

Field-Ionization Energy Spectra

Andrew J. Jason* and Albert C. Parr*

Department of Physics, The University of Alabama, University, Alabama 35486

Mark G. Inghram†

Department of Physics, The University of Chicago, Chicago, Illinois 60637

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Two models—resonance tunneling and surface-plasmon creation—which purport to explain structure observed in field-ionization energy spectra are discussed in terms of experimental evidence. The resonance-tunneling model is found to most adequately explain the major structure observed.

Lucas has suggested^{1,2} that the structure observed in field-ionization energy distributions^{3,4} is due to excitation of surface plasmons rather than to resonance tunneling.^{3,4} It is important to clarify the applicability of these two theories to the experimental situation, since interpretation of results from the atom-probe-microscope,^{5,6} field-ion-microscopy,⁶ and field-ionization-energy-analysis experiments are often strongly dependent on the theoretical model.

The surface-plasmon (SP) model is attractive since it appears to explain the experimental results, and if applicable would provide a direct method for experimental exploration of surface excitations. However, as outlined below we conclude that the resonance-tunneling (RT) model explains the experimental results whereas SP predicts behavior at variance with these results in several regards.

The apparent failures of RT (as listed in Table I of Ref. 2) can be dismissed by a more detailed consideration of the RT model. The RT calculation⁵ gives the field-ionization probability for an atom as a function of distance from the metal surface. Experimental data will be approximately related to this probability through multiplication by the rate of gas supply. Supply to the ionization region occurs in two ways⁶: (i) surface diffusion of fully or partially accommodated atoms from the shank of the tip and (ii) supply directly from the gas, enhanced by the interaction of the dipole moment with the electric field. Whichever mode predominates at any field or position, it is clear that with increasing field and hence increasing ionization probability, both sources of supply for any given ionization region will eventually decrease. Species diffusing along the shank will be removed by ionization before reaching the experimentally accessible tip apex; those from the gas phase will be ionized before reaching this region. Thus, even though there is a high probability for field ionization, no ions will be produced at these points.

These statements are represented graphically for regions near the surface in Fig. 1(a) and for the gas phase in Fig. 1(b). Here ionization near the surface means ionization within a distance $z = \phi/eF$ from the surface, where ϕ is the work function, F the field, and e the electronic charge. Ionization at larger distances will be termed "space" ionization. The functions increase initially with field because of dipole attraction. In space, supply to regions far from the tip, e.g., at distance z_3 , should increase more slowly with field and deplete more slowly at higher fields than near space regions, because of the lower field which varies inversely with the square of the distance from the tip center. Then, the ratio of space to surface supply is as shown in Fig. 1(c).

Figure 1(d) gives the ratio of space to minimum-distance ionization probabilities as calculated by the WKB approximation: $\exp(-0.68I^{3/2}/F)$ for ionization in space and $\exp[-0.68(I^{3/2} - \phi^{3/2})/F]$ for ionization at the critical distance (with energies in eV and F in $V/\text{\AA}$).⁷ Taking the decrease with distance from the surface into account modifies Fig. 1(d) into 1(e). Multiplying 1(c) by 1(e), yields Fig. 1(f), the ratio of space to surface current. If instead of the WKB probability the distributions predicted by RT are used (with z_1 , z_2 , and z_3 corresponding to the RT peaks), very little qualitative difference would occur in the plot of Fig. 1(f). This plot closely resembles the experimental results as given in Fig. 10 of Ref. 4 and reproduced as Fig. 3 of Ref. 2 and explains the peak intensity variation with field. In particular, the sharp rise in the secondary peak intensities with field observed at low fields is inherently due to the ionization of atoms away from the surface. This is not attributable to spurious resolution effects as suggested by Lucas; such effects can be shown to be small for this case and could not account for the observed variation over three orders of magnitude. The crossing of the curves at high fields is a consequence of gas supply to regions away from the sur-

