

## Auger Electron Ejection from Tungsten Surfaces by Low-Energy Ions\*

FRANKLIN M. PROPST AND EDGAR LÜSCHER

*Coordinated Science Laboratory and Physics Department, University of Illinois, Urbana, Illinois*

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Work on the study of the ejection of electrons from the surface of polycrystalline tungsten by  $\text{He}^+$ ,  $\text{H}_2^+$ ,  $\text{N}_2^+$ , and  $\text{O}_2^+$  is reported. The total yields and energy distributions of the Auger electrons ejected by ions of 50-, 100-, and 200-eV kinetic energy are measured. The influence of adsorbed gases at the tungsten surface on the yields and energy distributions is also studied.

### I. INTRODUCTION

THE study of the interaction of atomic particles with solid surfaces has received increasing attention. This paper reports work on the study of the ejection of electrons from the surface of polycrystalline tungsten by ions of helium, hydrogen, nitrogen, and oxygen. The total yields and energy distributions of the electrons ejected by ions of 50-, 100-, and 200-eV incident kinetic energy are given. The effect of adsorbed gases is also studied.

The process that gives rise to the ejected electrons is of the Auger type, represented schematically in Fig. 1. One electron from the conduction band of the metal neutralizes the ion near the surface. The energy released by the electron is absorbed by a second electron from the metal because the wave functions of the two electrons overlap. If the energy transferred to this second electron is large enough and its momentum properly oriented, this electron can escape from the metal. A few calculations of this process have appeared in the literature.<sup>1-8</sup>

A number of mechanisms are possible that could cause errors in the experiment: (a) reflection of the incident ions, (b) sputtering of positive and negative ions from the target surface, and (c) ejections of electrons from the collector surface by (i) ions reflected at the target, (ii) ions sputtered from the target, (iii) electrons ejected from the target, (iv) metastable atoms reflected or sputtered from the target, and (v) photons emitted by the incident ions as they impinge upon the target. All of these processes (with the exception of sputtered negative ions and electrons secondary to the primary Auger electrons) would give rise to saturation currents as the collector is made more negative with respect to the target. These saturation currents were a very small fraction of the primary electron currents in all cases to be reported here. It is also unlikely that negative ions are sputtered in appreciable quantity. Electrons ejected

from the collector by the primary Auger electrons could give rise to only small errors due to the small size of the solid angle that the target subtends at the collector. Another source of error is the loss of electrons through the aperture in the collecting sphere through which the ions enter. This can give rise to only small errors (1-2%) due to the small value of the solid angle that this aperture subtends with respect to a point on the target. In the present work, magnetic selection of the ions was employed. Thus, there is no error due to metastable atoms in the ion beam. There is possibly some error due to metastable ions in the beam. This error is small since the relative cross sections for production of metastable ions are very small.

### II. APPARATUS AND EXPERIMENTAL PROCEDURE

The experiment consists of measuring the total yield and the energy distribution of the ejected electrons as a function of the type and energy of the incident ions and the state of the tungsten surface. A schematic

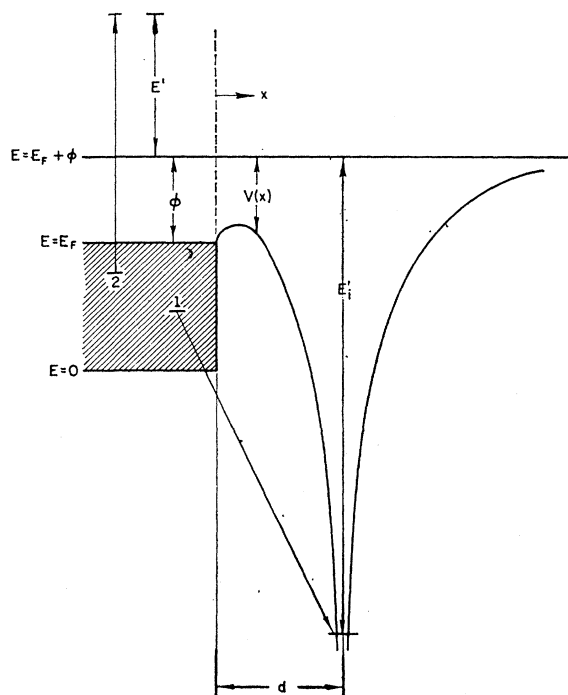


FIG. 1. Energy-level diagram for the ion-metal system, illustrating Auger neutralization of the ion.

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<sup>1</sup> H. S. W. Massey, Proc. Cambridge Phil. Soc. **26**, 386 (1930).

<sup>2</sup> Sh. Sh. Shekhter, Zh. Eksperim. i Teor. Fiz. **7**, 750 (1937).

<sup>3</sup> A. Cobas and W. E. Lamb, Jr., Phys. Rev. **65**, 327 (1944).

<sup>4</sup> P. A. Wolff, Phys. Rev. **95**, 56 (1954).

<sup>5</sup> H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).

<sup>6</sup> D. Sternberg, Ph.D. thesis, Columbia University, 1957 (unpublished).

<sup>7</sup> H. D. Hagstrum, Phys. Rev. **122**, 83 (1961).

<sup>8</sup> F. M. Propst, Phys. Rev. **129**, 7 (1963).

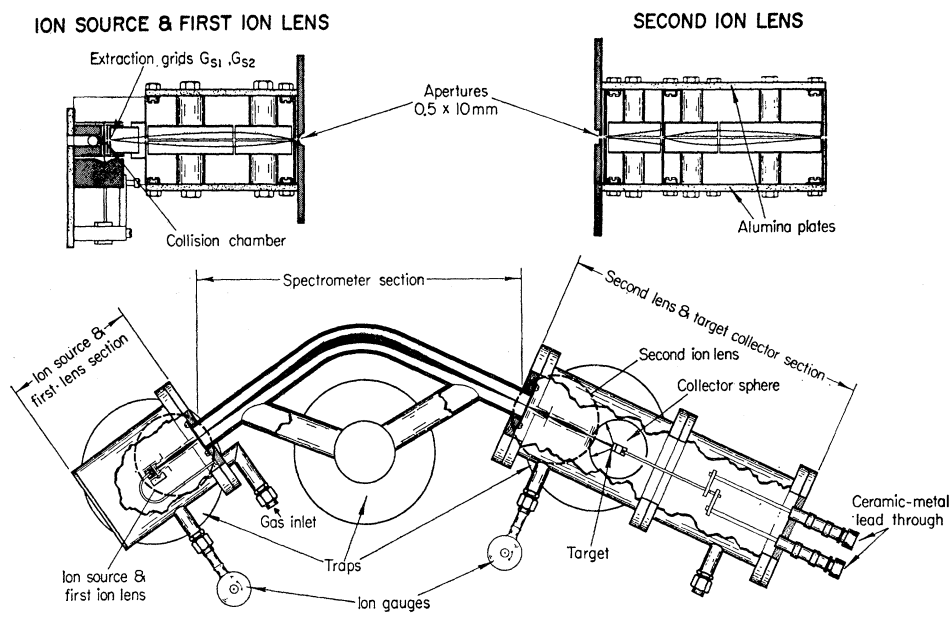


FIG. 2. Schematic diagram of the ion optics and the vacuum system.

