

## Mean Adsorption Lifetime of Rb on Etched Tungsten Single Crystals: Neutrals\*

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The mean adsorption lifetime has been measured for the fraction of adsorbed Rb which was desorbed as neutral atoms from an etched W surface. The lifetime was found to be greatly different from that obtained in the case of Rb ions. Experimental values have been found to be consistent with a theoretical model which assumes that, in a surface ionization process, the adsorbed particles may occupy either of two discrete states with distinctly different types of binding.

### I. INTRODUCTION

IN the surface ionization process, some of the adsorbed particles are desorbed as ions and some as neutral atoms. For steady-state conditions where desorption is balanced by additional incoming particles, the ratio of desorbed ion current density to desorbed atom current density is given by  $I_i/I_a = (\omega_i/\omega_a) \exp[e(\phi - I)/kT]$ .<sup>1</sup> The ratio of weight factors,  $\omega_i/\omega_a$ , is  $\frac{1}{2}$  for alkali metals,  $\phi$  is the surface electron work function, and  $I$  is the alkali ionization potential. Past work with the alkali metal-tungsten system, including experimental verification of the Langmuir-Saha equation above, was consistent with the hypothesis that there are both an ionic state and an atomic state of the adsorbed particle. This view was strongly supported by Taylor's<sup>2</sup> measurements which gave a different desorption rate for ions and atoms. Gurney,<sup>3</sup> however, has given theoretical arguments which imply that, in the adsorbed state, the alkali and surface interact in such a way as to make ion and atom indistinguishable. The relative probability of ion/atom desorption was assumed to be determined by relative valence electron probability density inside/outside the surface barrier. This view implies that experimental measurements of the mean adsorption lifetime for particles desorbed as ions would be the same as that measured for particles desorbed as neutral atoms.

The present work was designed to check this prediction. The mean desorption lifetime on "essentially clean," etched W crystals has been measured for Rb which was desorbed as Rb neutral atoms.<sup>4</sup> This was accomplished by using a second surface ionization filament to detect the neutral atoms from the surface under examination.

### II. EXPERIMENTAL

Most of the apparatus and methods have been described previously.<sup>4</sup> The major modification is shown

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<sup>1</sup> I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. (London) **A107**, 61 (1925).

<sup>2</sup> J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).

<sup>3</sup> R. W. Gurney, Phys. Rev. **47**, 479 (1935).

<sup>4</sup> The crystal preparation, surface cleanliness measurements, and ion lifetime measurements have been discussed by F. L. Hughes and H. Levinstein, preceding paper [Phys. Rev. **113**, 1029 (1959)].

in Fig. 1. A chopped Rb atomic beam impinged upon the etched tungsten filament,  $W_1$ . Neutral Rb atoms which were desorbed were permitted to drift with thermal energy to the second filament,  $W_2$ , where they were adsorbed a second time. The desorbed ions from the second filament were focused and accelerated by the electrode,  $A$ . After passing through  $A$ , the ion pulse was amplified by the secondary emission multiplier. The signal was passed into conventional electronic amplifiers and displayed on an oscilloscope in the same manner as for the ion pulse work which was previously described.<sup>4</sup> With the exception of a small Boltzman "tail," due to the thermal drift in part of the trajectory, the oscilloscope trace of the neutral pulse had the same appearance as that shown for the ion pulse.

### 1. Electronics

For Rb on etched tungsten ( $\phi = 5.25$  v), the ion/atom current density ratio is  $\approx 2.5 \times 10^4$  at  $1200^\circ\text{K}$ . In order to keep the surface coverage low, it was necessary to operate at about the same beam intensity as was used for the ion work.<sup>5</sup> In addition, the geometrical losses of neutral atom current between  $W_1$  and  $W_2$  was of the order of  $10^3$ . The additional gain required over that required by the ion work was thus of the order of  $10^6$ .

The additional amplification required was obtained

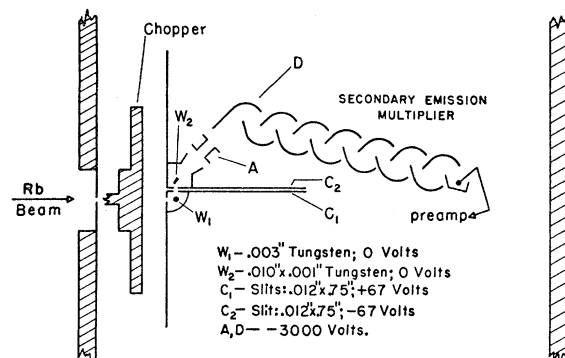


FIG. 1. Apparatus for measurement of neutral Rb adsorption lifetime.

<sup>5</sup> In this measurement, the coverage was about  $10^{11}$  atoms/cm<sup>2</sup>. Rb-Rb interaction effects are expected to be much less than the experimental error.



of discrete states ranging from the vacuum level down to  $\phi$  electron volts below the vacuum level. This will produce a band of ion states ranging from curve *A* to curve *C*. Curve *B* represents one of these states between the two extremes.

