## Surface States of Electrons on Liquid Helium

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We have measured the rate of escape of electrons from the surface of liquid  ${}^{4}$ He into the gas under the influence of an electric field. The rate of escape is orders of magnitude different, depending on whether the electrons were deposited on the surface from the liquid side or from the gas side.

In this Letter we report the first measurements of the lifetime of electrons in surface states on liquid <sup>4</sup>He. The surface acts as a barrier against the entry of electrons from the gas since an electron must acquire an energy of 1 eV to enter the conduction band of the liquid.<sup>1,2</sup> On the other hand it is attracted to the surface by the electrostatic image force. Cole and Cohen<sup>3</sup> used this model to predict a surface state in which the electron is localized outside the liquid within 100 Å of the surface. The ground-state energy is  $\approx 1 \text{ meV}$  below the vacuum level. Properties of electrons localized just inside the surface of the liquid have been investigated by the transport across the liquid-gas interface of electrons injected from a radioactive source immersed in the liquid.<sup>4-6</sup> There is an energy barrier that, at sufficiently low temperatures, limits the rate of escape from the liquid into the gas. This has been interpreted by a model in which the electron is localized just inside the liquid surface.4<sup>-6</sup>

We have deposited electrons on the surface from the gas side and also from the liquid side. In both cases we have measured the lifetime for escape into the gas under the influence of an electric field. This identifies, for the first time, what we believe to be the surface state outside the liquid as predicted by Cole and Cohen.<sup>3</sup> We find that electrons in this state have properties very different from those of electrons localized inside the surface of the liquid.<sup>4-6</sup>

Electrons were deposited on the surface from the gas side by making free electrons in a highvoltage negative corona discharge in the helium gas above the liquid and drawing them to a localized area on the surface by means of a metal anode immersed in the liquid. To put electrons on the surface from below, they were produced by thermionic emission from a heated W filament immersed in the liquid.<sup>7</sup> In both cases we measured the lifetime  $\tau$  for emission from the surface into the gas in the presence of a suitably oriented electric field. Under comparable conditions,  $\tau$  is of order 10<sup>-4</sup> sec for electrons introduced from above the surface and, depending on the temperature, ranges from 10 to 10<sup>3</sup> sec for those introduced from below.

The apparatus and circuit used are shown schematically in Fig. 1. Helium is contained in a closed cylindrical vessel about 10 cm high and 6 cm in diameter having glass walls and metal ends. The inner surface of the glass has a transparent conductive coating connected electrically to the ends so the container can be grounded. There are two 3-cm diam brass plates mounted,

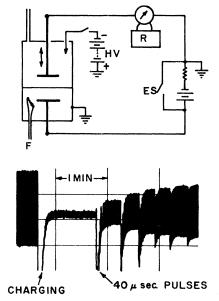


FIG. 1. <u>Above</u>: Schematic drawing of apparatus and measuring circuit; F, filament; ES, electronic switch for shorting out applied voltage; R, recorder driven by electrometer output; HV, voltage for corona discharge. The moving plate oscillates at 1 cps. <u>Below</u>: Recorder tracing showing signal before and after charging. Changes of amplitude due to escape of electrons during 40  $\mu$ sec pulses shorting out applied voltage are indicated. The height of the dark recorder tracing is the amplitude of the signal and indicates the variation of voltage at the electrometer input as the plate goes up and down. The electrometer is used in the "slow" mode and its response time is fast compared with the period of oscillation of the plate. one fixed and the other movable along the vertical axis. The upper plate, mounted on a stainless steel tube, can move up and down at 1 cps through 0.5 cm. It is used to measure the surface potential of the liquid when electrons are present as in the Kelvin method for determining work functions.<sup>8</sup> The plate is connected to a Keithley electrometer which, in turn, drives a strip chart recorder.

