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Spectroscopy of electrons in image-potential–induced surface states outside liquid helium

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We report a spectroscopic study of electronic transitions from the ground state to several excited states in the potential well lying outside the free surface of liquid helium formed by the long-range attractive-image potential and the short-range electron-atom repulsive potential. These electric dipole transitions were observed at frequencies from 130 to 220 GHz by measuring the microwave absorption derivative at fixed frequency as the splittings between states were tuned to resonance by an applied electric field $\mathcal{E}$. Transitions were observed between the ground state and the first through seventh excited states, and detailed measurements were made of the frequency versus $\mathcal{E}$ relation for transitions to the first and second excited states. Extrapolation of the respective data to $\mathcal{E} = 0$ yields splittings of 125.9 ± 0.2 and 148.6 ± 0.3 GHz and initial Stark-tuning rates of 2.3 ± 0.1 and 5.9 ± 0.4 GHz/(V/cm). The data can be fit satisfactorily by variational calculations based on a simple model potential which takes the origin of the image potential to lie 1.04 Å inside the liquid-helium surface. These calculations show the wave functions to be significantly compressed by the Stark-tuning fields; e.g., the second excited state is compressed at our highest fields to 1/2 of its original size. Measurements of the linewidth of the lowest transition as a function of the helium vapor density are reported. The peak-to-peak line width is 1.0 GHz at a vapor density of 5×10^{18} atoms/cm^3 and increases approximately linearly with increasing vapor density. A phenomenological theory of several mechanisms contributing to the linewidth is discussed.

I. INTRODUCTION

An electron in the vapor outside a liquid-helium surface is attracted toward the surface by the image force, whereas within a few angstroms of the surface the electron encounters a strong repulsive barrier arising from the Pauli exclusion principle. The potential well formed by the sum of the image potential and the repulsive barrier supports a series of bound electron states which are very similar to the s states of the hydrogen atom, but bound with four orders of magnitude less energy. The results of a preliminary spectroscopic study of transitions between the lowest bound state and the first two excited states in the presence of an external electric field were reported earlier.[1] The purpose of this paper is to report a significantly more detailed experimental study of these transitions over a wider range of frequencies and helium vapor pressures, and to present a comparison of the data with simple model calculations.

The possibility that the potential well outside a liquid-helium surface could support a series of bound electron states was first pointed out by Sommer.[2] The idea was independently rediscovered and further elaborated a few years later by Cole and Cohen[3] and by Shikin.[4] The first experimental investigations reported measurements of the mobility[5] and the trapping lifetime.[6] A subsequent experiment designed to measure both the mobility and trapping lifetime failed to yield evidence for the existence of the surface states.[7] A cyclotron-resonance experiment[8] confirmed the existence of surface states and supported the mobility measurements of Sommer and Tanner.[5] Two groups have recently performed mobility measurements which reveal that the surface-state electron (SSE) mobility parallel to the surface is appreciably reduced in the presence of a strong electric field pressing the electrons against the helium surface.[9,10] Several theoretical papers have been written on the possibility that the two-dimensional electron gas formed by the SSE might undergo a gas-to-solid transition at low temperatures and high densities.[11-14] Other theoretical papers have explored the effect of the electron-ripplon interaction on the mobility,[3,15] the transition to a polaronlike bound electron-ripplon state, i.e.,[15-17] the plasmon dispersion relation,[12,18,19] and a macroscopic density instability.[20] Cole has reviewed the work on SSE through 1973.[21]

In Sec. II, we present an elementary discussion of the bound electronic states in a "hydrogenic" approximation. We then describe the apparatus and experimental procedures in Sec. III followed by the principal experimental results in Sec. IV. In Sec. V we first discuss the splittings between states in the absence of perturbing fields and test several models of the liquid-helium surface for compatibility with our observed splittings. We then discuss the increase in the splittings between states in the presence of an electric field which presses the electrons against the helium surface. The experimental results are found to agree well with a simple variational calculation. Section VI contains experimental results on the spectroscopic line widths as a function of the helium vapor pressure and presents a comparison of the measurements with a phenomenological theory of the line width. Sections VII and VIII then conclude this work.

