

Particle ejection from ion-bombarded clean and reacted single-crystal surfaces

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A model based on a classical dynamical calculation of the impact of a 600-eV Ar^+ ion into a single crystal has been developed to the point where it compares quantitatively to a wide variety of experimental observables. Here, we make direct comparisons between experiment and theory for relative sputtering yields, energy and angular distributions of the ejected atoms, and multimer yields. The model is also extended from clean single-crystal surfaces to include adsorbate atoms and molecules. These results are compared to experimental SIMS studies aimed at sorting out the structure-sensitive factors that contribute to the cluster ion yield. In oxygen chemisorption on Ni(100), for example, the O_2^-/O^- yield is four times larger for a $c(2 \times 2)$ coverage than for a $p(2 \times 2)$ coverage, a value also predicted by the calculations. In molecular CO chemisorption, the ejection of CO is found to occur molecularly in both the experiments and in the calculations. In comparison to the calculations, a high value of $\text{Ni}_2\text{CO}^+/\text{NiCO}^+$ is consistent with a bridge-bonded CO structure at low coverage.

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I. INTRODUCTION

The elucidation of the chemistry of solid surfaces using low energy ion beams (500–5000 eV) as a probe has been a continuing goal of many groups over the last decade. Of particular interest is the development of secondary ion mass spectrometry (SIMS). Here, the momentum of the primary ion beam, usually Ar^+ is utilized to cause ejection into the vacuum¹ of various atomic and molecular species from the sample surface. Although each ionic impact event causes a great deal of chemical² and physical³ damage, the total dose is kept below 10^{13} ions cm^{-2} to avoid striking the same point on the surface more than once.¹ Although the technique is sensitive to fractions of a monolayer, the large amount of data obtained using the method are difficult to interpret in terms of the structure of the original surface.

Recent theoretical attempts to quantitatively describe the mechanism of the momentum deposition of the primary ion have been quite successful.⁴⁻⁹ The approach utilizes a standard classical dynamical treatment to model the response of a 250 atom microcrystallite.⁴ The calculation is capable of generating a variety of experimental observables including relative sputtering yields,⁴ energy,⁴ and angular⁵ distributions of the ejected atoms, multimer yields^{6,7} and surface damage information.⁴ The model has also been extended from clean single-crystal surfaces to include adsorbate atoms⁸ and molecules.⁹ Although the ionization probability of a given particle is not considered in the calculation, the method provides a necessary first step in generating any new model which does

include ionization. A general conclusion from this theoretical effort is that the surface morphology—the location of specific atoms with respect to each other—is a dominant factor in determining ejection mechanisms for a given system. A number of possible approaches to the elucidation of the surface structure seem feasible by experimentally examining the appropriate observables.

A direct comparison of our calculations to experimental studies of ejected neutral or ionic species, then, requires the use of single-crystal surfaces. Only a few of these systems have been experimentally examined at present. Our efforts have been directed towards a SIMS investigation of the Ni(100) (10) and Ni(111) (11) surfaces exposed to O_2 (10) and CO (12), since many other experimental techniques have also been employed to characterize these systems.

In this paper, we present a comprehensive comparison between the predictions of the molecular dynamics calculations and the experimental results obtained from clean and reacted single-crystal surfaces. As a rule, we find these comparisons are most successful when ratios of yields between different crystal faces or between adsorbates in different coverages are used, since ambiguities in the potential surfaces and ionization probabilities are minimized. We find the measured yields are quite sensitive to the crystal structure, coverage and site symmetry of adsorbates. Preliminary examples based on the chemisorption of O_2 and CO on Ni(100) illustrate these concepts and suggest a number of new approaches to surface characterization with SIMS.

TABLE I. Total yield of 600-eV argon ion on copper (100), (110), and (111).

Crystal face	Total number of trajectories	Total number of atoms ejected	Total yield	Relative yield ^a			
				Calculated	Experiment ^b Cu	Experiment ^b Ag	Experiment ^c Au
(100)	211	857	4.06	1.0	1.0	1.0	1.0
(110)	121	429	3.54	0.9	0.6	0.7	0.7
(111)	188	1222	6.50	1.6	1.8	1.6	1.5

^a Normalized to the (100) face.

