Isothermal ramped field-desorption of benzene from tungsten

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The binding of molecular benzene on clean (field-evaporated) tungsten surfaces at 78 K has been investigated as a function of electric field strength using a new ramped field-desorption technique. The resulting spectra, analogous to total pressure thermal desorption spectra (which do not mass analyze the desorbing species), show a physisorbed structure below 0.36 V/Å which increases continuously in area with increasing benzene coverage, a peak at 0.36 V/Å which grows until a saturation coverage is reached (and is thought to represent a physically adsorbed transition layer between chemisorbed and multiple layer physisorbed benzene at the surface), and a series of poorly resolved chemisorbed peaks (between ≈ 0.38 and 1.13 V/Å) whose detailed shape depends on the local morphology of the surface region being examined. By recording the image of the desorbing species over the narrow field ranges which define these distinct features, the crystallographic behavior of the physisorbed and chemisorbed layers on the surface has been visually determined with angstrom resolution.

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INTRODUCTION

The binding properties of adsorbates on metal surfaces has been a problem of continued interest to the surface scientist. Powerful surface analytic techniques have been employed for many years to study these interactions, with thermal desorption spectroscopy occupying a prominant place in such investigations. In this technique,[1] a surface is exposed to species whose binding characteristics are to be studied. Then, the temperature of the substrate is linearly increased with time, and the thermal desorption characteristics of the species determined by observing variations in the rate of desorption of neutrals from the substrate as a function of its temperature and coverage. In this paper we present a high-field analog of the thermal desorption measurement just described in which the rate of field-induced desorption of species, adsorbed on a metallic surface at cryogenic temperatures, is monitored by observing the ion current resulting from the application of a linearly increasing electric field.

It has been known for many years that the field-desorption process produces highly charged ions of a metallic substrate at cryogenic temperatures.[2] For many materials twofold, threefold, and even fourfold charged ions are observed, with the higher charge states usually dominating the mass spectrum at low temperatures.[2] However, as the substrate temperature is increased (and the field required for desorption correspondingly decreased), the abundance of ion species gradually shifts toward the lower charge states.[2] Above 300 K, for example, the singly charged ion dominates the mass spectrum of essentially all field-desorbing materials.[2] Extrapolating these results to the limit of thermal evaporation of the substrate at zero field, one expects to observe a progressive decrease in the abundance of the singly charged species and a corresponding increase in the production of neutral species. The indication is that the field-desorption process is strongly temperature dependent. In fact, it is often described as thermal activation over a field-reduced energy barrier at the

surface.[2] As a result, the "ramped field-desorption" spectra to be described were expected to resemble their thermal desorption counterparts at zero applied field. What was surprising, was their remarkable similarity.

In addition to recording ramped field-desorption spectra, it is also possible to photograph the spatial position of the ions produced over narrow field ranges. Consequently, the apparent crystallographic distribution of surface species corresponding to each distinct feature in the spectra has also been obtained.

In this investigation we will restrict our attention to benzene adsorption on (110) oriented tungsten at a fixed substrate temperature of 78 K. For simplicity, the total ion current from the specimen will be monitored as a function of applied electric field in analogy with total-pressure, thermal desorption measurements which also do not distinguish between different species desorbed from the surface.

EXPERIMENTAL TECHNIQUE

In order to generate the electric fields required to field desorb a species of interest from a metallic substrate, a field emitter specimen having an apex radius of 300–800 Å is usually used. Since it is also desirable to prepare a surface which is atomically clean and smooth by field evaporation[3] in vacuum, electric fields of the order of 6 V/Å must be achievable, requiring specimen potentials of up to 20 kV. For convenience, the specimen potenial is ramped at a rate of 100 V/s from zero up to a maximum which is several hundred volts below that previously found to cause gentle field evaporation of the substrate in vacuum. This insures that essentially all absorbed species (whose binding to the surface is weaker than the interatomic binding of the substrate atoms themselves) will be desorbed without changing the morphology of the substrate. This procedure is analogous to conventional thermal desorption at linearly increasing temperatures approaching, but well below, the melting point of the substrate.

To clean the surface of all extrinsic impurities, gentle field evaporation of the lattice can be initiated, followed by field-ion imaging to define the resulting, atomically perfect surface. The ability to completely clean the surface and precisely characterize its morphology on an atomic scale is an important asset of the high-field technique.

The upper portion of Fig. 1 shows, schematically, the instrumentation required for a ramped field-desorption analysis, while the lower portion details the instrumentation required for Imaging Atom-Probe (IAP) spectroscopy. The latter time-of-flight mass spectrometric technique, described elsewhere,[4] provides a method of identifying surface constituents by applying a high voltage pulse to the tip sufficient in magnitude to field-desorb species of interest.