II. HYDROGENIC APPROXIMATION

The potential energy of an electron outside a free surface of liquid helium consists predominantly of two parts: the long-range attractive image potential arising from polarization of the helium atoms and a short-range repulsive barrier to penetration into the liquid helium arising from the Pauli exclusion principle. The exclusion principle requires that the wave function of an excess electron in the liquid must be orthogonal to the wave functions of the core electrons on the helium atoms. The orthogonalization raises the electronic energy by about 1 eV, and consequently presents a strong repulsive barrier to penetration into the liquid helium.[22,23] The repulsive potential rises to its full value over a distance of a few angstroms as the vapor-liquid interface is traversed.

Another contribution to the energy of an electron above a free helium surface arises from interaction of the electron with helium atoms in the vapor.[24] This interaction raises the electron energy appreciably, but it can be shown that it raises the energy of all eigenstates by the same amount when the gas density is uniform. Consequently, the time-average splittings between bound states are unaffected by the vapor, although fluctuations in the vapor density do contribute to the line width as will be discussed below.

To illustrate the nature of the bound states and to obtain a first approximation to the binding energy, the spectroscopic splittings, and the Stark tuning rates, we take the helium surface to be planar, the helium density to change abruptly from the bulk liquid value inside the surface to zero outside the surface, and we assume an infinite repulsive barrier. The electronic potential is then $V(x)=\infty$ for $x\leq 0$; $V(x)=-Ze^2/x$ for $x>0$, where $z=(\epsilon-1)/4(\epsilon+1)$, as can be obtained from classical electrostatic considerations. The electrons are assumed to move freely in the y-z plane so the wave equations describing the motions parallel and perpendicular to the surface are separable. This leads to a wave function of the form $\Psi(\vec{r})=e^{i\vec{k}\cdot\vec{R}}\Phi_n(x)$, where $\vec{R}$ is a vector in the plane of the surface. The $\Phi_n(x)$ are then described by the one-dimensional Schrödinger equation

$$\frac{-\hbar^2}{2m}\frac{d^2\Phi_n}{dx^2}+V(x)\Phi_n=E_n\Phi_n\,, \tag{1}$$

which is identical to the radial wave equation for $rR(r)$ for s states of the hydrogen atom. Requiring the wave functions to vanish at the origin and at infinity then yields the hydrogenic eigenenergy spectrum

$$E_n=\frac{-mZ^2e^4}{2\hbar^2n^2}=\frac{-Z^2R}{n^2}\,, \tag{2}$$

where R is the rydberg. Since the dielectric constant of liquid helium is close to unity ($\epsilon=1.057\,23$),[25] the effective nuclear charge Z is small ($Z^2\approx 5\times 10^{-5}$) and the binding energy is small, $E_1\approx 0.6$ meV. The smallness of the binding energy ensures that the infinite-barrier approximation is reasonable. In this "hydrogenic" approximation the splittings between the ground state and the first two excited states are, in frequency units, 119.3 and 141.3 GHz. These splittings, expressed in temperature units, are 5.7 and 6.8 K, so at ≈1 K, where the experiments are performed, only the ground state has a significant thermal population.

In the mm-wave region corresponding to the splittings between bound states, it is convenient to perform experiments at a fixed frequency and to vary the spectroscopic splittings by Stark tuning. If an electric field $\mathcal{E}$ is applied perpendicular to the surface along the x axis, the electronic potential becomes $V(x)=-Ze^2/x+e\mathcal{E}x$. In the hydrogenic approximation, first-order perturbation theory yields the perturbation to the nth eigenenergy $\Delta E_n=e\mathcal{E}\langle x\rangle_n$, where $\langle x\rangle_n$ is the expectation value of x for the nth unperturbed eigenstate. Owing to the weak binding of the image potential, the values of $\langle x\rangle_n$ for the three lowest eigenstates have the remarkably large values 114, 456, and 1026Å, respectively. Consequently, the calculated *linear* Stark tuning rates are appreciable: 0.8 and 2.1 GHz/(V/cm) for transitions between the ground state and the first and second excited states, respectively. Thus, modest electric fields can tune the splittings by tens of GHz. It is interesting to note that because of the asymmetric potential, the eigenstates are not states of parity and the electric field produces a *linear* Stark effect. Note also that it is not possible to extend this calculation to higher electric fields by employing a second-order perturbation theory because even the weakest electric field radically changes the higher-energy eigenfunctions.