^b Measured at 2 keV by weight loss.¹⁵

^c Measured at 2 keV by weight loss.¹⁶

II. PROCEDURES

A. Calculational method

Details of the classical dynamical procedure have been described in detail elsewhere.^{4,6,8} In general, we solve Hamilton's equations in time for a model microcrystallite containing four layers with ~ 60 atoms/layer. Adsorbate atoms or molecules can be placed on top of this microcrystallite. The Ar^+ ion of energy 600 eV is then allowed to strike between 50–200 different points in an irreducible symmetry zone of the surface. The potential parameters have been published elsewhere.^{8,9}

B. Experimental method

The SIMS measurements are performed in a standard UHV chamber with a base pressure of 4×10^{-9} Pa. The crystal can be transferred in UHV to a HP 5950A ESCA spectrometer for determination of surface coverages. The primary ion beam is in all cases Ar^+ at 2000 eV with a maximum current density of 2×10^{-9} A cm^{-2} . The components of the SIMS/XPS apparatus have been described in previous publications.^{13,14}

III. CLEAN METAL SURFACES

A. Monomer yields

The classical dynamics treatment provides a direct measure of the yield of neutral Cu atoms ejected from a single-crystal surface. These yields are calculated by averaging the yields of the several hundred individual trajectories initiated over the symmetrically irreducible zone. This averaging is important since certain impact points yield no secondary particles at all, while others produce as many as 13 ejected atoms.^{4,6,7}

The model microcrystallite size is sufficient to contain all of the crystal motion which contributes to the ejection of particles. This aspect of the model allows direct comparison of yields calculated on these low index faces of copper as shown in Table I. Experimental studies by Magnuson and Carlston¹⁵ at 2 keV on these three faces give results which are in excellent agreement with the calculations when the numbers are normalized to the (100) face.

The absolute yields from Cu are somewhat different than the measured absolute yields, although our value of 4.0 atoms/ion on (100) versus the experimental value of 2.1 is not too unrealistic. We find that the absolute yields are quite

sensitive to the potential parameters, whereas the relative yields as reported in Table I are quite insensitive to changes in these parameters. In fact, when examined in this way, the importance of the surface morphology is most striking in that the same relative yields are also found for the low index faces of Ag¹⁵ and Au,¹⁶ as shown in Table I. Since no adjustments of potential parameters have been attempted in these studies, we only compare our results to experimental results when ratioing procedures can be employed which minimize the dependence on the interaction potential.

B. Secondary particle energy distributions

The distribution of the kinetic energies of the ejected particles can easily be computed using our model. In earlier work, we found the general shape of the curve to match quite well the experimental energy distribution of ejected neutral Cu atoms measured by Stuart and Wehner.¹⁷ The curve rises from zero at 0.0 eV to a maximum at an energy between 1–5 eV and then gradually falls off as $\sim E^{-1.6}$. The curve has a very long tail which extends to greater than 100 eV.

For the Cu(111) face, we now have calculated the energies of a collection of more than 1200 particles and can examine the shape of this curve under higher resolution conditions. As shown in Fig. 1, there is considerable structure in the curve including a peak at ~ 1.7 eV, a second peak or possibly a shoulder at ~ 2.7 eV and an early step at ~ 0.8 eV. Recent experimental energy distributions obtained by 30 keV Ar^+ on polycrystalline Cu are in remarkable agreement with all the features of this curve as shown in Fig. 1.¹⁸

A few earlier studies have also reported structure in the energy distributions which has been ascribed to "Focussons." Our analysis of the many individual trajectories clearly shows that the structure is not necessarily due to focussed collision sequences, rather that these are distinct, preferred mechanisms that cause given atoms to eject. Each atom thus has a characteristic energy distribution, which is not the same as the overall distribution. The resultant curve is then a superposition of a small set of preferred ejection mechanisms.

C. Angular distributions

The angular distribution of the ejected particles is strongly influenced by the crystal structure. Shown in Fig. 2 are the experimental¹⁹ and calculated angular distributions for Cu(100). The plots are made by putting a flat-plate collector above the surface. The radial distance corresponds to the polar deflection of the ejected particles. The agreement between