During ramped field-desorption analysis, the high voltage to the tip is increased by a linear ramp applied to the input of a programmable high voltage power supply.[5] A precision divider attenuates the high voltage output in order to drive the horizontal input of an x-y recorder so that its x axis will be proportional to the applied electric field. Since the electric field will scale linearly with the applied voltage:

$$F_{applied} = (F_0/V_0) \, V_{applied}$$

where V_0 is the measured tip voltage corresponding to a known applied field F_0. If $F_{applied}$ is needed only to within 15% or 20%, and the substrate is stable under field-ion imaging in helium, V_0 can be taken as the helium ion-image best image voltage (BIV) because the corresponding best image field F_0 is known to be 4.5 V/Å to this accuracy.[6] A further improvement in the accuracy of the field calibration (to perhaps ±3%) can be obtained by using a local, crystallographically dependent field strength measured for a specific region of the specimen by means of the energy distribution of field ionized hydrogen above the tip apex.[6] However, for the present investigation, the less accurate calibration was judged to be sufficient.

The desorbed ions, produced by the applied field, are accelerated by the field to a chevron channel-plate detector[4] having a gain sufficient to insure that single ion impacts can be recorded. The total amplified ion current is then routed through a rate meter whose analog output drives the vertical axis of the x-y recorder proportional to the number of ions desorbed per second. Since the desorbing ions travel almost radially from the tip to the chevron channel-plate detector, they will form, at the detector, a magnified image of their relative positions on the surface prior to desorption (provided that field-induced or thermally enhanced migration on the surface prior to desorption is negligible). If the detector is activated during selected portions of the ramp, its phosphor screen can be photographed to give "ramped desorption images" which will correspond to selected features observed in the desorption spectra on the x-y recorder.

To provide experimental flexibility, the tip to detector distance could be varied from approximately 3 to 12 cm. At the shortest extreme, almost all of the apex of the specimen accessible to field-ion imaging can be observed. At 11.8 cm, the radius of curvature of the spherically curved detector assembly, only 5% of the total imaged area can be observed, but IAP mass spectroscopy with good mass resolution is pos-
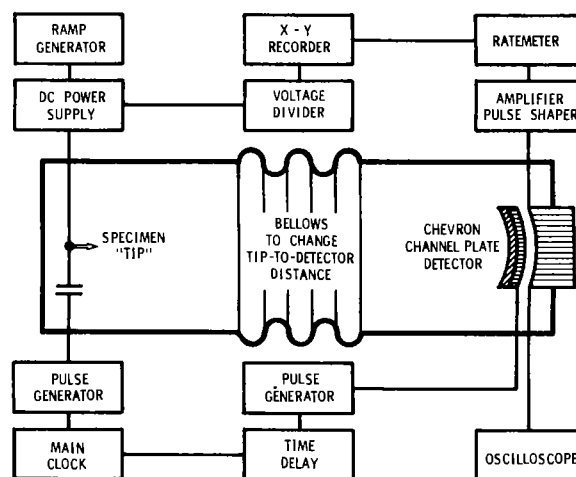

FIG. 1. A schematic diagram of the apparatus and instrumentation used to obtain ramped-desorption spectra (upper portion), and imaging atom-probe mass spectra (lower portion). The specimen "tip," a field emitter with a typical radius of 300 to 800 Å, is cooled to cryogenic temperatures by means of a closed cycle, liquid helium refrigerator (not shown).

sible. The limited viewing area at this position is actually an advantage in that only a small region of the surface will contribute to the ramp desorption spectra, making them less dependent on variations in the surface crystallography. It should be noted that the electric field strength at the surface is not an areal constant, but varies because of the macroscopic change in shape of the emitter with distance from its apex, as well as changes in local morphology.[7] Limiting the field of view of the detector to small angles near the emitter axis will, therefore, have the additional advantage of reducing any spread in the desorption fields due to variations in electric field strength at the surface. For these reasons, the 11.8-cm tip-to-detector distance was used for the measurements to be presented here.

Prior to benzene adsorption (and field calibration) the tungsten tips used in this study were field-evaporated at 78 K in vacuum to clean the surface and establish a stable end-form. It should be understood that the temperature at the surface of the specimen tip cannot be directly measured because of its angstrom dimensions. Seventy-eight degrees Kelvin is actually the temperature of the cold end of a commercial helium refrigerator[8] used to cool the specimen, but separated from it by an electrically insulating, thermally conducting, sapphire block. As a result, the actual temperature of the specimen surface was higher than 78 K by an estimated 2–10 K. The specimen, sapphire block, and helium refrigerator cold end were surrounded by a radiation shield held at 40 K. The tip apex was positioned behind a 2-mm-diam aperture in the radiation shield in order to allow the desorbing ions to reach the detector.