view of the apparatus is given in Fig. 2. The ions enter the sphere through a small aperture and impinge on the target. The ejected electrons are collected by this sphere. The voltage between the collector and the target is varied to accelerate or decelerate the electrons. The current at the sphere is recorded as a function of this voltage. The derivative of this retarding potential curve represents the energy distribution of the ejected electrons. The vacuum chamber is made of 304 stainless steel and can be baked at 400°C. The system is evacuated by three Edwards 2M4 mercury vapor pumps. A detailed description of the apparatus and experimental techniques is presented elsewhere.<sup>9</sup>

All of the measurements to be reported in this paper were made on a polycrystalline tungsten sample. The tungsten was cut from commercial rolled tungsten foil and electropolished in NaOH. It was found that flashing the sample to 2300°C for short periods of time (5–60 sec) did not produce “clean” conditions. Only after heating the sample to 1600°C for 6 days followed by flashing to 2400°C were clean conditions achieved.

### III. EXPERIMENTAL RESULTS: THE TOTAL ELECTRON YIELDS

The total electron yields for clean tungsten and tungsten with adsorbed gases as a function of the kinetic energy of the helium, nitrogen, hydrogen, and oxygen ions are shown in Fig. 3.

The behavior for the different ions will be discussed for each ion species individually.

#### A. Helium Ion ( $\text{He}^+$ )

The yields for  $\text{He}^+$  ions incident on the atomically clean tungsten surface obtained in the present work and those reported by Hagstrum<sup>10</sup> are given in the upper part of Fig. 3. The results reported by Hagstrum are in good agreement with those obtained here. The agreement is even more striking when we consider the loss of electrons through the aperture in the collector. Comparing the solid angles subtended at the target by the apertures in the apparatus described by Hagstrum<sup>11</sup> and in the present system, we find that our results should be higher than those obtained by Hagstrum by about 2%. This is approximately the difference between the two curves shown in Fig. 3. This amount is based on the assumption that the electrons are ejected from the target isotropically over angles. If the angular distribution were peaked in the direction of the surface normal, the difference would be somewhat greater.

The adsorption of both hydrogen and nitrogen on the surface decreases the electron yield. The degree of hydrogen coverage was measured using the flash filament technique and was approximately  $8 \times 10^{14}$  atoms per  $\text{cm}^2$ . The nitrogen coverage was  $2 \times 10^{14}$  atoms per  $\text{cm}^2$ . From Fig. 3 it is seen that an adsorbed nitrogen atom changes the yield of electrons ejected by  $\text{He}^+$  approximately three times more than an adsorbed hydrogen atom.

The results of the study of the influence of hydrogen and nitrogen adsorption on the Auger ejection of elec-

<sup>9</sup> F. M. Propst and E. Lüscher, *Rev. Sci. Instr.* **34**, 574 (1963).

<sup>10</sup> H. D. Hagstrum, *Phys. Rev.* **96**, 325 (1954).

<sup>11</sup> H. D. Hagstrum, *Phys. Rev.* **89**, 244 (1953).

trons by  $\text{He}^+$  by Hagstrum<sup>12</sup> cannot be compared directly with the present results because the gas coverages of the surfaces in the two experiments were different. In addition, Hagstrum found that, in the case of hydrogen, the target could not be cleaned immediately by flashing to high temperatures. He attributed this to diffusion of hydrogen out of the bulk of the tungsten. This effect was not observed in the present work until after very long exposure of the target to hydrogen.

### B. Hydrogen Molecular Ion ( $\text{H}_2^+$ )

The yields for  $\text{H}_2^+$  ions incident on clean and hydrogen-covered tungsten are also presented in Fig. 3. The yields for the clean surface were taken immediately after flashing the target to approximately 2200°K for several seconds. The amount of adsorbed gas was not more than 2% of the value for the "covered" target. The sharp increase in the yield with increasing incident kinetic energy of the ions might indicate that kinetic ejection is important at lower energies for  $\text{H}_2^+$ . One might expect this, since the lighter ions are more efficient at transferring kinetic energy to the electrons of the solid. It is interesting to observe that the difference between the yields for the clean surface and the covered surface is approximately constant over the range of energies presented. It is also important to note the very large fractional decrease in the yield due to the adsorption of hydrogen.

This behavior suggests that as in the case of  $\text{He}^+$  the adsorbed gas atoms on the surface affect the ejection mechanism in a fundamental manner.

### C. Nitrogen Molecular Ion $\text{N}_2^+$

The results for  $\text{N}_2^+$  are in striking contrast to those for  $\text{H}_2^+$ . Here as in the case of  $\text{He}^+$  there is a slight decrease in the yield with increasing ion energy. The change in the yield due to the adsorbed gas is the smallest of all of the systems studied. The total yield for  $\text{N}_2^+$  on atomically clean tungsten is almost identical to that for  $\text{H}_2^+$  at 50-eV ion kinetic energy. This is as we might expect, since the ionization potentials for the two ions are almost the same. However, this value (0.026) is surprisingly low. The ionization potentials for  $\text{H}_2$  and  $\text{N}_2$  are 15.6 eV and 15.5 eV, respectively. The ionization potential for Ar is 15.8 eV. The yield for  $\text{Ar}^+$  ions of 50-eV incident kinetic energy is 0.098 or approximately four times the value for  $\text{H}_2^+$  and  $\text{N}_2^+$  at the same kinetic energy. This small value for the total yield might be due to excitation of the vibrational states of the molecule. If all of the energy released in a transition is not absorbed by an electron but a fraction is transferred to the molecular vibration, more low-energy electrons will be produced than in the case of the noble gas ion with approximately the same ionization potential. These low-energy electrons have a

<sup>12</sup> H. D. Hagstrum, Phys. Rev. **104**, 1516 (1956).