III. APPARATUS AND PROCEDURES

Two different microwave absorption cells which yield equivalent results have been employed in the experiments. One cell is a right circular cylinder of radius 1.1 cm and height 0.32 cm; the other is a rectangular box $2.2\times 1.32\times .19$ cm^3. Microwaves are coupled into and out of the cells by two tapered wave guides oppositely placed on the side walls. One wave guide is terminated by our detector, an InSb bolometer[26] which is operated in the liquid helium. The other leads to a standard wave guide which carries 0.1 μW of mm-wave radiation to the cell from the source, a Schottky barrier diode doubler driven by an appropriate klystron. The electron source is a 0.001-cm-diam thoriated tungsten filament. The top and bottom surfaces of the cells are electrically isolated from the sides which are grounded to the incoming wave guide. The cells are placed in a vacuum-tight can which is then immersed in a pumped helium bath capable of cooling to 1.2 K.

A typical experimental run consists of condensing sufficient helium into the vacuum can to half fill the cell at 1.2 K. The voltages on the top and bottom plates are adjusted so the helium surface is at a small positive potential of the order of 1 V. The center of the filament is biased so electrons are attracted only toward the helium surface and cannot reach the top plate or the walls of the cell. The filament is then briefly heated to charge the helium surface with approximately 10^7 electrons/cm^2 until their space-charge potential cuts off further current to the surface. The filament is then turned off, and the voltage between the top and bottom plates is swept by a triangular wave form applied in a way that maintains the helium surface at the same positive potential. This procedure enables us to vary the perpendicular electric field acting on the electrons without allowing the number on the surface to change. In this manner, charge can be held on the surface for hours. Simultaneously with the above potentials, a small 100-kHz sine-wave voltage (about 0.1 V) is applied across the plates through a transformer. The bolometer output is synchronously demodulated at 100 kHz, yielding dA/dV, the derivative of the microwave absorption with respect to the voltage across the cell. The absorption derivative is fed into one axis of an x-y recorder while the dc potential difference between the plates is applied to the other axis. All the results reported here have been obtained in the small-signal, low-density limit where both nonlinear and collective effects are negligible.

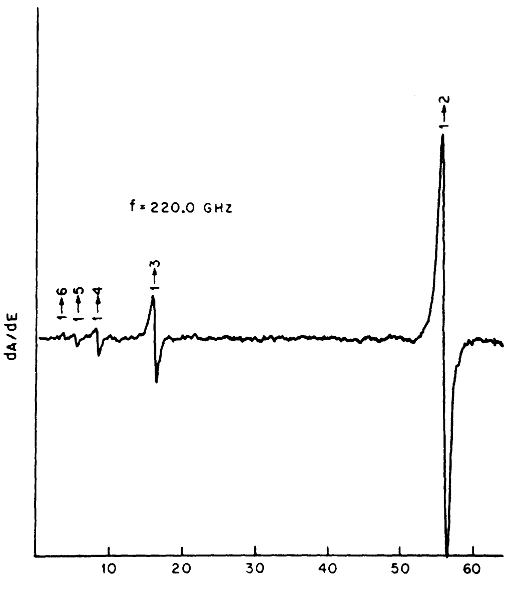

FIG. 1. Experimental recording of mm-wave absorption derivative vs the potential difference across the experimental cell taken at a frequency of 220 GHz and temperature of 1.2 K. The linear Stark effect is employed to tune the splittings between bound electronic surface states on liquid helium to resonance with the applied radiation. The $1\rightarrow 2$, $1\rightarrow 3$, ... transitions are analogous to the Lyman α, β, ... transitions of the hydrogen atom.

IV. EXPERIMENTAL RESULTS

Figure 1 shows an experimental trace taken at 220 GHz. The larger absorption-derivative signal is due to transitions from the ground state, $n=1$, to the first excited state, $n=2$; the smaller signals arise from transitions between the ground state and the second through fifth excited states. Traces taken with higher gain display additional transitions to the sixth and seventh excited states. The observed lines will display a small systematic shift in position with increasing surface charge density unless the cell is exactly half full of helium.[27] The liquid-helium level is carefully adjusted until there is no shift in line position with changes in surface charge density. A series of traces similar to Fig. 1 are then taken over a wide range of frequencies. The frequency is measured to 0.2% accuracy with an absorption-type wavemeter, while the positions of the line centers are readily established to within ±0.2 V from the traces. A plot of resonance frequency versus potential difference across the cell at resonance is presented in Fig. 2 for the $1\rightarrow 2$ and $1\rightarrow 3$ transitions. Linear extrapolation of the lowest data points to $V=0$ yields 125.9 ± 0.2 GHz for the unperturbed splitting between the ground and first excited states. Similarly, we obtain 148.6 ± 0.3 GHz for the splitting between the ground and second excited states at $V=0$. Both of these splittings are significantly larger than predictions based on the simple hydrogenic approximation.