Benzene was adsorbed on the tip apex by means of the retractable capillary dosing assembly shown in Fig. 2. Dosing was accomplished by throttling valve C in Fig. 2, retracting the capillary, and establishing a stable benzene flow. The increase in background pressure of the vacuum system (above the resulting "base" pressure of 8×10^{-9} Torr) was assumed to be proportional to benzene partial pressure and was used to establish identical flow conditions during successive dosing
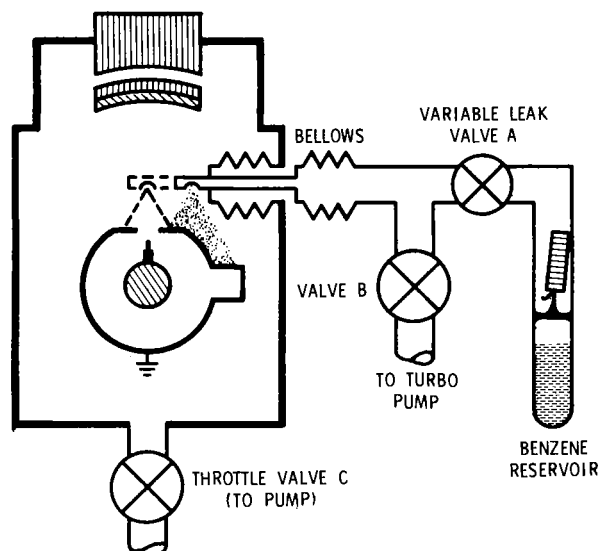
FIG. 2. A schematic drawing of the benzene doser used in this study. Two bellows are used so that the benzene reservoir, valve A, and valve B can remain stationary when the capillary dosing tube is extended or retracted. In the retracted position of the capillary dosing tube (shown in solid lines), benzene vapor cannot strike the tip apex directly. When extended (dotted lines) benzene vapor reaches the tip apex through a 2-mm-diam aperture in the cryogenically cooled, grounded shield that surrounds the tip assembly which is cooled to 78 K. The curved Chevron channel plate detector appears in the upper part of the figure, but the bellows which is used to change the tip-to-detector distance is not shown.

experiments. Benzene from the ambient background was not observed to field-desorb from the tip apex at least for adsorption times comparable to those requiring to establish a stable benzene flow ($\approx$ 5 s).

Typically, after a background pressure of 1×10^{-7} Torr of benzene was established, the capillary was extended to the position shown by the dotted lines in Fig. 2. As a result, benzene could adsorb directly on the tip apex for a given, well-defined time. The capillary was then retracted and the benzene flow immediately discontinued by closing leak valve[9] A in Fig. 2 and evacuating the capillary assembly through valve B. Throttle valve C was then opened, and the chamber evacuated to better than 2×10^{-9} Torr before ramp-desorbing the tip. Since the dosing time was accurately known, and the sticking coefficient of benzene of tungsten can be considered to be unity at 78 K, the actual benzene exposure could, in principle, be determined if the benzene pressure at the exit aperture of the dosing capillary was known. Since the pressure was not known the actual benzene exposure could not be determined. However, relative doses and dosing reproduceability were known to the accuracy to which the product of benzene partial pressure and dosing time could be controlled (better than 0.5%).

In order to assure the purity of the benzene used in this study, American Petroleum Institute reference standard benzene (greater than 99.8 mol%) was purchased in an evacuated, sealed pyrex ampoule with an internal break-tip seal.[10] Pressures better than 8×10^{-10} Torr were achieved in the vacuum system prior to fracturing the break-tip with a pyrex-encased kovar rod, manipulated by an external magnet.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 is a composite of several ramped field-desorption spectra taken from tungsten at 78 K under a variety of experimental conditions. The orientation of the tip and the extent of the desorption area can be seen in the field-ion micrograph of Fig. 4(a). The essential features of the ramp desorption spectra were observed to be independent of temperature below 100 K where benzene migration on the tip apex was determined to be negligible.

Spectra G and H of Fig. 3 resulted from an identical benzene exposure. Spectrum A of Figure 3 resulted from one-half of this exposure. Spectra B–F were recorded after spectrum A without redosing the tip apex with benzene. Spectrum I was recorded after spectrum H, again without redosing. Spectra A–G were all taken between 0 and 3.56 kV (1.5 V/Å). Spectra H and I were taken between 0 and 10 kV (3.8 V/Å), although only the portion of spectrum H between zero and 3.56 kV is shown in Fig. 3.