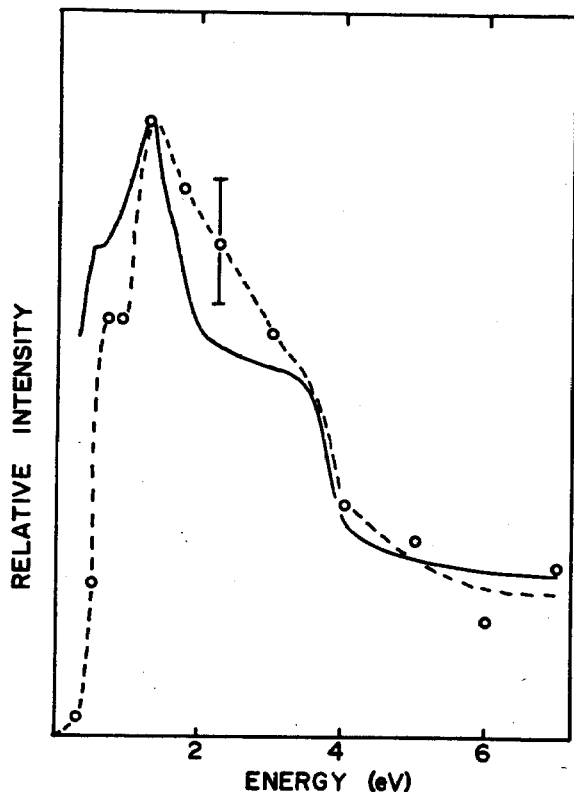


FIG. 1. Energy distribution of ejected Cu atoms. The solid line is our best reconstruction of the data presented in Ref. 18 for 30-keV Ar^+ ion bombardment of polycrystalline Cu. The dotted lines are our calculated values for 600-eV Ar^+ ion bombardment on Cu(111). The peaks have been normalized to the same height.

the experimental and calculated distributions is quite good. The fourfold symmetry of the (100) face is immediately apparent from the angular distributions of the ejected particles. From our calculations we can determine that the fourfold holes on the (100) face constrain the path of the ejected atoms, and their trajectories proceed, on the average, in the (001) plane perpendicular to the surface, thus causing the intense spots in the $\langle 110 \rangle$ direction. The angular distributions of the ejected particles from the (110) and (111) faces of copper reflect the appropriate symmetry and are also in good agreement with experimental results.

D. Multimer formation

Molecular clusters have been observed to be ejected from metal surfaces for many years. The calculational procedure has provided a qualitative understanding of the mechanism of cluster formation.^{6,7} For the clean metals, we find the atoms in the surface layer which ultimately make up a cluster are not necessarily ejected at the same time. The cluster establishes its identity over the solid and does not necessarily consist of atoms that were nearest neighbors on the surface. The quantitative predictions of the model concerning the relative amounts of dimers and trimers are in reasonable agreement with experiment. The Cu_2/Cu and Cu_3/Cu ratios as measured by secondary neutral mass spectrometry (SNMS) are shown in Table II.²⁰ The comparison of the actual yields calculated from an average of the Cu(100) and Cu(110) faces are in excellent agreement for the dimers and in qualitative agreement

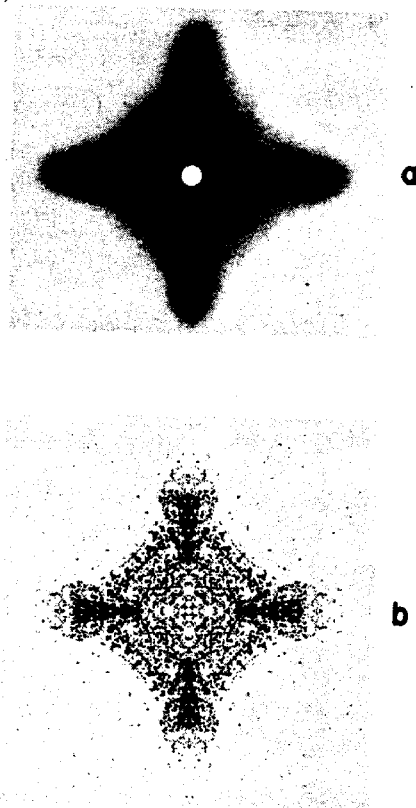


FIG. 2. Angular distribution of ejected atoms from Cu(100) by Ar^+ ion bombardment at normal incidence. Panel (a) is the experimental result taken from Ref. 19 for 4-kV Ar^+ ions. Panel (b) is our calculation for 600-eV Ar^+ ions.

for the trimers. The deviation between experiment and calculation for the trimers could arise from the use of an overly strong potential to describe Cu_3 or from the possibility that some of the Cu_3 molecules could dissociate before reaching the detector. The experimental number might be somewhat low since the fragmentation of Cu_3 during ionization was assumed to be negligible. The structural features of the experimental sample were not well defined; as we shall see, these numbers change considerably with surface morphology.