The measured Stark tuning rates at low voltages are 2.3 ± 0.1 GHz/V for the $1\rightarrow 2$ transition and 5.9 ± 0.4 GHz/V for the $1\rightarrow 3$ transition. If we convert the applied voltages to electric fields by dividing them by the cell height (0.318 cm), we find that the measured tuning rates are about 10% less than those predicted in the "hydrogenic" approximation in Sec. II. However, the ratio of the measured tuning rates is 2.6 ± 0.2, in good agreement with 2.67, the value expected from the "hydrogenic" first-order perturbation calculation. The relative absorption cross sections of the two resonances are in the ratio 5:1, in agreement with that expected for electric-dipole transitions between the "hydrogenic" eigenstates. In Sec. V we discuss more realistic models of the helium surface which yield predicted splittings and Stark tuning rates that are in closer agreement with experiment.

V. MODEL CALCULATIONS

To make a more realistic calculation of the expected splittings, we need to treat the case of a finite barrier to electron penetration into the liquid. However, if we proceed in the usual fashion and attempt to match the wave function and its derivative across the surface, we encounter mathematical difficulties arising from the singularity in the Coulomb potential. In the remainder of this section we review model calculations designed to circumvent this difficulty.

Huang *et al.* have calculated the helium atom density distribution in the vicinity of the liquid-vapor interface, then self-consistently calculated the binding energy of a surface-state electron.[28] They obtained a binding energy of 9 K which corresponds to a ground-state–to–first-excited-state splitting of 140 GHz, which is again 10% too large. Their article did not contain enough detail to allow the reader to critically examine their calculation.

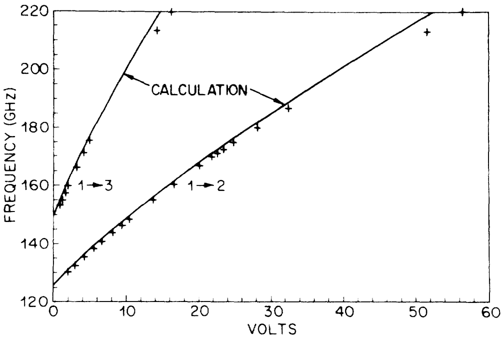

FIG. 2. Plot of transition frequencies vs voltage across the experimental cell. The crosses are measured data points while the solid curves are the result of the variational calculation based on a simple model potential described in the text. The curvatures in the plots arise from compression of the electronic wave functions by the electric field which presses the electrons against the helium surface.

Cole and Cohen reasoned that the image-potential concept should not be valid at distances from the liquid-vapor interface that are less than the interatomic spacing in the liquid. For simplicity of calculation they simply truncated the $1/x$ potential at a distance b from the interface and kept the potential constant at $-Ze^2/b$ for $0 \leq x \leq b$. With this model and a 1-eV repulsive barrier, the parameter b must be ≈10 Å to yield a ground-state–to–first-excited-state splitting equal to the observed value. Such a large value of b is not consistent with the assumptions underlying the model.[29]

We choose to approximate the potential at the helium surface by $V(x) = 1.0$ eV for $x \leq 0$ and $V(x) = -Ze^2/(x+\beta)$ for $x > 0$. This is treating the potential outside the surface as if the image potential has its origin a small distance β inside the liquid. For this model potential the eigenfunctions become simply the "hydrogenic" wave functions matched in slope and magnitude at the helium surface to an exponential decaying into the liquid. Using a method pointed out by Sanders and Weinreich,[30] the eigenenergy of the nth state is then given by

$$E_n = E_n^0 + \frac{\hbar^2}{2m}\left[\beta - \left(\frac{\hbar^2}{2mV_0}\right)^{1/2}\right][\Psi_n^{0\prime}(0)]^2, \tag{3}$$

where E_n^0 is the hydrogenic eigenenergy and $\Psi_n^{0\prime}(0)$ is the slope of the hydrogenic eigenfunction at the helium surface. The adjustable parameter β takes the value 1.04 Å when the $1 \to 2$ splitting is set equal to the experimentally determined value (125.9 GHz) at $\mathcal{E} = 0$. With β equal to 1.04 Å the calculated value of the $1 \to 3$ transition becomes 148.7 GHz which agrees with the experimental value of 148.6 ± 0.3 GHz.