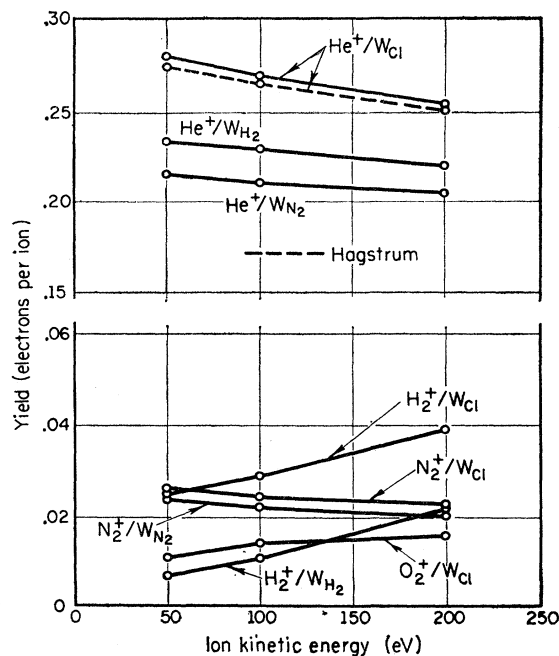


FIG. 3. Variation of the electron yields with the kinetic energy of the incident ions. The subscript "cl" indicates the atomically clean surface. The subscripts  $\text{H}_2$  and  $\text{N}_2$  indicate that the surface is covered by hydrogen or nitrogen, respectively.

lower probability of escape. Thus, the external yield would be lower than in the case of the noble gas ion.

### D. Oxygen Molecular Ion $\text{O}_2^+$

The yields for  $\text{O}_2^+$  ions incident on atomically clean tungsten are also given in Fig. 3. The value of the yield is markedly lower than that of the noble gas ion with approximately the same ionization potential. Xenon has an ionization potential of 12.1 eV and an electron yield of 0.017 for 50-eV ion kinetic energy.  $\text{O}_2$  has an ionization potential of 12.5 eV and an electron yield of 0.011 at the same kinetic energy. Again we must consider the possibility of excitation of vibrational levels and the binding of the molecule to the tungsten surface.

## IV. EXPERIMENTAL RESULTS: THE ELECTRON ENERGY DISTRIBUTIONS

### A. Helium Ion $\text{He}^+$

The energy distributions of electrons ejected from atomically clean tungsten by  $\text{He}^+$  ions of 50-, 100-, and 200-eV incident kinetic energy are shown in Fig. 4 (a). These results are in reasonable agreement with those reported by Hagstrum.<sup>10</sup> Figure 4 (b) shows a comparison between the distribution obtained here and that obtained by Hagstrum for  $\text{He}^+$  ions of 100-eV kinetic energy. The distribution obtained in the present work extends to slightly higher energies than those reported by Hagstrum. There is also a small difference between

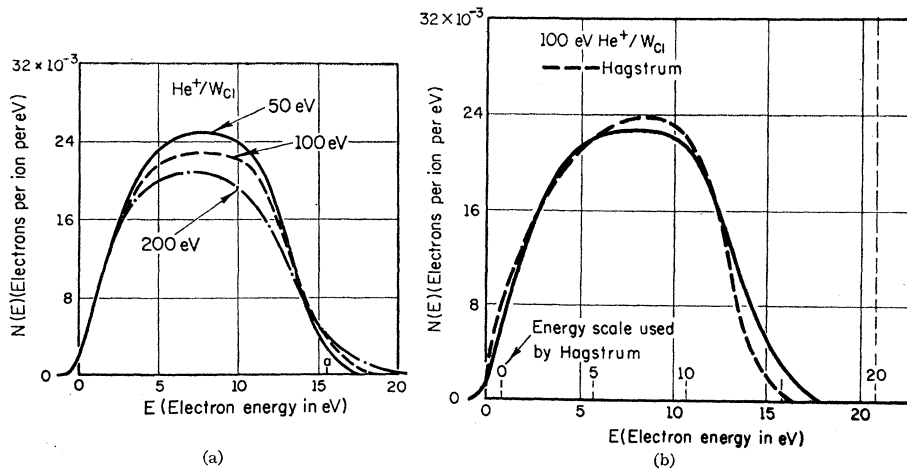


FIG. 4. (a) Energy distributions of electrons ejected from atomically clean tungsten by  $\text{He}^+$  ions of 50-, 100-, and 200-eV incident kinetic energy. The point labeled "a" indicates the value of  $E_i - 2\Phi$  for  $\text{He}^+$  ions. (b) Comparison of the energy distribution obtained in the present work with that reported by Hagstrum (see Ref. 10). The distribution is that for  $\text{He}^+$  ions of 100-eV kinetic energy incident on atomically clean tungsten. The lower dashed curve has been normalized to agree with the more recent value for the total yield reported by Hagstrum.

the position of the energy scale. The curves are drawn so that the low-energy edges are superposed. Hagstrum determined the zero point of the energy axis by retarding potential measurements on the thermionic current from the target. In the present work, we have used the Auger electron distribution itself to determine this zero point. This latter procedure was adopted in order to facilitate comparison of the distributions for the atomically clean surface with those of the gas-covered surface. The adsorption of both hydrogen and nitrogen changes the work function of tungsten. Thus, the contact potential determined by thermionic measurements does not apply to the gas-covered surface.

The energy distributions of electrons ejected from hydrogen-covered and nitrogen-covered tungsten by

$\text{He}^+$  are shown in Figs. 5 (a) and 5 (b). These distributions are compared with those for the atomically clean surface in Figs. 6 (a)–6 (c). It is seen that the distributions for the clean and hydrogen-covered surface change with the kinetic energy of the ions in a similar manner. The maximum values of these distributions decrease significantly with increasing kinetic energy of the ions. The most pronounced change in these distributions occurs near their maxima. On the other hand, the maxima in the distributions for the nitrogen-covered surface show very little dependence on the energy of the ions and most of the change in the distributions occurs at higher electron energies. The effect of the adsorption of hydrogen and nitrogen is illustrated in Figs. 7 (a) and 7 (b), where the difference between the distributions for the clean surface and the gas-covered surface is plotted. The effect of the adsorbed gas atoms is that a greater fraction of the electrons are excited with lower energies. Since the escape probability decreases with the energy of the electrons, the increase in the low-energy portions of the distributions is not as great as the decrease in the high-energy portion. The symmetry of the curves for the change due to hydrogen adsorption [Fig. 7 (a)] tends to substantiate the arguments for the potential character of the ejection mechanism.

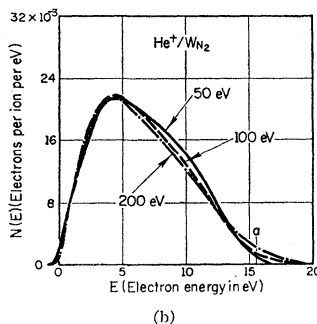
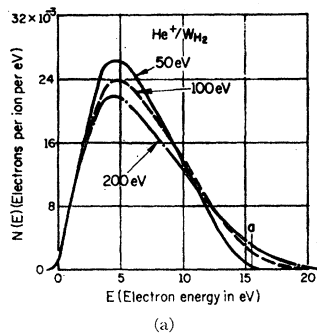


FIG. 5. Energy distributions of electrons ejected (a) from hydrogen-covered tungsten and (b) from nitrogen-covered tungsten by  $\text{He}^+$  ions of 50-, 100-, and 200-eV incident kinetic energy. The point labeled "a" is the value of  $E_i - 2\Phi$  for  $\text{He}^+$  ions.