PHYSICALLY ADSORBED BENZENE

The sharp peak in the spectrum of Fig. 3(A) with a maximum at 0.84 kV (0.36 V/Å) and an onset threshold of 0.55 kV (0.2 V/Å), is due to a developing coverage of benzene at the surface since this peak grows with benzene exposure [see Fig. 3(G)]. In Fig. 3(G), this peak has developed a shoulder (at 0.75 kV or 0.32 V/Å) which is broadened toward lower desorption fields. The shoulder reflects the formation of multiple layers of physically adsorbed benzene since it continues to increase in area (and shift toward lower fields) with increasing benzene coverage. The shift toward lower fields suggests that physically adsorbed multilayers of benzene have formed. A benzene molecule in a physically adsorbed multilayer is bonded only by weak, van der Waals forces to its benzene neighbors. Because of this weak interaction, and any thermal insulation from the substrate provided by underlying multilayers, benzene molecules in the outermost layer are readily removed at low fields. As the multilayer thickness increases, benzene molecules in the outermost layer will be more easily removed and the corresponding peak in the ramped desorption spectrum will shift toward lower fields. The sharp peak at 0.84 kV (0.36 V/Å) which grows in amplitude with increasing exposure only up to some maximum value, is thought to represent a distinct binding state of physically adsorbed benzene. It probably reflects the formation of a physically adsorbed transition layer(s) between chemisorbed and multiple layer physisorbed benzene at the surface. Such an explanation has also been suggested to explain a feature seen in thermal desorption spectra (for adsorbates other than benzene).[11]

Repeatedly ramping the surface after dosing with benzene as in Fig. 3(G) following field evaporation "cleaning" of the surface resulted in a (physisorbed) structure resembling that of Fig. 3(G). In each ramp, the field corresponding to the maximum amplitude of the sharp peak, the "shoulder," and the low field desorption threshold, remained stable to within 0.03 V/Å. However, during several ramps, the area under the sharp peak was observed to become less than or even equal to the area of the shoulder, and often the two features merged [see, for example, the peak at 0.93 kV in Fig. 3(H)].

BENZENE DESORPTION FROM TUNGSTEN - 78K - 11.85 kV (He BIV)
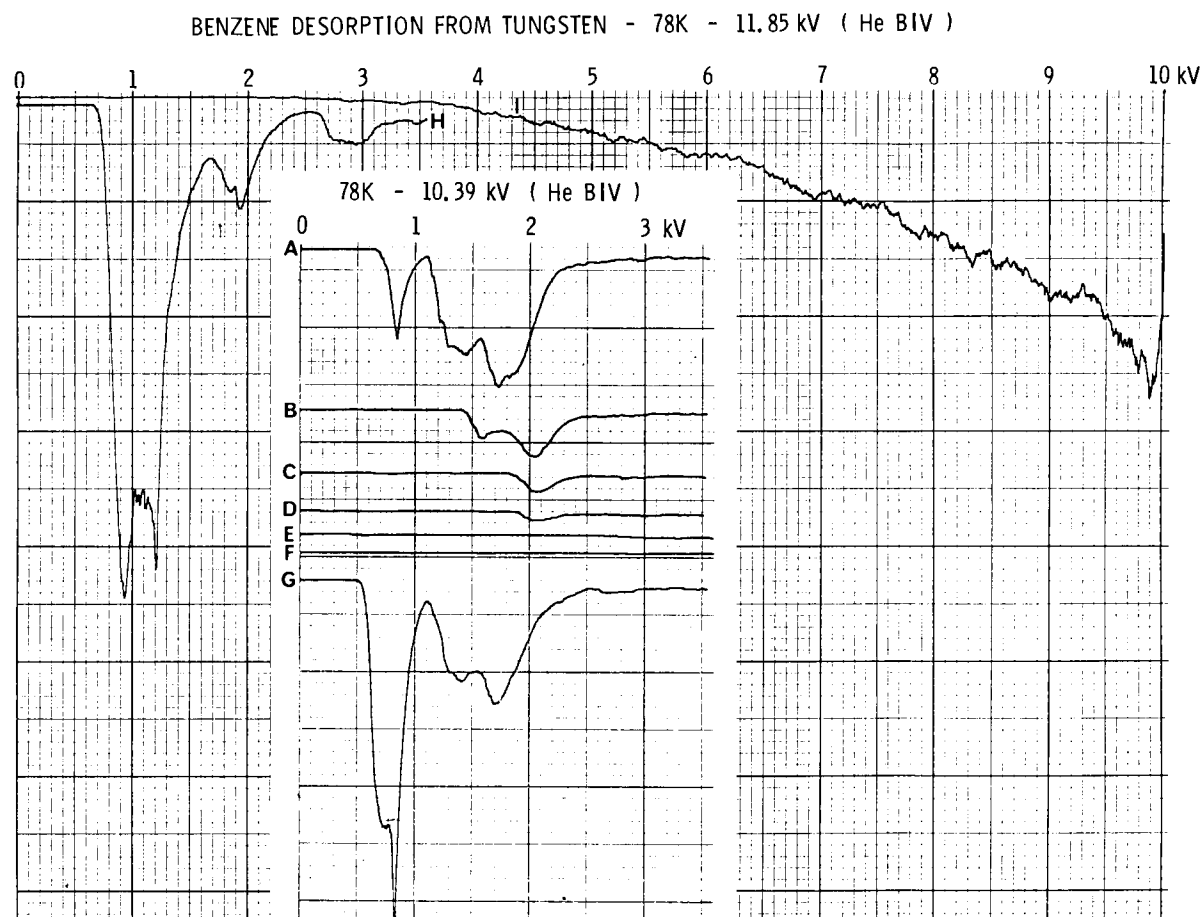
78K - 10.39 kV (He BIV)

