

data of Madden, Ederer, and Codling.³

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Field Calibration Using the Energy Distribution of Field Ionization*

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The accuracy of data obtained by field-ion microscopy is often limited by a $\pm 15\%$ uncertainty of converting measured voltages into field strengths. Plotting the difference of relative energy deficits of free-space ionized H_2 , D_2 , or Kr for sets of two applied voltages against the logarithm of the voltage ratios yields a field factor k . The surface field $F_0 = V/k\mathbf{r}_t$ is obtained with the 3% accuracy by which the tip radius \mathbf{r}_t can be known. The method is applicable to all metals accessible to field-ion microscopy.

Field-ion microscopy¹ is increasingly used for quantitative investigations of surface phenomena such as field adsorption of noble gases,² or surface migration and surface binding energy³⁻⁵ of individual atoms. All the data obtained require knowledge of the field strength F_0 at the tip surface, yet only the applied voltage V can be measured with any accuracy. A proportionality factor $\beta = F_0/V$ may be calculated for the quite unrealistic spherical case, or the better approximation of electrode geometry by confocal paraboloid, hyperboloid, or sphere-on-cone configurations. However, in real experiments the tip geometry is more complicated, with local radii

varying over the emitting area and usually unknown shapes of the tip shank. Thus an experimental determination of β directly from emission data is most desirable. It may be surprising that essentially all field-ion data available are based on a calibration by Müller and Young,⁶ who, assuming the validity of the Fowler-Nordheim equation, used field electron emission from a field-evaporated tip to determine the best image field (BIF) of tungsten in helium to be about $4.5 \text{ V}/\text{\AA}$, with a small dependence on the tip radius. The accuracy of this calibration was estimated to be not better than $\pm 15\%$, although for a given tip the best image voltage can be reproduced to within 1

or 2%.

Experimental ionization fields of all other image gases such as Ne, Ar, and H₂ are based on comparison of the BIF for helium, using the same tip. It has further been tacitly assumed that the helium BIF of any other refractory metal is also 4.5 V/Å, and the experimental evaporation fields of sixteen different metals^{7,8} are derived from this one field calibration.

This situation is unsatisfactory as field-ion-microscopical measurements are becoming more precise, and the chemically specific effects of directional wave functions and their interaction with field-adsorbed gases can no longer be neglected.⁹

We present in this paper a new method of field calibration that is based on field ionization and will be applicable to all metals that give stable field-ion images. We use the energy distribution of field ionization in free space, some 30 to 150 Å above the tip surface. This regimen can be reached with hydrogen or deuterium at all refractory metals, as field ionization lifts off the surface at $F_0 > 2.9$ V/Å.¹⁰ For the nonrefractory metals, for which hydrogen-promoted field evaporation might pose a problem, krypton may be employed advantageously.

If x is the distance from the tip surface of radius r_t to which the voltage V is applied, the field strength in space may be described by the hyperboloid approximation¹¹

$$F(V, x) = V/k(r_t + 2x), \quad (1)$$

which makes the field at the surface

$$F_0(V) = V/k r_t, \quad (2)$$

an equation commonly used.¹² Free-space ionization depends essentially on the field at the gas molecule only, and not upon the property of the surface. The position x_i where free-space ionization peaks at a certain field $F(V_i, x_i)$ moves outward with increasing applied voltage V_i , so that

$$F(V_1, x_1) = F(V_2, x_2) = \dots = F(V_i, x_i). \quad (3)$$

Compared to the energy eV_i an ion would have if it originated at the surface, an ion formed at x_i has an energy deficit given by

$$\begin{aligned} \Delta E(V_i, x_i) &= e \int_0^{x_i} F(V_i, x) dx, \\ &= e \int_0^{x_i} \frac{V_i}{k(r_t + 2x)} dx, \\ &= \frac{eV_i}{2k} [\ln(r_t + 2x_i) - \ln r_t], \end{aligned} \quad (4)$$

$$\frac{\Delta E(V_i, x_i)}{eV_i} = \frac{1}{2k} \ln \left(1 + \frac{2x_i}{r_t} \right). \quad (5)$$

Using Eqs. (1) and (3) we can write for two different applied voltages V_1 and V_2

$$\frac{V_1}{V_2} = \frac{1 + 2x_1/r_t}{1 + 2x_2/r_t}, \quad (6)$$

and we eliminate x_i and r_t from Eqs. (5) and (6):

$$\frac{\Delta E(V_1, x_1)}{eV_1} - \frac{\Delta E(V_2, x_2)}{eV_2} = \frac{1}{2k} \ln \left(\frac{V_1}{V_2} \right). \quad (7)$$

Thus the geometrical field factor k may be experimentally determined by measuring energy deficits $\Delta E(V_i, x_i)$ at various applied voltages V_i .