### B. Molecular Ions of Hydrogen, Nitrogen, and Oxygen ( $\text{H}_2^+$ , $\text{N}_2^+$ , $\text{O}_2^+$ )

The energy distributions of electrons ejected from atomically clean tungsten by  $\text{H}_2^+$ ,  $\text{N}_2^+$ , and  $\text{O}_2^+$  ions of 50-, 100-, and 200-eV incident kinetic energy are shown in Figs. 8 and 9. At 50-eV kinetic energy, the distributions for  $\text{H}_2^+$  and  $\text{N}_2^+$  are almost identical. Since these ions have the same ionization potential, it seems probable that the ejection mechanism for the two ions are similar. As the ion kinetic energy is increased, the distributions for  $\text{H}_2^+$  increase and extend to higher energies. This is as one would expect if kinetic ejection

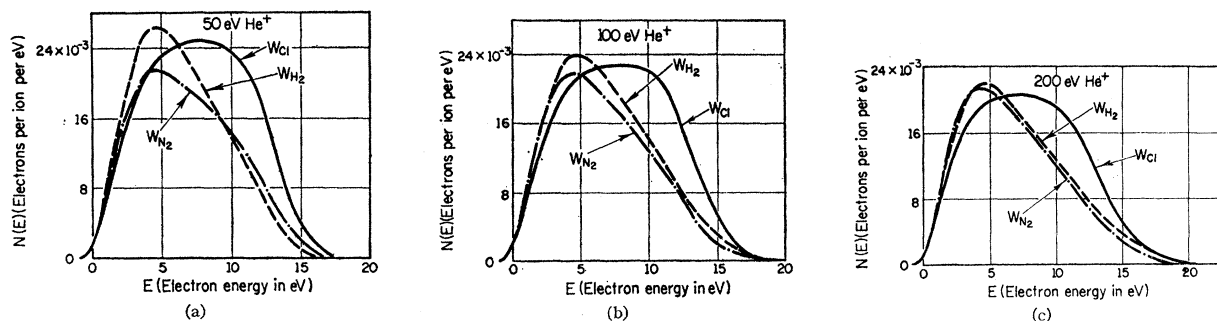


FIG. 6. Energy distributions of electrons ejected from atomically clean, hydrogen-covered, and nitrogen-covered tungsten by  $\text{He}^+$  ions of (a) 50-eV, (b) 100-eV, and (c) 200-eV incident kinetic energy.

were present. In contrast, the distributions for  $\text{N}_2^+$  ions do not change significantly with increasing ion energy. This indicates that kinetic ejection by  $\text{N}_2^+$  does not become important until higher kinetic energies of the ions are reached. On the basis of a simple hard-sphere model, the threshold for kinetic ejection by  $\text{N}_2^+$  would be 14 times higher than for  $\text{H}_2^+$ . It is interesting to note that the upper energy limits of the distributions of electrons ejected by  $\text{H}_2^+$  and  $\text{N}_2^+$  ions of 50-eV kinetic energy are in good agreement with the limit of  $E_i - 2\Phi$  ( $E_i$  = ionization energy of the ion and  $\Phi$  = work function of the metal) predicted by energy conservation applied to the simple model depicted in Fig. 1. This suggests that some of the processes take place while ions retain the molecular form and that all of the energy released is absorbed by an electron from the metal. However, the low value of the yield indicates that the fraction of processes which take place in this manner is small.

The upper energy limit of the electron distribution for oxygen molecular ions  $\text{O}_2^+$  of all energies is in marked disagreement with the  $E_i - 2\Phi$  value. Oxygen is also adsorbed in the atomic form with relatively high binding energy ( $\sim 5$  eV per atom). It is possible that a fraction of the processes take place in such a way that not only the ionization energy but also the binding energy is transferred to a single electron. Again, the low value of the total yield indicates that this fraction is small.

The effect of the adsorption of hydrogen on the energy distributions of electrons ejected by  $\text{H}_2^+$  is shown in Figs. 10 and 11. The energy distributions for the covered surface show a dependence on the kinetic energy of the ions analogous to that for the clean surface. Adsorbed hydrogen decreases the total yield and shifts the energy distribution towards lower energies.

The influence of adsorbed nitrogen on the electron energy distributions by  $\text{N}_2^+$  is represented in Figs. 12 and 13. In contrast to the case of hydrogen, the adsorption of nitrogen causes small changes in the distributions. The adsorption of nitrogen shifts the distributions slightly toward lower energies, but otherwise they are not changed significantly.

## V. DISCUSSION AND CONCLUSIONS

### A. Yields and Energy Distributions

Calculations of the ejection of electrons from tungsten by  $\text{He}^+$  have been given previously.<sup>5,8</sup> The agreement with the experimental distribution is reasonably good. A more complete treatment, starting from first principles, is complex and requires further investigation.

The situation for molecular hydrogen ions  $\text{H}_2^+$  is even more complicated. The interaction of hydrogen with tungsten (bound states) and dissociation of  $\text{H}_2^+$  have to be taken into account. The binding energy of a hydrogen atom on tungsten is 3 eV,<sup>13</sup> the dissociation energy of the  $\text{H}_2$  molecule is 4.5 eV,<sup>13</sup> and the first ionization potential of  $\text{H}_2$  is 15.5 eV. In Fig. 14 the potential energy curves for the initial and final states of the  $\text{H}_2^+$  ion incident on the tungsten are represented.

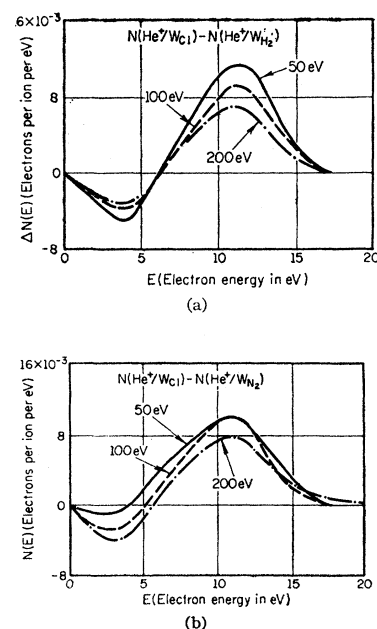


FIG. 7. Change in the energy distributions of electrons ejected from tungsten due (a) to the adsorption of hydrogen, and (b) to the adsorption of nitrogen. The curves are for  $\text{He}^+$  ions of 50-, 100-, and 200-eV incident kinetic energy.