FIG. 3. Ramped desorption spectra obtained by field desorbing benzene at 78 K from a tungsten specimen whose orientation and surface structure is shown in the helium ion-micrograph of (a). Spectra G and H resulted from identical benzene exposure. Spectrum A resulted from one-half this exposure. Spectra B–F were recorded after spectrum A without redosing the tip apex with benzene. Spectrum I was recorded after spectrum H again without redosing. Spectra A–G were all taken between 0 and 3.56 kV (1.5 V/Å).

Spectra H and I were recorded between 0 and 10 kV (3.8 V/Å), although only the portion of spectrum H between 0 and 3.56 kV is shown. Field calibration was accomplished by recording the best image voltate (10), 39 kV for spectra A–G, 11.85 kV for spectra H–I) during helium ion-imaging of the substrate. The helium best image voltage (He BIV) was associated with a field strength of 4.5 V/Å. Any other field, resulting from a given specimen potential, was then obtained by a direct, linear proportionality.

The variation in area of the physisorbed structure under identical dosing conditions suggests that the number of species detected was not constant. This raises the possibility that dissociation of molecular benzene occurs to some statistically variable degree, most probably in those multilayers closest to the surface either during, or prior to, desorption at 78 K. Dissociation would be expected to be most probable in the physisorbed layers which are closest to the tungsten surface because these would be the more tightly bound layers. Dissociation of molecular benzene in these layers would produce a variable number of surface species available for desorption, independent of benzene exposure, resulting in a relative variation in the area of the physisorbed structure for identical coverages. Dissociation phenomena can also be used to explain the occurrence of features seen in successive ramp desorption spectra initiated immediately after the first spectra, but without additional benzene exposure (Fig. 3(B)–(F)]. These results will be discussed in the next section dealing with chemisorbed benzene.

It is interesting to note that the application of nanosecond desorption pulses to remove species from the outermost physisorbed layer results primarily in the detection of mass 78 ($C_6H_6^+$), together with a small abundance (less than 5%) of

mass 39 (probably $C_6H_6^{2+}$). This result is consistent with a dissociation process occurring only within those physisorbed layers in closest proximity to the surface.

It is also interesting to note that the overall appearance of the thermal desorption spectra recorded by Cratty and Hansen for thermal desorption of molecular benzene from polycrystalline tungsten[12] closely resembles the ramped desorption spectra of Fig. 3. Particularly striking is the occurrence of two physisorbed peaks in the thermal desorption spectrum [see, for example, Fig. 3(G)]. Such similarities warrant further investigation into a detailed comparison of field and thermal desorption mechanisms. However, it should be stressed that a fundamental difference exists between any field desorption measurement at low substrate temperatures and its thermal counterpart at zero field. In field desorption, one detects only positive ions, the primary species produced by the desorption process; whereas, in thermal desorption, species are primarily removed from the surface as neutrals.

At the field strengths normally encountered in field-ion microscopy (>2 V/Å), neutral production is expected to be particularly improbable; but at much lower fields (viz. during field-desorption of weakly bound multiple layers of physically adsorbed gases) desorption of neutral species may not be in-

significant. Unfortunately, measuring the abundance of low energy neutrals from field-desorbing multilayers is very difficult since the number of species removed from a typical 1000 Å surface area is limited, and post-ionization of low energy neutrals (for detection purposes) is usually a very inefficient process.