Since the electrons are so weakly bound and their wave functions extend so far above the helium surface, the wave functions are significantly compressed by moderate applied electric fields. To take proper account of this compression in the calculation of the Stark tuning rate, we have employed a variational calculation which uses exponentially decaying polynomials as trial functions. The groundstate trial function is first normalized, then the expectation value of the Hamiltonian (which now contains the electric-field term) is minimized with respect to the spatial extent of the wave function (which for the ground state is the effective "Bohr radius" of the state). The trial function for the first excited state is then normalized and orthogonalized to the ground-state wave function which has been compressed by the applied electric field. The expectation value for the Hamiltonian is then calculated and minimized. Minimizing the Hamiltonian requires finding the appropriate root of a cubic equation for the ground state, a sixth-order equation for the first excited state, and so forth. Hence, we have found the roots numerically, and with the same program have calculated the slopes of the perturbed wave functions at the helium surface. These slopes are used in Eq. (3) as before to correct the eigenenergies for the finite penetration of the wave functions into the liquid helium. To convert the calculated fields to potential differences we use classical electrostatics and treat the cell as an infinite parallel-plate capacitor half filled with liquid helium. The resulting energy differences as a function of voltage for the $1 \rightarrow 2$ and $1 \rightarrow 3$ transitions are plotted as the solid curves in Fig. 2. It is clear from Fig. 2 that although the theory does lie consistently above the data, the variational calculation yields close agreement with the experimental data points for all frequencies up to about 180 GHz. At still higher frequencies the calculated splittings progressively deviate from the measured values. (Note that β was the only adjustable parameter in the calculation and it was fixed at 1.04 Å to fit the observed $1 \rightarrow 2$ transition frequency at $\mathcal{E} = 0$.) To illustrate the compression of the wave functions, we find that a modest field of 100 V/cm reduces the expectation values of x to 93%, 70%, and 51% of their $\mathcal{E} = 0$ values for the $n = 1$, 2, and 3 states, respectively.

VI. LINEWIDTH

We have investigated the variation of the $1 \rightarrow 2$ transition linewidth as a function of temperature from 1.3 to 1.6 K. We observe an approximately linear dependence on the helium-atom density in the vapor outside the surface. We attribute this linear dependence to two mechanisms (to be explained in greater detail below) of approximately equal importance. One is a direct scattering process in which the parallel momentum (with respect to the surface) of the electron is changed, resulting in a loss of phase between the perpendicular eigenstates. This process of phase loss is reminiscent of those which contribute to the T_2 relaxation times in spin resonance. The other source of linewidth is due to the fact that the electron is moving through a fluctuating potential, namely, the helium atoms in the vapor. Since these are distributed randomly, the electron—as it moves through the gas—interacts with a varying number of atoms, causing the difference between the energy levels to fluctuate. Because the electron moves quickly, these fluctuations are quite fast and are partially averaged out by a motional narrowing effect.

Figure 3 shows the results of our studies of linewidth variation with helium-atom density in the vapor. The data points were taken at three different frequencies and low electron densities ($\sim 10^6$ electrons/cm^2) to eliminate collective effects. They have been converted from the peak-to-peak voltage splitting of our experimental curves using the measured value of $d\nu/dV$ obtained from Fig. 2. As can be seen, the results show a linear dependence on the gas density. We attribute the nonzero intercept to the effects of inhomogeneous broadening owing to small nonuniformities in the perpendicular electric field in the experimental cell. The slope of the data points in Fig. 3 is approximately 1.2×10^{-10} Hz/(particles/cm^3).