<sup>13</sup> R. Gomer, *Field Emission and Field Ionization* (Harvard University Press, Cambridge, Massachusetts, 1961), p. 119.

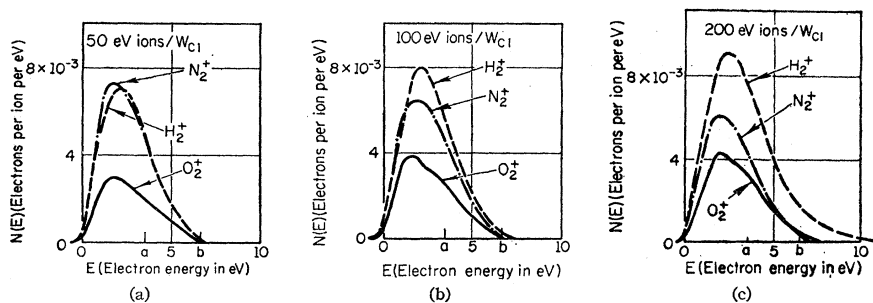


FIG. 8. Energy distributions of electrons ejected from atomically clean tungsten by  $H_2^+$ ,  $N_2^+$ , and  $O_2^+$  ions of (a) 50-eV, (b) 100-eV, and (c) 200-eV incident kinetic energy. The point labeled "a" is the value of  $E_i - 2\Phi$  for  $O_2^+$  ions. The point labeled "b" is the value of  $E_i - 2\Phi$  for  $H_2^+$  and  $N_2^+$  ions.

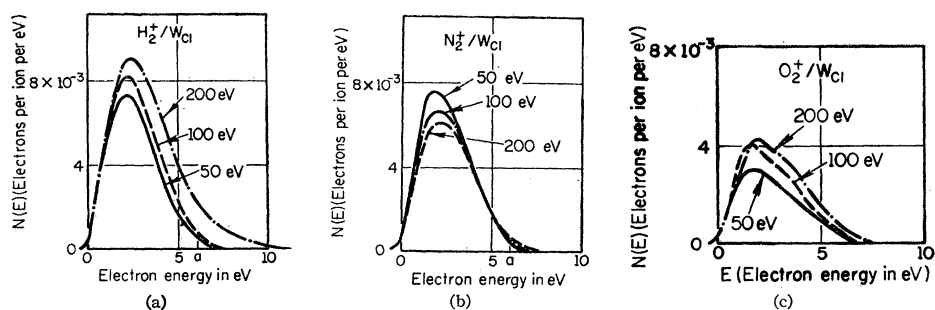


FIG. 9. Energy distributions of electrons ejected from atomically clean tungsten by ions of 50-, 100-, and 200-eV incident kinetic energy. The point labeled "a" is the value of  $E_i - 2\Phi$  for the ions. (a)  $H_2^+$  ions; (b)  $N_2^+$  ions; (c)  $O_2^+$  ions

The three systems are (1)  $H_2^+ + ne_m$ ,  $H_2^+$  ion in the ground state plus  $n$  metallic electrons in the ground state; (2)  $H_2 + (n-2)e_m + e_k$ ,  $H_2$  molecule in the ground state plus  $n-2$  metallic electrons plus one free electron; and (3)  $2H + (n-2)e_m + e_k$ , two hydrogen atoms in the ground state plus  $n-2$  metallic electrons plus a free electron. There are also two holes in the metal in systems 2 and 3, but this does not enter into the present considerations. For large distances of the ion from the surface the potential energy for system 1 is chosen to be zero. System 2 is derived from the first system by removing an electron from the metal, neutralizing the ion with this electron, and absorbing the excess energy with a second electron from the metal. If both electrons are taken from the Fermi level, the potential for this state of the system for large separation is  $E_i - 2\Phi$  lower than the potential for system 1. This corresponds to the state of system 2 with lowest potential energy corresponding to the  $n^2$  combinations of the two electrons taken from the metal. There is a band of  $n^2$  states extending upward from the lowest level. The states of system 3 are obtained in a similar manner. The results are the same except that all of the states are shifted upward on the potential scale by an amount

equal to the dissociation energy of the  $H_2$  molecule (4.5 eV). The levels that lie above the curve for the initial state correspond to electrons that cannot escape from the metal. In the approximation of the Franck-Condon principle, transitions occur vertically between potential curves. The kinetic energy (outside of the metal) of the free electron is given by the difference in potential between the curves for the initial and final states at the distance from the surface at which the transition occurs. The curves of Fig. 14 exhibit a large number of degenerate levels and a large number of resonant states. The situation is even more complicated than shown in the figure. We have not included the vibrational states of the  $H_2$  molecule. In fact, system 3 corresponds to the highest vibrational level of the molecule in system 2.

In comparison to the case of the noble gas ion ( $Ar^+$ ) with approximately the same ionization energy as  $H_2^+$ , there is a large increase in the density of the final states with potential curves close to the potential curve of the initial state. Transitions to these states give rise to excited electrons with lower kinetic energies. Since the probability of escape is smaller for low-energy electrons,<sup>8</sup> the yield is decreased because of these additional states. There is also a large increase in the number of states that correspond to bound electrons. The relative values of the matrix elements between the various states determine the magnitude of this decrease in yield. However, the qualitative behavior of a decreased yield is independent of these relative values.

Finally, we see that the binding energy of the hydrogen atoms to the tungsten surface does not introduce the possibility of the excitation of electrons with ki-

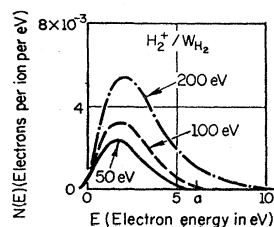
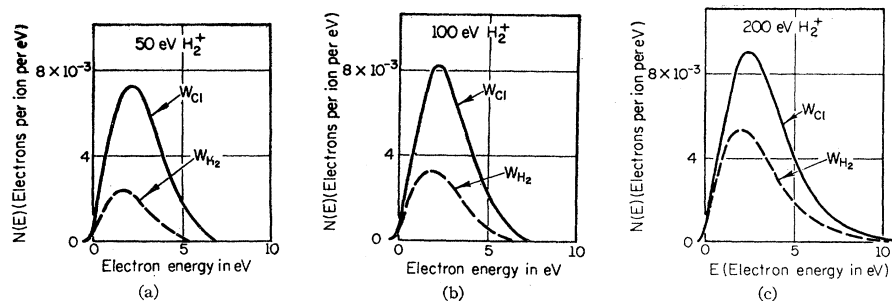


FIG. 10. Energy distributions of electrons ejected from hydrogen-covered tungsten by  $H_2^+$  ions of 50-, 100-, and 200-eV incident kinetic energy. The point labeled "a" is the value of  $E_i - 2\Phi$  for  $H_2^+$  ions.