CHEMISORBED BENZENE

In Fig. 3(A) and (G), between approximately 1.1 (0.45 V/Å) and 2.5 kV (1.2 V/Å) a structure is seen apparently composed of several unresolved peaks. The structure grows with increasing benzene exposure, up to some maximum exposure, after which a sharp peak at 0.84 kV (0.45 V/Å) appears. The lack of growth with increasing exposure, and the relatively high desorption fields suggests that the structure is associated with chemisorbed benzene at the surface. This implies that the structure can be associated with benzene desorption from various crystallographic regions of the surface and/or multiple binding states within a specific region. Preliminary measurements obtained by aperturing the detector to observe only one crystal plane at a time support this interpretation. In addition, ramped desorption images (described in the next section) clearly show (for some ramped desorption spectra) field-desorption from the center of the (110) plane.

In a previous paragraph, it was suggested that dissociation of molecular benzene may be occurring in physisorbed layers closest to the tungsten surface. This assumption is reinforced by the results of repetitive ramping over the chemisorbed field range without redosing the surface. For example, Fig. 3(B) shows a ramp desorption spectrum taken one minute after the spectrum of Fig. 3(A) without reexposing the surface to benzene. The physisorbed peak structure of Fig. 3(A) is absent (as expected) but unexpected structure is observed within the field range associated with chemisorbed species. The spectra of Fig. 3(C) and (D), taken one minute after those of Fig. 3(A) and (B) (without redosing the surface), again show structure within the chemisorbed field range. However, the structure progressively shifts toward higher fields and decreases in amplitude until [in Fig. 3(E)] all structure has disappeared. The spectrum of Fig. 3(F) was taken twenty minutes after that of Fig. 3(E) (again without redosing the surface). The lack of discernable structure during this ramp indicates that readsorption from the gas phase, or migration over the specimen surface from outside of the region sampled by the detector, cannot be responsible for the structure seen in the spectra of Fig. 3(B)–(D). Accordingly, the structure is most probably due to a tightly bound benzene residue remaining on the surface after dissociation of the parent species during a previous ramp. But the question arises as to why dissociation products formed during a portion of a given ramp would not desorb later in that ramp, particularly since any structure observed in following ramps always occurs near the middle of the field range (indicating only moderate binding). One possibility is that at a given temperature, the product of electric field strength and time in that field is the governing parameter in determining the probability of field-induced desorption, not just field strength alone. This possibility is supported by the ramp spectra of Fig. 3(H) and (I). In Fig. 3(H), the same tungsten tip used for the ramps of Fig. 3(A)–(G) was field evaporated

to a larger radius, and benzene adsorbed under the same dosing conditions which produced the spectrum of Fig. 3(G). The voltage was then ramped to 10 kV (3.8 V/Å) but the spectrum recorded only between 0 and 3.56 kV. The next ramp, shown in Fig. 3(I) (and taken one minute after reaching 10 kV without redosing), displays no structure over the fields characteristic of physisorbed *or chemisorbed* benzene. The implication is that the first ramp (to 3.8 V/Å) established a high enough field for a long enough time to desorb any dissociation products formed at lower fields. An interesting corollary is that upon reaching and remaining at 3.8 V/Å in the second ramp [Fig. 3(I)], the ion current did not immediately reach quiescent value, but decreased gradually over a period of one minute to the final value recorded. This further suggests that a finite length of time is required in order to remove all bound species at a particular value of the applied electric field.

In order to attempt to discover the identity of the species desorbing at the maximum field reached in Fig. 3(I), another ramp to 10 kV was initiated (after cleaning the surface by field evaporation, and redosing with benzene). A spectrum, similar to that shown in Fig. 3(H), was obtained indicating similar surface processes had occurred. But now, instead of ramping to 10 kV as was done to record the spectrum of Fig. 3(I), several 2 kV (50 ns wide) desorption pulses were applied to the specimen, biased to 8 kV dc. The resulting imaging atom-probe mass spectra showed the presence of carbon, indicating that a carbonaceous layer resulted from initially ramping the benzene covered tungsten surface to 10 kV. As a result, the gradual reduction in ion current observed at 3.8 V/Å during the ramp of Fig. 3(I) can most probably be associated with field-desorption of a tightly bound carbon residue.