Assuming the line to be Lorentzian, i.e., signal $\sim \Delta\nu / (\Delta\nu^2 + \nu_{sc}^2)^2$ where $\Delta\nu = \nu - \nu_{1\rightarrow 2}$, we can extract from the slope of Fig. 3 a scattering frequency per helium atom. This is $(\sqrt{3}/2) \times 1.2 \times 10^{-10}$ Hz/(atom/cm^3). The extrapolated residual linewidth for the 148 GHz data points at zero gas density is approximately 300 MHz which corresponds to a root-mean-square variation of the electric field of the order of 0.3 out of 35 V/cm.

Before going into greater detail concerning the scattering process mentioned above we should eliminate the most obvious possibility for the linear dependence of the linewidth on gas density, namely, a simple scattering process whereby an

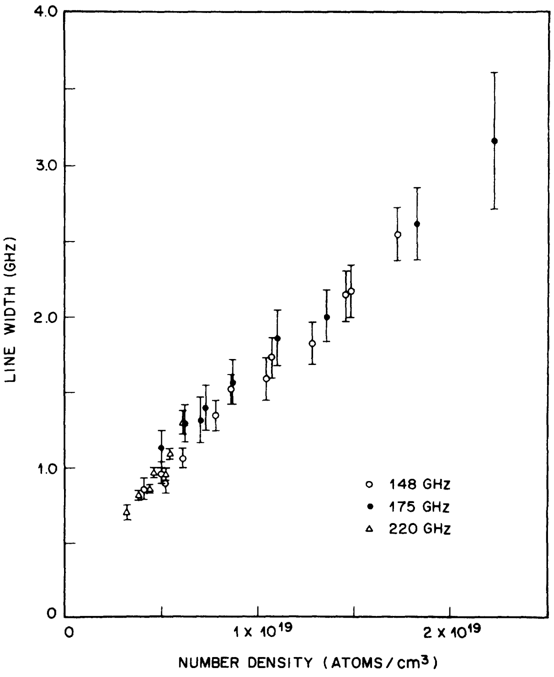

FIG. 3. Plot of peak-to-peak linewidth (in GHz) measured for the $1 \rightarrow 2$ transition vs the helium vapor density in the experimental cell.

electron in the excited state is deexcited to the ground state by a collision with a helium atom. Using a point-interaction pseudopotential, $V_0\delta(\vec{r}-\vec{r}_a)$, where $V_0=2\pi a_s\hbar/m$ (a_s is the scattering length for the electron-helium scattering), we have calculated this rate and find it to be

$$4\pi^2\frac{\hbar}{m}a_s^2\int_0^\infty \Phi_1^2(z)\Phi_2^2(z)\,dz\,,$$

where $\Phi_1(z)$ and $\Phi_2(z)$ are the eigenfunctions for the ground and first excited states, respectively, and the other symbols have their usual meanings. When evaluated, this expression gives approximately 0.1×10^{-10} Hz/particles/cm^3, which is too small by a factor of 10 to explain the data.

The scattering process mentioned at the beginning of this section is one in which the phase relation between the excited state and ground state is destroyed even though the electron is not actually deexcited. To calculate this we take the electron wave function to be a superposition of the two states,

$$\Psi=e^{i\vec{k}\cdot\vec{R}}[\Phi_1(z)+\Phi_2(z)e^{i\omega_{12}t}]\,,$$

and ask what a scattering event in which only the parallel momentum direction is changed, i.e., $\vec{k}\to\vec{k}'$, will do, assuming a single helium atom located at r_a.

We initially consider the two states separately. From standard scattering theory we can write the scattered wave function as a sum of the initial part plus a scattered part,

$$e^{i\vec{k}\cdot\vec{R}}\Phi_j(z)\to[e^{i\vec{k}\cdot\vec{R}}+a_jf(R)]\,\Phi_j(z),$$

where $j=1,2$, $f(R)$ is an outgoing cylindrical wave, and a_j is the scattering amplitude for the jth perpendicular state. Note that the a_j depend on Φ_j because the probability of interaction with a helium atom is proportional to $|\Psi|^2$ at that helium atom which is of course different for different perpendicular states. Thus the superposition of the two states would give

$$\begin{aligned}e^{i\vec{k}\cdot\vec{R}}[\Phi_1(z)+\Phi_2(z)e^{i\omega_{12}t}]&\to[e^{i\vec{k}\cdot\vec{R}}+a_1f(R)]\,\Phi_1(z)+[e^{i\vec{k}\cdot\vec{R}}+a_2f(R)]\,\Phi_2(z)e^{i\omega_{12}t}\\&=[e^{i\vec{k}\cdot\vec{R}}+\tfrac{1}{2}(a_1+a_2)f(R)]\,[\Phi_1(z)+\Phi_2(z)e^{i\omega_{12}t}]+\tfrac{1}{2}(a_1-a_2)f(R)[\Phi_1(z)-\Phi_2(z)e^{i\omega_{12}t}]\,.\end{aligned}$$