The validity of our method rests on the assumption, as expressed in Eq. (3), of an essentially fixed field strength at which free-space field ionization peaks. We believe this statement to be acceptable because under high-field conditions complete ionization occurs on the first approach towards the tip. The gas supply function to the critical volume element is simple, as the kinetic energy of the polarized molecules is $kT + \frac{1}{2}\alpha F^2$, that is, essentially a function of F only. The kinetic energy for the typical condition of H₂ or D₂ at 3 V/Å is 0.25 eV, large compared to kT . There is no complication by molecules rebounding from the shank. The efficient thermal accommodation to the low tip temperature prevents these molecules from reaching the near-apex region before being ionized.

We employed a 60°, second-order focusing mass spectrometer, an improved version of the device used by Barofsky and Müller.¹³ A small area of the field-ion image is selected by a probe hole in the screen, and the spectrum is displayed on a phosphor screen after amplification with a microchannel plate. The energy resolution is 2 eV. Ion spectra are photographed, and energy deficits at the distribution peak found by microdensitometry are determined. Table I gives experimental data for D₂ ions from a tungsten tip. The difference of relative energy deficits for two applied voltages is plotted against the logarithm of the voltage ratios. The resulting straight line corroborates our assumption of Eq. (3). From its slope k is determined within about 1%. For this particular tip and the crystallographic area seen through the probe hole, about (531) which lies half-way between (110) and (311), the field factor is $k = 7.95$.

TABLE I. Experimental data for a tungsten tip.

i	V_i (V)	$\Delta E(V_i, x_i)$ (eV)	$10^2 \frac{\Delta E(V_i, x_i)}{eV_i}$	V_i/V_1	$\ln(V_i/V_1)$	V_i/V_2	$\ln(V_i/V_2)$
1	10 400	120 \pm 2	1.154
2	11 140	176	1.586	1.071	0.0687
3	11 760	229	1.951	1.131	0.1229	1.056	0.0542
4	12 420	285	2.30	1.194	0.1775	1.115	0.1088
5	13 190	350	2.65	1.268	0.238	1.184	0.1689
6	13 930	413	2.97	1.339	0.292	1.250	0.224
7	14 500	472	3.26	1.394	0.332	1.302	0.264
8	15 000	519	3.46	1.442	0.366	1.346	0.298

Ring counting in a field-ion micrograph of this tip gives a local radius of $r_t = 375 \text{ \AA}$. The tip had been field evaporated at 78°K with $V = 16.9 \text{ kV}$. According to Eq. (2) the evaporation field is 5.70 V/\AA , and the helium best-image field is 4.70 V/\AA , values accepted in Ref. 1 but considerably lower than the 6.70 V/\AA evaporation field obtained with another, more recent Fowler-Nordheim field-emission calibration by van Oostrom.¹⁴

Using $r_t = 375 \text{ \AA}$ and Eq. (5) we can localize the peak of the field ionization of D_2 at the various voltages of Table I. As an example, for $V_1 = 10\,400 \text{ V}$, ionization peaks at $x_1 = 37 \text{ \AA}$, where the field according to Eq. (1) is 2.92 V/\AA . For the highest voltage used, $V_8 = 15\,000 \text{ V}$, ionization peaks at the same field at $x_8 = 137 \text{ \AA}$.

Similar preliminary experiments were made with an iridium tip. At the vicinity of the (001) plane the radius was 634 \AA , the evaporation field at 78°K was 5.5 V/\AA , and BIF for helium 4.3 V/\AA .

It should be pointed out that the data obtained are not sensitive to a particular form of the field equation as given in Eq. (1). As long as we consider ionization at a distance much less than $\frac{1}{4}$ tip radius away from the surface, any other approximation will give nearly the same result. For instance, if the field near the tip surface is written as $F = F_0 [r_t / (r_t + x)]^{4/3}$ as used in Ref. 6, the field factor k derived from the data of Table I will be 2% larger.