RAMPED DESORPTION IMAGING

If the chevron channel-plate detector is activated during a specific portion of a ramp, a desorption image corresponding to the equivalent field range can be photographed on its phosphor screen fiber-optic output window. Under the assumption that surface migration does not occur prior to (or during) desorption, the resulting image will display the distribution of species on the surface corresponding to desorption over the selected field range. Figure 4(a) shows a helium field-ion micrograph of the (110) tungsten surface used to obtain the ramps of Fig. 3(H)–(I). Figure 4(b) shows the image corresponding to the physisorbed structure in the spectrum shown in Fig. 3(H), over the range 0.6 (0.2 V/Å) to 1.0 kV (0.4 V/Å) for a dosage time of 55–60 s at a benzene background pressure of 1×10^{-7} Torr. The nonuniform distribution of image spots shows that the physisorbed benzene structure of Fig. 3(H) did not result from uniform benzene coverage on the surface. Instead, the image of Fig. (4b) suggests that at 78 K adsorption at these coverages is characterized by somewhat localized, "islandlike" formations perhaps resulting from short range migration (tens of angstroms) over the surface. However, the distinct localized features of the image also indicate that the adsorbed benzene is immobile over long distances (hundreds of angstroms), since such mobility would result in a more uniform image spot density. At higher coverage (1×10^{-7} Torr of benzene for 110 s) a more uniform benzene layer

is produced as indicated by the ramped desorption image of Fig. 4(c). For greater benzene coverages (indicated by an increase in the area of the physisorbed structure and a shift toward lower fields), the appearance of the physisorbed image remained essentially the same.

Ramped desorption images of physisorbed benzene taken twenty minutes after an initial image (without benzene redosing), show no image spot density. Repeating the experiment, but keeping a potential of 950 V on the specimen during the twenty-minute wait between images also produced no image spot density. This is a strong indication that gas phase readsorption, and thermal (or field-induced thermal) migration over the imaged area of Fig. 4(a) is not significant at 78 K.

In Fig. 4(d), the ramped desorption image corresponding to chemisorbed benzene is shown for fields between 0.38 (1.0 kV) and 1.13 V/Å (3.0 kV). The field range was chosen, somewhat arbitrarily, to include only those features of the ramped spectrum of Fig. 3(H) which were associated with chemisorbed benzene at the surface. The arrow in Fig. 4(d) points to benzene desorption from the exact center of the (110) plane which corresponds to the sharp peak at 0.45 V/Å in Fig. 3(H). The lack of disorption image spots immediately around the (110) pole in Fig. 4(d) may suggest: (1) preferential dissociation of benzene in this highly terraced region of the surface, resulting in products tightly bound to the surface and incapable of being desorbed over this field range, or (2) previous removal of species from this region during ramping over the physisorbed peaks.

If dissociation of molecular hydrogen, found to be more highly probable in the highly terraced region of the lattice surrounding the (110) pole of a tungsten tip[13] is, indeed, a general phenomena, then possibility (1) above may be the correct explanation for the lack of image spots in this region.

SUMMARY AND CONCLUSION

The binding of molecular benzene (at 78 K) on clean, tungsten surfaces has been investigated as a function of electric field strength using a new ramped field-desorption technique. In this technique, a tungsten field-ion specimen "tip" cleaned by field-evaporation (at 5.7 V/Å), and characterized by helium field-ion microscopy (at 4.5 V/Å), is subjected to a linearly increasing electric field following benzene adsorption from the gas phase. The rate of field induced desorption of surface species (as positive ions) is plotted as a function of applied field on an x-y recorder, producing spectra remarkably similar in appearance to those produced by thermal desorption at zero field.

In the ramped desorption spectra of benzene, three prominant, reproducible features can be identified, including: (1) a low-field (0.32 V/Å) feature which increases continuously in area with increasing benzene exposure and is associated with physically adsorbed benzene multilayers; (2) a sharp peak at 0.36 V/Å which grows with benzene dosage until a saturation coverage is reached (and is assumed to represent another binding state of physically adsorbed benzene at the surface, and (3) a series of poorly resolved peaks between $\approx$ 0.38 and 1.13 V/Å which grow with benzene