Inspecting the last expression, we see that if $a_1=a_2$, then the scattering event will in no way perturb the coherence of the initial superposition and thus will have no effect on the linewidth. On the other hand, if $a_1\neq a_2$, the electron can undergo a process whereby the phase between the two parts of the wave function changes by π. This is sufficient to disturb the coherence of the oscillation and thus contributes to the linewidth. The probability for this is simply $(\frac{1}{2}|a_1-a_2|)^2$ in the above notation.

Calculation of this rate using the above pseudopotential gives

$$\nu_{sc}=\frac{\pi^2\hbar}{m}\,a_s^2\left(\int_0^\infty\Phi_1^4\,dz+\int_0^\infty\Phi_2^4\,dz-2\int_0^\infty\Phi_1^2\Phi_2^2\,dz\right)\,.$$

Numerically this yields $\nu_{sc}=0.3\times10^{-10}$ Hz/particle/cm^3. Thus out of a total scattering frequency of 1×10^{-10} Hz/particle/cm^3 we are able to explain 40% by scattering processes.

In order to explain the rest of the linewidth we now must consider the shifts of the actual energy levels caused by the presence of helium atoms in the vapor. Because of the multiple scattering aspects of this problem we will only estimate this term roughly.

Using first-order perturbation theory and taking $V(R)=\sum_{\text{atoms}}V_0(\vec{r}-\vec{r}_a)$ we find immediately

$$\langle\Delta E_n\rangle=\langle(\Psi_n|V|\Psi_n)\rangle=\left\langle\sum V_0|\Psi(r_a)|^2\right\rangle,$$

where $\langle\;\rangle$ indicates an average over atomic positions. If we assume no correlation between the positions of the electron and helium atoms (reasonable at such low helium densities), we can replace the sum by $N(1/V)\int dr_a$ where V is the volume of the system and the integral is to average over all possible positions of the atoms. This gives $\Delta E_n=NV_0/V$, thus showing that the presence of the helium vapor will cause a constant shift of the energy levels. However, because of the random nature of the vapor, the electron will sometimes be interacting with more or less atoms, leading to a fluctuation in ΔE_n which, we will see, depends on Φ_n.

We need to evaluate

$$\langle\Delta E_{12}^2\rangle=\langle(\Delta E_1-\Delta E_2)^2\rangle=\langle\Delta E_1^2\rangle+\langle\Delta E_2^2\rangle-2\langle\Delta E_1\Delta E_2\rangle\,.$$

Now

$$\begin{aligned}\langle\Delta E_1^2\rangle&=\left\langle\sum_{\vec{r}_i,\vec{r}_j}V_0^2|\Psi_1(r_i)|^2|\Psi_1(r_j)|^2\right\rangle\\&=\sum_{r_i}V_0^2|\Psi_1(r_i)|^4+\sum_{i\neq j}V_0^2|\Psi_1(r_i)|^2|\Psi_1(r_j)|^2\\&=V_0^2\frac{N}{V}\int_0^\infty|\Psi_1(r)|^4\,d\vec{r}+V_0^2\frac{N(N-1)}{V^2}\left(\int_0^\infty|\Psi_1(r)|^2dr\right)^2\\&=V_0^2\rho\int_0^\infty\Psi_1^4(r)\,dr+V_0^2\rho^2,\end{aligned}$$

where $\rho = N/V$, and we have dropped the absolute value signs since $\Psi(r)$ is real.