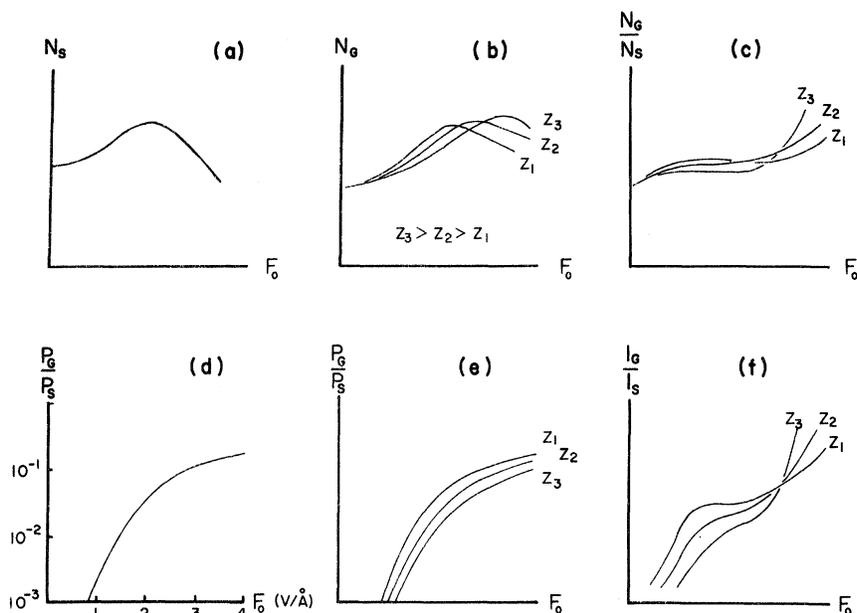


FIG. 1. Plots of supply and ionization probability as a function of field used in estimating the relative ion currents as a function of field. (a) Plot of N_s , the density of molecules at the surface, vs field. (b) Plot of the N_G , the density of molecules in the gas phase, at various positions z_1 , z_2 , and z_3 vs field. (c) Plot of the ratio N_G/N_s at various positions z_1 , z_2 , and z_3 vs field. (d) Plot of the calculated ratio of space to surface ionization probability vs field in $V/\text{\AA}$. (e) Same as (d) except for various positions z_1 , z_2 , and z_3 . (f) Plot of the ratio of the space to surface ionization current vs field. All the plots except for (d) are schematic. (d) is calculated from the WKB formulas given in text.

face.

Items 2, 7, and 8 of Table I in Ref. 2, which note the independence of observations on substrate and imaging gas, are understandable by the RT model. To first order the peak spacings should be independent of gas or substrate. The essential features determining the peak spacings are the electric field and the location of the sharp decrease of the electronic potential energy near the surface. These are closely sample independent, as can be shown by model calculations. The tunneling barrier shape does not affect RT predictions, since interference of the electron waves does not occur in classically forbidden regions.

Damped distributions at lower fields are expected with the RT model, as well as with the SP theory. The ionization probability gives a peak-to-valley ratio which decreases with field. Additional damping is provided by the statistical nature of the small currents and possibly by the breakdown of the RT assumption of plane-wave states for the tunneling electron at low final energies.

The weaker structure observed with Ne in place of H_2 at the same field is included in the RT model. Applying WKB ionization probabilities, secondary peak intensities should be the same for two gases if the fields are in the ratio of the $3/2$ power of the ionization potentials.⁸ Experimental evidence indicates that this rule approximately holds for hydrogen, neon, and helium.

SP predicts that any ion originating near the surface will leave the tip region with energy losses corresponding to plasmon excitations. A violation of this prediction is found to occur in the field ion spectra of hydrogen. The species H_3^+ which is

seen from about 2 to 3 $V/\text{\AA}$ contains no secondary peaks in its energy distribution and remains sharp at all fields despite the presence of large secondary structure in the H_2^+ spectrum.^{4,7} H_3^+ appears with a critical energy deficit of 8.2 eV (relative to 11.1 eV for the critical deficit of H_2^+) and is clearly due to a surface reaction, since its intensity is strongly dependent on substrate temperature. The H_3^+ ion intensity varies linearly with gas pressure and is hence not due to gas-ion collisions. The onset rate with energy deficit of the H_3^+ peak is similar to that of H_2^+ , and hence H_3^+ does not have a longer formation time than H_2^+ .

Experimental results also show another effect which argues against the SP model. Comparison of small-tip ($\sim 100 \text{\AA}$) and large-tip ($> 300 \text{\AA}$) distributions at similar fields shows an attenuated high-energy deficit structure for the small tip. An example of this is given in Figs. 9(e) and 9(g) of Ref. 4. Despite a higher surface field for the small tip the distribution decays more rapidly with energy deficit than does the large-tip spectrum. The RT model accounts for this, since ionization can occur at large distances from the surface. The field of the smaller tip decreases more rapidly with distance than does that of the larger, with a consequent smaller ionization probability. The SP model cannot account for this effect, since to first order it is insensitive to the field behavior far from the surface.

It is thus demonstrated that (i) ions which can only be created near the surface do not show secondary structure, (ii) ions can be created far from the surface and these ions constitute the high-energy deficit structure of the distributions,

TABLE I. Summary of discrepancies between RT theory and experiment alleged by Lucas in Ref. 2. Numbers 9 and 10 list additional effects not explained by the SP model.

Observations	Interpretation by RT model
Peak spacings	
1. Independent of imaging gas	No first-order dependence expected, since probability of tunneling and transmission to metal are approximately factorable.
2. No pressure effect	None expected—ionization is a single-atom event as deducible from magnitudes of current and pressure.
3. No crystal-face effect	No first-order effect expected, since spacings are determined by potential between surface and atom.
4. Same peak spacings for W, Pt, Mo	Same as No. 3 above.
Peak intensities	
5. Damped distributions at low fields	RT calculations predict decrease in peak to valley height with decreasing field. Statistical noise causes further apparent damping.
6. I_I/I_S increases with field; crossing of first three loss curves	Due to supply considerations. In particular, low-field behavior is not explicable by SP but is due to ionization away from surface.
7. High-field behavior; decay of parent peak and broad distribution	Due to relative increase of space ionization with subsequent depletion of sample near surface.
8. Weaker structure with Ne in place of H ₂	Higher ionization potential for Ne.
9. No structure in H ₃ ⁺ distributions	Ions formed only near surface. Defect of SP.
10. Tip radius effects in high-energy deficit structure	Differing electric field for space ionization. Not explained by SP.

and (iii) the RT model can explain the observed spectra when material supply is taken into account. The evidence for these points is summarized in Table I.