FIG. 11. Energy distributions of electrons ejected from atomically clean and hydrogen-covered tungsten by  $H_2^+$  ions of (a) 50-eV, (b) 100-eV, and (c) 200-eV incident kinetic energy.



netic energy in excess of  $E_i - 2\Phi$ . The image potential shifts the potential curve for the initial state downward so that the maximum distance between the potential curve for this state and the curve for the lowest state in system 3 is never appreciably greater than  $E_i - 2\Phi$ . Detailed knowledge of the interaction curves for the molecule and molecular ion with the surface is required to predict exactly the maximum value of the kinetic energy of the excited electrons. On the basis of this model, we expect the total yield for  $H_2^+$  ions to be appreciably less than the total yield for  $Ar^+$  ions. We also expect the maximum kinetic energy of the ejected electrons to be approximately  $E_i - 2\Phi$ . The effect of the additional states introduced by the vibrational states of the hydrogen molecule can be illustrated qualitatively following a procedure similar to that outlined by Hagstrum<sup>5</sup> and making the following assumptions: (1) The transition probabilities are independent of the initial energies of the two participating electrons. (2) The transition probabilities are independent of the excitation of the hydrogen molecule. (3) The electrons are excited isotropically over a solid angle of  $4\pi$ . (4) The molecule is not excited into the continuum of dissociated states. The excited states of the hydrogen molecule are given by

$$E_v(v) = hc\nu_0(v + \frac{1}{2}) - hc x(v + \frac{1}{2})^2, \quad (1)$$

where  $v$  is the vibrational quantum number,  $\nu_0$  is the vibrational wave number ( $4395 \text{ cm}^{-1}$ ),  $x$  is the anharmonic constant ( $118 \text{ cm}^{-1}$ ),  $c$  is the speed of light, and  $h$  is the Planck constant. The calculated energy distributions for  $H_2^+$  and  $Ar^+$  based on these assumptions are represented in Fig. 15. The ratio of the total

yields predicted by this calculation is 3.1 and the experimental value is 3.8. We emphasize that the calculation is only qualitative and does not give proper values for the total yield for either ion. However, it illustrates the effect of additional states.

The considerations for the  $N_2^+$  ion are similar to those for the  $H_2^+$  ion. Although the dissociation energy of  $N_2$  is twice as great as the dissociation energy of  $H_2$ , the vibrational levels are approximately twice as dense in  $N_2$ . Thus, we expect approximately the same results

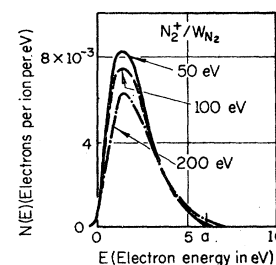
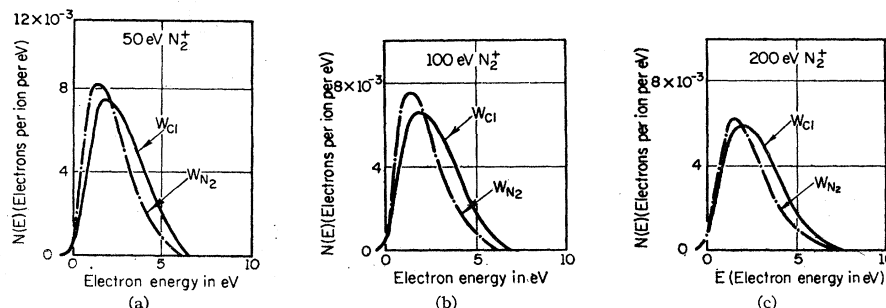


FIG. 12. Energy distributions of electrons ejected from nitrogen-covered tungsten by  $N_2^+$  ions of 50-, 100-, and 200-eV incident kinetic energy. The point labeled "a" is the value of  $E_i - 2\Phi$  for  $N_2^+$  ions.

for the two ions when there is no kinetic ejection present. This is found to be the case for ions of 50-eV kinetic energy or lower.

The arguments for oxygen molecule ions  $O_2^+$  are analogous to those above. However, there is now the possibility that some processes occur that result in excited electrons with kinetic energy greater than  $E_i - 2\Phi$ . This is due to the large binding energy of oxygen on tungsten. In Fig. 16 the potential curves for the following three systems are shown: (1)  $O_2^+ + ne_m$

FIG. 13. Energy distributions of electrons ejected from atomically clean and nitrogen-covered tungsten by  $N_2^+$  ions of (a) 50-eV, (b) 100-eV, and (c) 200-eV incident kinetic energy.



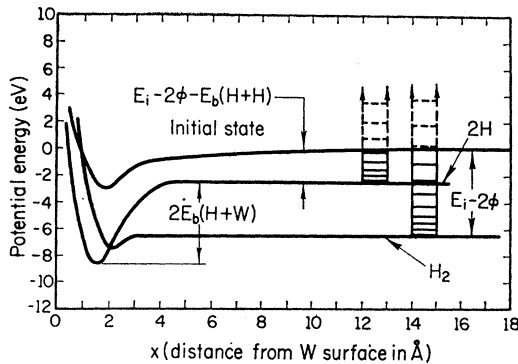


FIG. 14. Potential energy curves for the initial and final states for the  $H_2^+$  ion incident on tungsten.  $E_i$  is the first ionization potential of the  $H_2$  molecule,  $\Phi$  is the work function of tungsten,  $E_b(H-H)$  is the binding energy of the  $H_2$  molecule, and  $E_b(H-W)$  is the binding energy of the hydrogen atom on tungsten.

( $O_2^+$  ion in the ground state plus  $n$  metallic electrons in the ground state, which is the initial state); (2)  $O_2 + (n-2)e_m + e_k$  ( $O_2$  molecule in the ground state plus  $n-2$  metallic electrons plus a free electron); (3)  $2O + (n-2)e_m - e_k$  (two oxygen atoms plus  $n-2$  metallic electrons plus a free electron). The curves of Fig. 16 have been drawn to make the value of  $E_m$  (the maximum kinetic energy of the excited electrons) equal to the experimentally determined value of 6.5 eV. This allows an estimate of the binding energy of oxygen on tungsten of approximately 5.5 eV. This value agrees with the binding energy of 5 eV reported by Becker and Brandes.<sup>14</sup> We emphasize again that the estimate is approximate, since we do not know the form of the

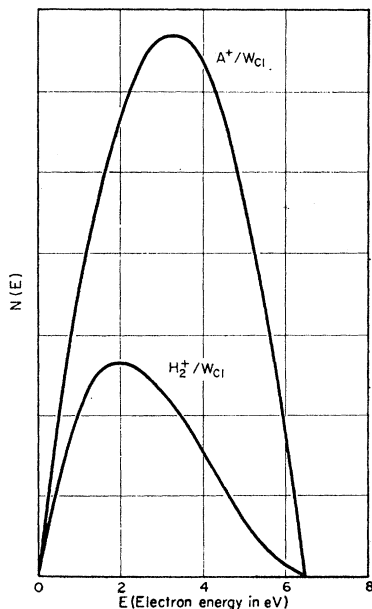


FIG. 15. Calculated energy distribution of electrons ejected by  $H_2^+$  and  $Ar^+$ .

interaction of the molecule and the molecular ion with the surface. Thus, we have a qualitative explanation for the experimentally determined facts that the total yield for  $O_2^+$  ions is lower than for the noble gas ion of the same ionization energy ( $Xe^+$ ) and that the  $E_i - 2\Phi$  limit is violated.