Similarly,

$$\langle \Delta E_2^2 \rangle = V_0^2 \rho \int_0^\infty \Psi_2^4(r)\, dr + V_0^2 \rho^2 \ ,$$

$$\langle \Delta E_1 \Delta E_2 \rangle = V_0^2 \rho \int_0^\infty \Psi_1^2 \Psi_2^2\, dr + V_0^2 \rho^2 .$$

Thus we have

$$\langle \Delta E_{12}^2 \rangle = \rho V_0^2 \int_0^\infty (\Psi_1^2 - \Psi_2^2)^2\, d\vec{r}.$$

Taking $\Psi_n = (2/R_0) e^{-R^2/R_0^2} \Phi_n(z)$ we can evaluate this expression, finding

$$\langle \Delta E_{12}^2 \rangle = 0.9 \rho V_0^2 / R_0^2 a_0.$$

This form for Ψ is, of course, completely ad hoc and is only meant to enable us to estimate the order of magnitude of this fluctuating term. If we use $R_0 = 260$ Å (chosen so that the average kinetic energy of the electron parallel to the surface is kT for $T = 1.3$ K), then we find $\langle \Delta E^2 \rangle^{1/2}/h = 40$ GHz, for $\rho = 10^{19}$ atoms/cc.

Since our linewidth is many times less than this and has a linear dependence on gas density, whereas this term would predict a square-root dependence, it is clear this term by itself is unable to explain our observations. However, since the electron is presumably moving rapidly through the helium vapor, we can reasonably expect some type of motional narrowing to take place if the correlation time of the fluctuations is rapid enough. In this case the correct formula for the linewidth would be $\Delta\omega = \langle \Delta E_{12}^2 \rangle \tau_c / \hbar^2$, where τ_c is the correlation time of the fluctuations.

Using the same wave function as above, a reasonable estimate for τ_c should be R_0 / V_{th} where V_{th} is the average velocity parallel to the surface. This gives

$$\Delta\omega = \frac{0.9 \rho V_0^2}{R_0^2 a_0} \frac{R_0}{\hbar^2 V_{\text{th}}} \ ,$$

which has the correct ρ dependence.

Treating R_0 as an adjustable parameter and demanding $\Delta\omega/2\pi = 0.6 \times 10^{-10}$ Hz/particle/cm^3, we find $R_0 = 1200$ Å. In view of the difficulty of performing more exact calculations, we feel this simple model indicates that the remaining fraction of the linewidth dependence can be satisfactorily explained by this motionally narrowed fluctuating term.

In attempting to fit our lines we have used both Lorentzian and Gaussian line shapes. We find that the line is clearly fit better by the Lorentzian, although the wings are not quite as large as they should be. This could be easily explained by the motional narrowing since we do not know the actual fluctuation spectrum due to the electron moving through the background gas.

In summary, we feel that our linewidths can be reasonably explained by a combination of processes involving the electron interacting with the helium atoms in the vapor. Approximately half the linewidth comes from direct scattering processes while the rest is due to a motionally narrowed fluctuating term which comes about because the electron is moving through a gas and thus interacting with a variable number of helium atoms.

VII. DISCUSSION

Our experimental study of electronic transitions between bound states outside liquid helium provides a sensitive probe of the electronic potential in the vicinity of the surface. In the absence of externally applied fields, the electronic potential originates from electric polarization of the helium atoms and from the repulsive electron-atom interaction owing to the Pauli exclusion principle. Consequently, the electronic potential is governed by the density distribution of the helium atoms in the vicinity of the liquid-vapor interface, and surface-state electron spectroscopy can be considered a sensitive probe of the density distribution. Several calculations of the density distribution at the liquid-vapor interface have been published recently.[31-34] We want to encourage others to test their density distributions by using them to calculate the eigenenergy spectrum for surface-state electrons and comparing their results with the measured values reported here. Thus far, the best fit to the experimental data was obtained with our rather primitive model potential together with a variational calculation to treat the effect of an electric field.

We would like to emphasize the pedagogical appeal of this system. The eigenstates are obtained from the one-dimensional Schrödinger equation which, with appropriate boundary conditions, yields s-state hydrogenic eigenfunctions. The corresponding eigenenergy spectrum has bound-state energies proportional to an effective Rydberg divided by n^2. An applied electric field can be treated approximately by a first-order perturbation calculation which yields the "physical" result that the eigenenergies are raised by $e\mathcal{E}\langle x \rangle_n$. The states lack parity and provide an interesting example of a physical system which displays a linear Stark effect. Also, a variational calculation of the Stark effect embodies the very "physical" concept that the electric field compresses the unusually fluffy electronic states.

Taken together, we feel that these factors make the surface-state electrons an exceptionally simple and instructive quantum-mechanical system.

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