A) TUNGSTEN FIELD-ION IMAGE   C) RAMPED DESORPTION IMAGE

B) RAMPED DESORPTION IMAGE   D) RAMPED DESORPTION IMAGE
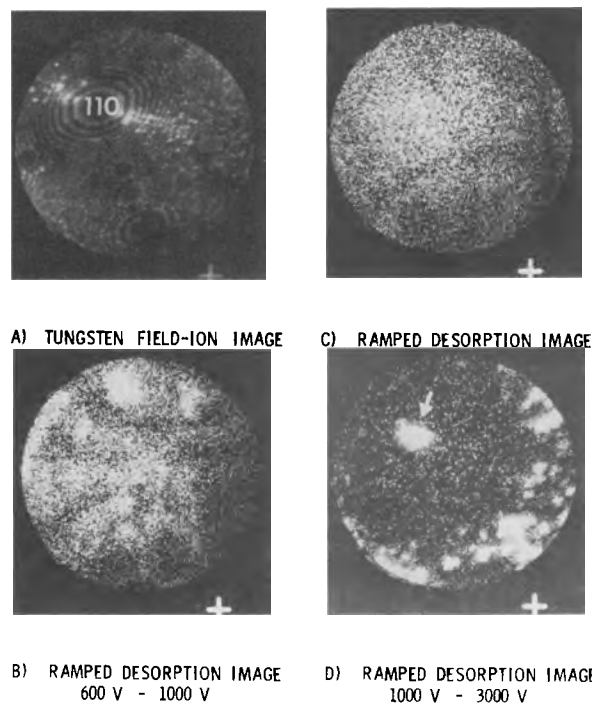   600 V - 1000 V   1000 V - 3000 V

FIG. 4. (a) A field-ion micrograph of tungsten at 78 K taken just before the desorption spectrum of Fig. 3(H). The micrograph shows the (110) oriented specimen "tip," and the region of the surface seen by the chevron detector during the desorption ramps of Fig. 3(H)–(I). The same tip (having a slightly smaller radius of curvature) was used to obtain the spectra of Fig. 3(A)–(G). (b) A ramped desorption image corresponding to the relative position on the surface, of the desorbing species which produced the physisorbed, multilayer structure of Fig. 3(H) between 0.6 (0.2 V/Å and 1.0 kV (0.4 V/Å). The nonuniform image spot denstiy indicates that the corresponding structure in the spectrum of Fig. 3(H) does not result from a uniform physisorbed layer of benzene on the surface. Furthermore, it indicates that long-range migration of adsorbed benzene is improbable since such mobility would lead to a more uniform image spot density. (c) A ramped desorption image corresponding to the physisorbed structure of Fig. 3(H), but at twice the benzene exposure |i.e., twice the benzene exposure which produced the ramp desorption spectra of Fig. 3(G) and (H)|. The uniform image spot density indicates that the physisorbed multilayer is areally uniform at the surface. (d) a ramped desorption image corresponding to the chemisorbed peaks of Fig. 3(H) between 1.0 (0.4 V/Å) and 3.0 kV (1.3 V/Å). Included are image spots due to the peak at 1.2 kV (0.45 V/Å) and identified with benzene desorption from the center of the (110) plane (indicated by an arrow). A lack of image spot density in the highly terraced region surrounding the (110) pole may be due to preferential dissociation of the benzene molecule into tightly bound residues which do not desorb over this field interval (see text).

exposure up to some maximum dosage, and are associated with a monolayer of chemisorbed benzene on the surface. Dissociation of molecular benzene within the first physically adsorbed layer and within the chemisorbed layer appears to be highly probable. Dissociation within the chemisorbed layer results in the production of a tightly bound carbonaceous layer on the surface which is only desorbed at fields approaching 3.8 V/Å. No evidence is seen for the dissociation of molecular benzene within the outermost physically adsorbed multilayers at 78 K.

By photographically recording the impact of individual field-desorbing species over the field ranges corresponding to the distinct features of the ramp spectra, the distribution of the species on the surface which produced these features were obtained. The resulting "ramped-desorption images" show developing areal uniformity in the physisorbed benzene multilayer as a function of benzene dosage, but crystallo-

graphic specificity only within the chemisorbed layer. From such images it was concluded that benzene migration (with or without an applied electric field) is negligible at 78 K.

Further application of the technique to other adsorbate-substrate systems seems warranted. One exciting possibility is the observation of the binding of biomolecular layers to metallic substrates. A more detailed comparison between ramped desorption spectra and their well understood thermal counterparts at zero field is also warranted, and should serve to more precisely characterize the nature of the field desorption event.

ACKNOWLEDGMENTS

[1]See, for example, P. A. Redhead, Vacuum **12**, 203 (1962) and G. Ehrlich, Adv. Catal. **14**, 255 (1963).

[2]E. W. Müller and T. T. Tsong in *Field Ion Microscopy Principles and Applications* (Elsevier, New York, 1969).

[3]*Field evaporation* is a term introduced by Müller (Ref. 2) to describe, specifically, the removal of *lattice atoms* (as positive ions) in a high electric field at temperatures usually below one-half of the melting temperature of the substrate. Field evaporation is a specific case of *Field-desorption* which refers to the field-induced removal of *any* substrate species.

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