## B. Influence of Gas Adsorption

In general, the yields and energy distributions of electrons ejected from metal surfaces by low-energy ions are strongly dependent on the nature and density of the adsorbed gases on the surface. As a possible mechanism to explain this effect, we assume that the adsorbed gas atoms introduce localized electronic states at the surface of the metal from which the primary Auger electrons can scatter. These states are illustrated schematically in Fig. 17, where we show an excited state of the electron around the adsorbed atom at an energy  $W$  above the ground state of the electron. In the cases of adsorbed hydrogen and nitrogen, these ground states are so far below the vacuum level that one would not expect them to participate strongly in the direct Auger transitions. However, as an electron excited in an Auger process leaves the metal, it can scatter from an electron in the ground state around an adsorbed atom, exciting this electron to the higher state. In such a process, the primary electron loses an amount of energy equal to  $W$ . The energy distribution of electrons ejected from the gas covered surface would then consist of the two parts:

(1) The portion of the electrons that escape from the metal without scattering from the surface states. The energy distribution of these electrons would be

$$[1 - f(E)]N_{e1}(E), \quad (2)$$

where  $f(E)$  is the scattering fraction and  $N_{e1}(E)$  is the energy distribution of electrons ejected from the clean

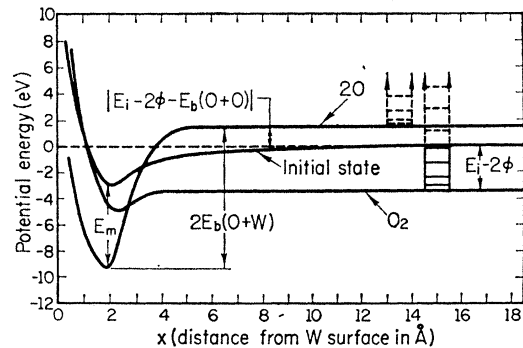


FIG. 16. Potential energy curves for the initial and final states for the  $O_2^+$  ion incident on tungsten.  $E_i$  is the first ionization potential of the  $O_2$  molecule,  $\Phi$  is the work function of tungsten,  $E_b(O-O)$  is the binding energy of the  $O_2$  molecule, and  $E_b(O-W)$  is the binding energy of the oxygen atom on tungsten.

<sup>14</sup> J. A. Becker and R. G. Brandes, *J. Chem. Phys.* **23**, 1323 (1955).



surface. The scattering fraction,  $f(E)$ , is given by

$$f(E) = n_a \sigma(E), \quad (3)$$

where  $n_a$  is the density of adsorbed atoms and  $\sigma(E)$  is the scattering cross section.

(2) The portion of the electrons that scatter and escape from the metal with an energy  $E - W$ , where  $E$  is the original kinetic energy of the scattered electron.

In the energy range  $E_m - W \leq E \leq E_m$ , where  $E_m$  is the maximum kinetic energy of ejected electrons, only the electrons that escape without scattering contribute to the energy distribution of electrons ejected from the gas covered surface. If the scattering cross section  $\sigma$  is constant over this energy range, the energy distribution for the gas covered surface will be a constant fraction of the energy distribution for the clean surface in this energy range. Figure 18 (a) shows a comparison between the energy distribution of electrons ejected from hydrogen-covered tungsten and  $0.36N_{el}(E)$  for  $\text{He}^+$  ions of 50-eV incident kinetic energy. The two curves coincide for energies within approximately 4.5 eV of the maximum kinetic energy. Figure 18 (b) shows the same curves for 50-eV  $\text{He}^+$  ions incident on clean and nitrogen-covered tungsten. These curves coincide for energies within approximately 5.5 eV of the maximum energy. This indicates that the excited states lie 4.5 and 5.5 eV above the ground states for adsorbed hydrogen and nitrogen, respectively. The amount of adsorbed hydrogen used in the present work corresponds to approximately  $8 \times 10^{14}$  atoms/cm<sup>2</sup>. From

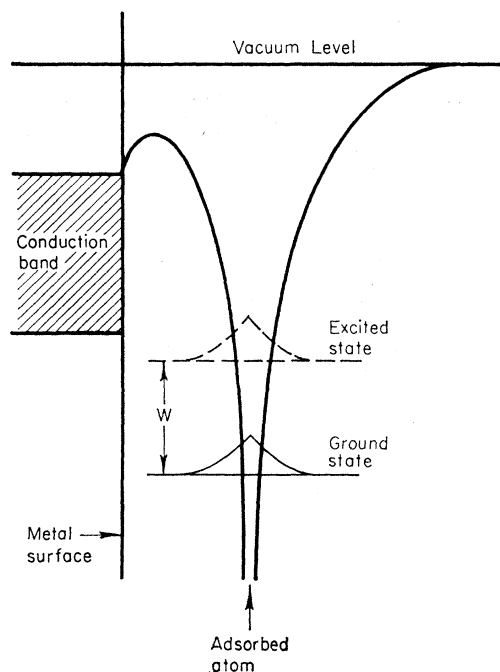


FIG. 17. Schematic diagram of the ground and excited electronic states of an adsorbed atom.