From simple manipulations with the SP formalism or application of first-order perturbation theory, it is apparent that neither the acceleration nor the velocity of the ion has appreciable effect on plasmon creation. The entire effect as predicted by SP is a consequence of the sudden appearance of an ion at z_0 . Removal of the ion at any experimentally achievable rate only provides for the establishment of an unperturbed plasmon state in the metal by the disappearance of the interaction at $t = \infty$. This can also be seen by inspection of Eq. (30) of Ref. 2, where the electric field does not explicitly enter into the plasmon excitation probability. In order to conserve energy an ion thus created simultaneously with a plasmon must be born at a distance greater than $z \approx (I - \phi + h\omega)/eF$, where ω is the plasmon frequency. This will not affect the distribution shape unless the probability of electron

tunneling at a given z is enhanced by plasmon excitation.

If it is nonetheless assumed that excitation occurs during the ion's flight, difficulties appear concerning the time over which the transition is presumed to occur. If the scattering time of the slowly moving ion is much larger than the plasmon period, the scattering is adiabatic and will not induce transitions. If the scattering is presumed sufficiently rapid to be nonadiabatic, general rules concerning the motion of low-energy heavy particles in coupled systems are violated. In molecular systems these rules correspond to the Franck-Condon principle, which forbids changes in velocity or position of the nuclei constituting the molecule during an electronic transition. Because of the similarity of a molecular transition with the proposed scattering of the coupled ion-surface system, the Franck-Condon principle would be expected to apply. Since the coupling is weaker in the plasmon case than in most molecular systems, heavy-particle rigidity would be expected

to be more rigorous.

These difficulties arise from the use of a classical ion trajectory in the SP calculation. In general, such a treatment is invalid at the low energies which the ion attains during its interaction with the surface. A quantum-mechanical treatment of the problem is necessary in order to correctly assess the probability of plasmon excitation using the SP interaction Hamiltonian.

The corrections for ion recoil given in Ref. 2 are furthermore difficult to accept since they result from the artificial insertion of an abrupt onset of the potential at some time after the actual creation of the ion. Such an onset is responsible for inducing transitions and thus corresponds to the creation of the ion at some $z > z_0$. This produces a smaller transition probability but is not an estimate of the effect of recoil.

The above discussion implies that the time scale is not given by the ion acceleration time relative to the plasmon period, since the rate of ion removal does not affect the predictions of SP. In this regard, a further factor to be considered is the ratio of the atomic lifetime for ionization (given approximately by $0.005Fe^{34/F}$ in atomic units, where F is in $V/\text{\AA}$) to the plasmon period (about 3 a. u.). Since this ratio is large under experi-

mental conditions, the possibility that ionization in this case is adiabatic with respect to plasmon excitation should be considered.

It is unclear why the results of the RT model should be doubted. The calculation is straightforward and simple. The pseudopotential model of the atom-metal potential configuration on which RT relies has been used extensively for calculating surface properties. While additional refinements are always desirable for specific situations, only the most rudimentary features of the pseudopotential model need be retained in order to predict the existence of secondary structure. Specifically, the potential near the surface need only decrease appreciably (compared to the energy of the tunneling electron) within a distance less than the electron wavelength. This will produce a region of appreciable reflectivity for the electron waves and consequent resonance conditions. The small electron reflection coefficients calculated by other models are sufficient to produce the effect as calculated by the RT theory.⁴

While it is possible that plasmon excitation occurs during field ionization, evidence indicates that the main aspects of the observed structure are adequately predicted by RT and the results of the SP model do not correspond with experimental results.

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Static Equilibrium Conditions for a Rigid-Ion Crystal*

L. L. Boyer[†] and J. R. Hardy

Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508

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The equilibrium requirements for a static ionic crystal impose a number of constraints on the short-range forces which become increasingly more important when one is dealing with complex structures. These constraints are presented and discussed for a general rigid-ion lattice, and a specific discussion is presented for the wurtzite structure.

In a lattice composed of rigid ions we have two types of forces; the long-range Coulomb interactions between the constituent ions and the short-range forces acting between relatively close neighbors which are essential to prevent the structure from collapsing. If we assume central short-range

forces then, for any structure, we must ensure that the static lattice is in equilibrium, both with respect to any macroscopic strain and also with respect to relative motion of the constituent sublattices (i. e., internal strain). For the more complex crystal structures this leads to a number of