Once the field factor k is determined, the accuracy of field calibrations depends on the precision by which r_t can be measured by ring counting. Since this is not very accurate at small tip radii, one can make use of the peak free-space ionization field of the calibration gas ($F_i = 2.92 \text{ V/\AA}$ for D_2) and determine the effective tip radius

by using Eqs. (1) and (5):

$$r_t = \frac{V_i}{2.92k \exp(2k \Delta E_i / eV)} \quad (8)$$

With this method the determination of the field at the surface as well as the effective radius of any tip can be made as accurate as the ring counting method is for a large tip, that is about $\pm 3\%$.

The described procedure using free-space field ionization provides us with an urgently needed method for the experimental determination of the field strength at the surface of a field-ion emitter under operational conditions. As the ions originate in a zone about $\frac{1}{10}$ to $\frac{1}{3}$ tip radius above the surface, possible local field enhancements due to atomic lattice steps, as well as the periodic ionization structure of the Jason effect,^{15,16} are washed out. On the other hand, regional differences in field strength due to the variation of local tip radius in the field evaporation end form are now measurable. With the second and third ionization potentials of the metals fairly well known, and the local fields determined by our method, we can apply the image force theory of field evaporation^{1,17} towards the determination of work functions of perfectly clean crystal planes of all metals accessible with field-ion microscopy.

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Coupling between Electrostatic Ion Cyclotron Waves and Ion Acoustic Waves

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We have observed the linear coupling between an electrostatic ion cyclotron wave and an ion acoustic wave near the second-harmonic ion cyclotron frequency for propagation of an electrostatic ion wave along a magnetic field, where the wave number perpendicular to the magnetic field k_{\perp} exists.

Recently, the propagation of electrostatic ion waves in a magnetic field has been investigated by many authors.¹⁻⁵ For propagation oblique to the magnetic field, Hirose, Alexeff, and Jones investigated in detail the behavior of the wave near the ion cyclotron frequency.¹ Properties of perpendicular propagation were also shown by Ohnuma *et al.*^{2,4} and Ault and Ikezi³ who detected the collisional effect at the ion cyclotron frequency² and the collisionless one at its harmonics.^{3,4} The dispersive character of the ion mode propagating almost parallel to the magnetic field near the fundamental ion cyclotron frequency has been reported by some authors.⁵ Levin and Oleson show this character by coil excitation,⁵ in contrast to other reports (mesh excitation). In this Letter, the propagation parallel to the magnetic field is investigated in detail especially near the ion cyclotron frequency and its harmonics.

The simplified experimental setup is shown at the top of Fig. 1. The experiments are performed with a QP machine⁶ on an argon plasma produced by a PIG plasma source. The plasma dimension is about 4 cm in diameter and 10 m in length with a density of $1.0 \times 10^{10} \text{ cm}^{-3}$ and an electron temperature of 4.5 eV. The wave was excited by a mesh (6 cm in diameter) aligned perpendicular to the magnetic field, and was detected by another one (2 cm in diameter) movable along the plasma column. Wave patterns of parallel propagation were displayed on an X-Y recorder by using an

interferometer technique.

Typical experimental wave patterns are shown at the bottom of Fig. 1. They show that two kinds

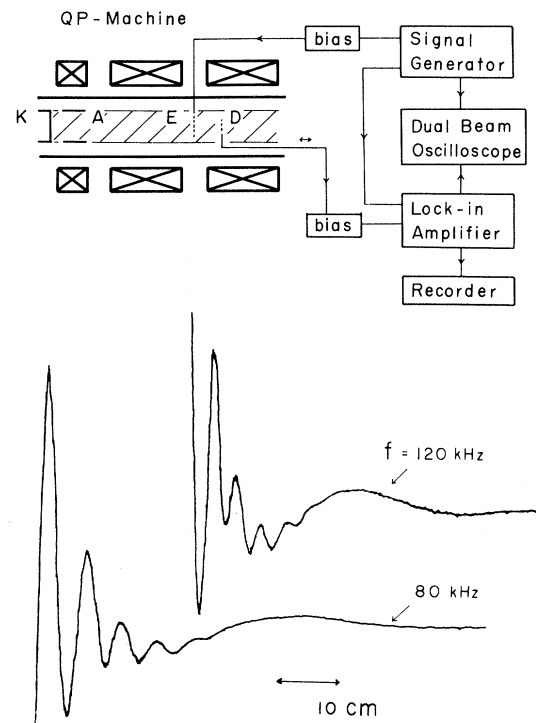


FIG. 1. Block diagram of the experimental setup, and the typical wave patterns obtained by a lockin amplifier.