adsorption isotherm of H, $\sigma_H = n_H \lambda_{th} \exp(E_a/k_B T)$, where σ_H and n_H are surface and volume densities of H, respectively, with the surface binding energy E_a and the thermal de Broglie wavelength $\lambda_{th} = (2\pi\hbar^2/m_H k_B T)^{1/2}$, where m_H is the atomic hydrogen mass. V and A are volume and surface area of the sample cell. The effective recombination rate coefficient K_s^{eff} is expressed in terms of surface and volume recombination rate coefficients, K_s and K_v, as $K_s^{eff} = AK_s + VK_v\lambda_{th}^{-2} \exp(-2E_a/k_B T)$ [3].

[1] Corresponding author. Present address: Research Center for Higher Education, Ropponmatsu 4-2-1, Chuo-ku, Fukuoka 810-8560, Japan. E-mail: toshikaz@rc.kyushu-u.ac.jp

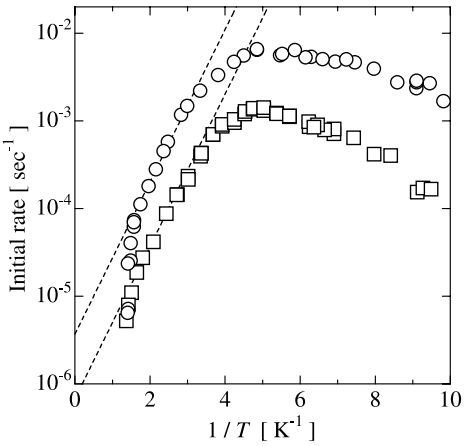

Fig. 1. Temperature dependence of the initial slopes of normalized SSE density decay cuves. Circles and squares correspond to the data for 50 and 30 discharge pulses. The dashed lines are proportional to $e^{2E_{\rm a}/k_{\rm B}T}$.

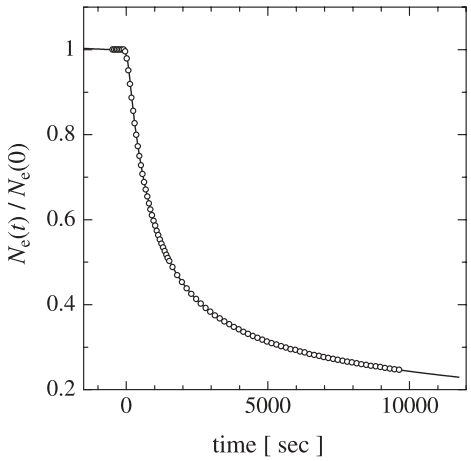

Fig. 2. An example of measured normalized SSE density decay (circles) at $T = 0.398$ K and its fitting to Eq.(5) (solid line).

One of the important observed properties of SSE density decay curves is when these are normalized by the initial SSE density, all the normalized curves become independent of $N_{\rm e}(0)$ as far as experimental conditions such as temperature and $N_{\rm H}(0)$ are the same. Such type of solution is obtained only when the first term of Eq.(2) is negligible, i.e, the decrease of $N_{\rm H}$ is governed by H–H recombination.

To determine the order of reaction n, we plot the temperature dependence of initial slope v_0 of the normalized SSE decay curve (Fig.1)

$$v_0 = (1/N_{\rm e}(0))\,|dN_{\rm e}/dt|_{t=0} = -K_{\rm e}(\alpha N_{\rm H}(0))^n. \qquad (4)$$

The main temperature dependence of v_0 comes from the exponential character in α. At high temperatures that the second term in Eq.(3) dominates, v_0 is approximately proportional to $e^{nE_{\rm a}/k_{\rm B}T}$. The dashed lines in Fig.1 are proportional to $e^{2E_{\rm a}/k_{\rm B}T}$, where well establised value $E_{\rm a}/k_{\rm B} = 1.0$ K for H on liq.^{4}He is used. For $1.5 < 1/T < 3.0$ K^{-1}, these lines fit the data well. Thus our model describes the data for this temperature range and $n = 2$. In the following we discuss the data within this temperature range. Neglecting the first term in Eq.(2) and taking $n = 2$, the sloution for $N_{\rm e}$ is

$$N_{\rm e}(t)/N_{\rm e}(0) = e^{-K_{\rm e}\alpha^2 N_{\rm H}^2(0)t/\left(K_{\rm s}^{\rm eff}\alpha^2 N_{\rm H}(0)t+1\right)}. \qquad (5)$$

With two adjustable parameters $K_{\rm e}$ and $N_{\rm H}(0)$, measured decay curves are fitted to Eq.(5). The values needed for $K_{\rm s}^{\rm eff}$ are obtained from Arai *et al.* [4] The data is described well by Eq.(5) and the fitting result gives $K_{\rm e} = (5 \pm 3) \times 10^{-14}$ cm^4/sec.

The reaction for $n = 2$ is expressed as H + H + $e^- \rightarrow H^-$ + H + 0.75 eV. Since we estimated that the direct three body collision frequency coefficient is two orders of magnitude smaller than our measured value of $K_{\rm e}$, we propose as a possible mechanism the following stepwise reaction. (i) $H + H \rightarrow H_2(v, J)$, (ii) $H_2(v, J) + e^- \rightarrow H + H^-$. The first step is the surface H recombination. $H_2(v, J)$, where v and J are the vibrational and rotational quantum number of H_2 molecule, is an early product of recombination which is rovibrationally excited. The second step is dissociative attachment (DA) of an electron to $H_2(v, J)$. DA proceeds via a formation of negative molecular ion H_2^- whose energy is above its dissociation limit. Since our reaction takes place on the liquid helium surface, $H_2(14, 4)$ is the prime candiate. $H_2(v, J)$ whose energy is lower than $H_2(14, 4)$ may leave the surface as soon as it is formed because its formation energy exceeds the surface binding energy of the molecule. Details will be discussed elswhere. [5]

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