To deposit electrons on the surface of the liquid from above a voltage of order 200 V is applied between upper and lower plates with the lower plate positive. Several kilovolts, the exact value depending on the gas pressure, is then applied to the corona discharge lead at the upper right in the housing. Electrons produced by the discharge are transported through the gas as free electrons since helium has no stable negative ions. They are drawn toward the lower plate and stop at the liquid surface where they are confined by the electrostatic potential to lie in the area vertically over the plate. The field due to the sheet of charge which builds up at the surface decreases the field between the surface and the upper plate and increases that between the surface and the lower plate until the potential of the surface reaches that of the upper plate. Any more charge landing on the surface would make the surface more negative than the upper plate. The resulting field would tend to draw electrons away from the surface into the gas. Under these conditions, as we will show, the electrons leave the surface in about 100  $\mu$ sec and would not be present for the subsequent operations in the experiment. The lower half of Fig. 1 shows a recorder tracing describing these operations. The moving plate originally senses the voltage difference of 200 V applied between upper and lower plates. After the electrons from the corona discharge have landed, the signal decreases since the surface potential is now nearly equal to that of the moving plate. The corona discharge is now shut off for the remainder of the experiment. As long as the positive voltage is maintained on the bottom plate the electrons remain on the surface. To measure the rate of escape from the surface, the voltage on the bottom plate is briefly shorted to ground by an electronic switch; 40  $\mu \sec$  for the trace in Fig. 1. During the time that both plates are at the same potential the surface with its sheet of electrons is negative with respect to both plates and the electrons can leave the surface and enter the gas. From the known mobility<sup>9</sup> of electrons in helium gas we know that their

transit time to the upper plate is then short compared to the time that the plates are at the same potential. After this interval the positive potential is again on the bottom plate and the amplitude of the recorder tracing indicates the number of electrons still remaining on the surface. In this way the amount of charge escaping during a short interval can be measured. By varying the length of the pulse controlling the electronic switch this can be studied over a wide range of conditions. We have shown that the electrons leave the surface by going through the gas and not by lateral motion along the surface to the container wall by applying a negative voltage to the wall sufficient to prevent any electrons from reaching it. This gives the same decay characteristics as with the container grounded. During the early part of the decay the charge decreases approximately exponentially with time according to the formula:  $q(t) = 0 \exp(-kt)$ . Here t is the total time that the plates have been grounded as the result of the application of one or more pulses to the electronic switch. The exponential decay accounts for about two thirds of the total charge originally present. At later times the decay becomes progressively slower than the formula predicts. We have used the approximate exponential form to obtain an average rate constant k valid for the early part of the decay. The circles in Fig. 2 show k (inverse of  $\tau$ ) for electrons deposited on the surface from the gas.

To put electrons on the surface from below we

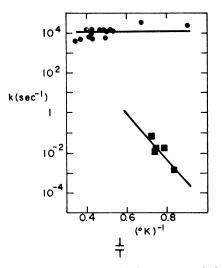


FIG. 2. Rate constant, k, for escape of electrons from the surface into the gas in the presence of a field as a function of temperature. Circles represent electrons deposited from above surface; squares represent electrons deposited from liquid side.

used thermionic emission from a thoriated W filament immersed in the liquid as described by Spangler and Hereford.<sup>7</sup> The filament is shown schematically in Fig. 1. Voltage was again applied between top and bottom plates but this time the top plate was positive so that the electrons were drawn upward to the surface. Electrons collect at the surface and some are localized there until the surface potential is equal to that of the negative bottom plate. Then the filament current is shut off and the voltage left on between the plates so that there is a field drawing electrons into the gas. As they escape, the change in surface potential is indicated on a recorder tracing. The main difference from the previous result where the electrons were deposited from the gas is that the rate constant is much smaller. The squares in Fig. 2 show k for this case. As before, the initial field was of order 100 V/cmfor all points.

We shall refer to the electrons deposited on the surface from above as being in "outside" states, and those deposited from the liquid side as being in "inside" states. For the outside states we found a weak field dependence of k such that k increases with increasing field. This is shown by the data in Table I. This, together with the absence of any observable activation energy suggests that these electrons escape from the surface by tunneling. We have not yet investigated the field dependence of k for the inside states.

We tentatively identify the outside states as those described by Cole and Cohen's image potential model.<sup>3</sup> This inside states appear to be those studied by Bruschi, Maraviglia, and Moss<sup>4</sup> and by Schoepe, Probst, and Dransfeld<sup>5,6</sup> in their experiments with the current injected into the liquid from a radioactive source. The activation energy, indicated by the data in Fig. 1 for the inside states, is  $E/k_{\rm B} = 27^{\circ}$ K. This lies between the values reported by the two groups above. It is clear that the outside and inside states are

Table I. $k$ as a function of initial field, $E_0$ .	
E <sub>0</sub> (V/cm)	k (sec <sup>-1</sup> )
70	$0.6 \times 10^4$
105	1.0
140	1.3
210	1.7

different. In addition to the large difference in rate constants we observe the outside states both above and below the lambda point of helium, whereas the effects reported in Refs. 4-6 could be observed only below the lambda point.

The observations on the electrons in the outside states raise several questions which will be discussed in an article now in preparation. These include the kinetics of the escape from the surface and the effects of the condenser force exerted by the electrons on the liquid.

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