The atom level represents the potential as an atom moves closer to the surface. Judging from the magnitude of the experimental neutral desorption energy, the binding appears to be due to exchange forces.

Transitions between ion and atom states are possible at points where the potential curves cross. Very little is known about the potential shapes and relative positions of the potential minima. For the potentials shown in Fig. 3, there are so many crossing points that there is access to and from any ion-atom level.

The inset in Fig. 3 shows the diagram in terms of transition and desorption probabilities/second. The transitions  $P_1$  and  $P_2$  are included to account for the possibility of ion-atom interchange. With initial ion and atom surface concentrations  $n_i$  and  $n_a$ , respectively, the time variation in these concentrations is given by

$$\begin{aligned}\dot{n} &= -(P_a + P_2)n_a + P_1n_i, \\ \dot{n}_i &= P_2n_a - (P + P_1)n_i.\end{aligned}\quad (1)$$

Owing to the number of parameters involved, the general solutions of Eq. (1) cannot be used. It is possible, however, to show that the equations are consistent with the experimental situation. The following boundary conditions were applied:

(a) Assume that the ion and atom pulse time decay is a true exponential and that the lifetime variation with  $1/T$  is a true exponential. Within experimental error this assumption is valid. However, semilogarithmic plots covering many decades are usually necessary in order to be certain

(b) Assume that the Langmuir-Saha equation is valid under pulse conditions. This assumption will be valid if the particles have time to come into quasi-equilibrium with the lattice.<sup>4</sup>

From (b), we have

$$I_i/I_a = P_i n_i / P_a n = (\omega_i / \omega_a) \exp[e(\phi - I) / kT], \quad (2)$$

and

$$n_i = (\omega_i P_a / \omega_a P_i) \exp[e(\phi - I) / kT] n_a = \beta(T) n_a. \quad (3)$$

Equation (1) becomes

$$\dot{n}_a = -(P_a + P_2 - P_1 \beta) n_a, \quad (4)$$

and

$$\dot{n}_i = -(P_i - P_2 / \beta + P_1) n_i.$$

The experimental desorption probabilities will be given by

$$\begin{aligned}P_a(\text{experimental}) &= P_a + P_2 - P_1 \beta, \\ P_i(\text{experimental}) &= P_i - P_2 / \beta + P_1.\end{aligned}\quad (5)$$

Equation (5) satisfies the part of condition (a), concerning exponential pulse decay. However, the condition on the temperature dependence of lifetime can be satisfied only if (1)  $P_1, P_2 \ll P_i, P_a$ ; or if (2)  $P_2 / P_1 = \beta$ .

Since  $P_1$  and  $P_2$  represent electronic transitions which are expected to occur in  $\approx 10^{-16}$  sec, the first possibility is unlikely. If the desorption probabilities are written in the form

$$P_{i,a} = (\tau_{i,a}^0)^{-1} \exp(-Q_{i,a} / kT), \quad \text{and} \quad P_2 / P_1 = \beta, \quad (6)$$

then the experimental boundary conditions are satisfied. Since  $\Delta Q = \phi - I + Q_i - Q_a$ , where  $\phi$  and  $I$  are now expressed in electron volts, Eq. (3) can be written

$$\beta = (\omega_i \tau_i^0 / \omega_a \tau_a^0) \exp(\Delta Q / kT) = P_2 / P_1. \quad (7)$$

Equation (7) has the form to be expected from statistical mechanics. The pre-exponential factor should represent the ratio of the densities of the vibrational states in the ion and atom levels. Becker's<sup>13</sup> calculation for the ratio,  $n_i / n_a$ , under steady-state conditions produced a term resembling  $\beta$ .

### 1. Effects of Retarding Field

As is shown in Fig. 1, a retarding field was applied to  $W_1$  to suppress ion evaporation. Originally, it was intended to operate  $W_1$  with a low accelerating field. Under those conditions, however, it was found difficult to prevent stray ions from entering the space of  $C_2$ . The following considerations show that the neutral-lifetime results will not depend on field polarity.

The effect on the ion-surface potential depth caused by an applied exterior field will be of the form of a Schottky term,  $e(eE)^{1/2}$ , since the potential is primarily an image potential. From thermionic electron emission from the etched surface, the term was found to be less than 0.01 eV, with a  $C_1 - W_1$  potential difference of 50 volts. The field effect on the neutral atom-surface potential should be much less.

Therefore, the energy diagram will be the same as before. Equations (3) and (4a) are still valid and the result is  $P_a(\text{experimental}) = P_a$ . The ion state population thus furnishes a reservoir of particles but does not affect the neutral evaporation rate.

### IV. CONCLUSION

The mean desorption lifetime of Rb has been measured for Rb desorbed as neutral atoms from "essentially clean," etched  $W$ . The values were different from the lifetime measured for Rb desorbed as ions.

The data have been found to be consistent with a model which assumes that, in surface ionization, ion and atom states are discrete and different. The ion state is primarily due to image forces. The atomic state appears to be due to exchange forces.

### V. ACKNOWLEDGMENTS

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<sup>13</sup> J. A. Becker, Ann. N. Y. Acad. Sci. 58, 723 (1954).