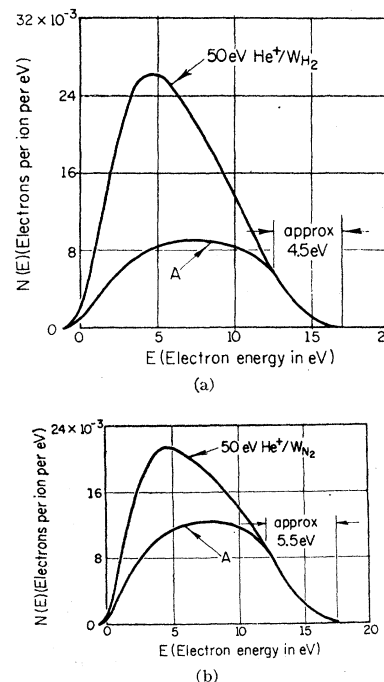


FIG. 18. Comparison of (a)  $N(E)_{\text{H}_2}$  with  $0.36N_{el}(E)$  and (b)  $N(E)_{\text{N}_2}$  with  $0.5N_{el}(E)$ , where  $N(E)_{\text{H}}$ ,  $N(E)_{\text{N}}$ , and  $N_{el}(E)$  are the energy distributions of electrons ejected from hydrogen-covered, nitrogen-covered, and clean tungsten by  $\text{He}^+$  ions of 50-eV incident kinetic energy.

this we deduce a cross section  $\sigma$  of approximately  $8 \times 10^{-16}$  cm<sup>2</sup>.

We can make a rough estimation of the total energy distribution of electrons ejected from the gas covered surface by assuming that the electrons that scatter from the surface states escape from the metal with the reduced probability of escape appropriate to the reduced energy. In this approximation, the total energy distribution is given by

$$N_{\text{covered}}(E - W) = [P(E - W)/P(E)]f(E)N_{el}(E) + [1 - f(E - W)]N_{el}(E - W), \quad (4)$$

where  $P(E)$  is the probability of escape and  $N_{el}(E)$  is the energy distribution for the clean surface. In Fig. 19, we show a comparison between this function and the energy distribution of electrons ejected from hydrogen-covered tungsten by  $\text{He}^+$  ions of 50-eV incident kinetic energy. The escape probability used in this calculation is that derived on the assumption of an isotropic angular distribution of the excited electrons.<sup>5</sup> The calculation is obviously crude; however, it is seen that the qualitative features of the experimental distribution are reproduced.

The fraction of electrons scattered from the high-energy portions of the distributions is greater for hydrogen than for nitrogen (for the coverage used in the present work). In contrast to this, at lower electron energies the distribution for the hydrogen-covered surface is higher than the distribution for the nitrogen-covered surface. This may be due to the fact that the surface state for the adsorbed nitrogen atoms is at a lower energy than the surface state for the adsorbed

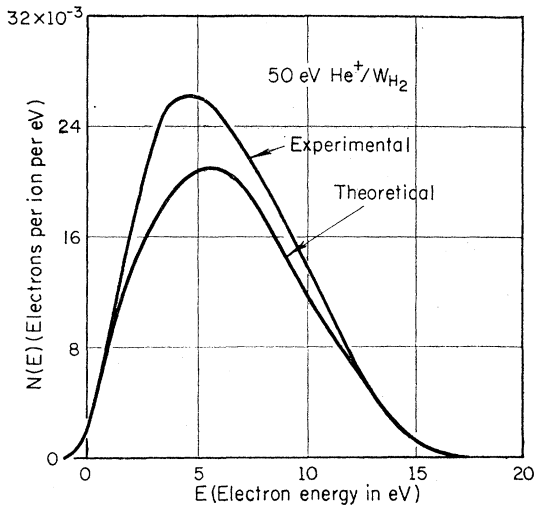


FIG. 19. Comparison between the theoretical [Eq. (4)] and experimental energy distribution of electrons ejected from hydrogen-covered tungsten by  $\text{He}^+$  ions of 50 eV incident kinetic energy.

hydrogen atoms. Thus, a greater fraction of the electrons that scatter from the nitrogen state will result in electrons that cannot escape from the metal. We note that electrons not in the critical cone of escape<sup>8</sup> can also scatter from the surface states and give rise to electrons which can escape. These electrons would also contribute to the low-energy portion of the distributions.<sup>15</sup>

For  $\text{H}_2^+$  ions incident on hydrogen-covered tungsten, the argument is the same. Since the excited state for adsorbed hydrogen is approximately 4.5 eV above the ground state, all electrons with enough energy to escape from the metal can scatter inelastically from an electron in a surface state. The scattering cross section increases as the energy of the electron decreases. Thus, we would expect the adsorption of hydrogen to cause a large reduction in the distribution of electrons ejected by  $\text{H}_2^+$  ions. This is found experimentally as shown in Fig. 11. Only the electrons above 4.5-eV external kinetic

<sup>15</sup> We note that localized electronic surface states at an energy  $W$  below the Fermi level would give similar effects. Again, the minimum amount of energy that an electron could lose in a collision is  $W$ . Thus in the energy range from  $E_{\text{max}} - W$  to  $E_{\text{max}}$  the energy distribution of electrons ejected from the gas-covered surface would be some fraction  $f$  times the distribution for the clean surface. The other arguments are essentially the same. However, in this case, when the external kinetic energy of the scattered electron is greater than  $W$  plus the work function  $\Phi$  of the metal, there is the possibility that both the scattered and the scattering electron can escape from the solid, thus giving rise to a greater preponderance of low-energy electrons.

energy can suffer an inelastic collision and still give rise to electrons with enough energy to escape from the metal. This again gives rise to a lower yield in the case of the hydrogen-covered surface.

For  $\text{N}_2^+$  ions incident on nitrogen-covered tungsten, the situation is somewhat different. An electron must have an energy greater than  $W$  above the Fermi level in order to lose energy in an inelastic collision with a surface state. Thus, electrons with external kinetic energy less than  $W - \Phi$  cannot suffer such collisions. Therefore, we expect the portion of the electron distribution between 0 and  $W - \Phi$  not to change by a great amount upon the adsorption of a gas that introduced levels at an energy  $W$  below the Fermi level. In Figs. 12 and 13, we see that the distributions for  $\text{N}_2^+$  ions incident on tungsten do not change greatly below about 2 eV when nitrogen is adsorbed. This indicates that the level for adsorbed nitrogen is approximately 6.5 eV above the ground state. For a nitrogen-covered tungsten surface with incident  $\text{He}^+$  ions the value found is 5.5 eV. It is likely that the level is approximately 6 eV above the ground state and fairly broad. The qualitative explanation of the small change in the distribution when nitrogen is adsorbed (which is in striking contrast to the case for  $\text{H}_2^+$  ions incident on hydrogen-covered tungsten) is still valid.

This mechanism gives a qualitative explanation for (1) the large change in the distribution of electrons ejected by  $\text{H}_2^+$  due to the adsorption of hydrogen; (2) the relatively small change in the distribution of electrons ejected by  $\text{N}_2^+$  due to the adsorption of nitrogen; and (3) the relative values of the distributions of electrons ejected from hydrogen- and nitrogen-covered tungsten by  $\text{He}^+$  ions.

In conclusion, it is possible to explain the experimental results assuming the excitation of vibrational states in the molecule ions and the scattering of the excited electrons from surface states, which are introduced by adsorbed gas atoms. We emphasize that the models are tentative.

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