Our calculations show that the cluster formation probability depends strongly on how densely the surface atoms are packed. Recent experimental studies have been completed on Ni(100), (110), and (111) where the relative yields of $\text{Ni}_2^+/\text{Ni}^+$ and $\text{Ni}_3^+/\text{Ni}^+$ have been determined.²¹ The experiments were fortunately completed under conditions appropriate for comparison to our calculations, i.e., ultrahigh vacuum with low Ar^+ ion doses to avoid surface damage. The published results are shown in Table III for comparison with our calculations.

When the ratios are normalized to the (100) face, the

TABLE II. Theoretical and experimental comparison of the Cu_2/Cu and Cu_3/Cu ratio.

	(100) + (110)	polycrystalline ^a
Cu_2/Cu	0.134	0.104
Cu_3/Cu	0.013	0.001

^a Experimental data taken from Ref. 20.

TABLE III. Multimer yield ratios for the three low-index orientations.

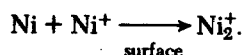
Ratio	Crystal face		
	(100)	(110)	(111)
Cu ₂ /Cu	1.0 (37/765) ^c	0.7 (14/401)	2.3 (107/953)
Ni ₂ ⁺ /Ni ⁺ ^b	1.0	0.6	1.8
Cu ₃ /Cu	1.0 (6/765)	0 (0/401)	1.9 (14/953)
Ni ₃ ⁺ /Ni ⁺ ^b	1.0	0.2	6.3

^a Normalized to the (100) face.

^b From Ref. 21.

^c The absolute number calculated for each species is given in the parenthesis.

agreement is quite encouraging. Of special interest is that the comparison of neutral molecule ratios to ion molecule ratios appears to be valid, and that the surface structure is more important in determining the relative yields than is the chemical nature of the target. The first observation suggests that, in accord with the mechanisms proposed for neutral dimer formation, that the ionic species form in an analogous fashion



We have confirmed the second point by altering considerably the interaction potential parameters of the dimer. Although absolute yields change drastically, the relative yields observed on the different faces are not strongly altered.

IV. ADSORBATES ON METALS

A. Atomic oxygen adsorption

Since the earlier investigations by Benninghoven using SIMS,¹ the interaction of oxygen with metal surfaces has been investigated with this technique by many groups. Because the cluster ion yields are usually enhanced in the presence of oxygen adsorption, a great deal of data is possible to obtain, although it is usually not possible to quantitatively interpret the results in terms of the surface structure. In this section, we examine the chemisorption of oxygen on Ni(100) and compare the results to classical dynamical calculations for atomic oxygen.

Many types of molecular cluster ions are observed to be ejected from Ni(100) exposed to a saturation exposure (~200 L) of oxygen. In our experiments we find, for example, Ni⁺, Ni₂⁺, Ni₃⁺, O[±], O₂[±], NiO[±], Ni₂O⁺, NiO₂⁻, and Ni₂O₃⁻. The calculational model provides insight into how these clusters arise. For the case of oxygen on Cu(100), the atomic trajectories have been calculated for oxygen placed in various coverages and adsorption site positions. The analysis clearly shows that the clusters form over the crystal surface after the components of the cluster eject in a more or less independent manner. The mechanism of cluster formation is completely analogous to that proposed for the clean metals. Considerable rearrangement of atoms on the surface that form the cluster is possible; the species are not lifted out of the surface intact, although considerable local atomic order is preserved. Since the constituent atoms of a cluster originate from a localized region

on the surface, the incorporation of oxygen into a nickel crystal to form NiO(100) should affect the Ni cluster yields. In our experiments we find that the Ni₃⁺ trimer yield is more dramatically reduced than is the Ni₂⁺ dimer yield, since the expanded NiO crystal statistically has fewer Ni atoms in the localized region. All of the clusters observed in SIMS have been found in the calculations to form by this "over the surface" mechanism.

Aside from its obvious structural implications, this mechanism also provides insight into the mechanism of ionization of the clusters. It is now believed that ions are ejected from the surface in their original charge state²² and that the low observed experimental ion yields are a consequence of reneutralization. Regardless of the ionization mechanism, however, there are both ions and neutrals that are ejected for each primary ion that impacts the surface. In accord with our model, then, the molecular cluster ions, must form over the surface as a result of collisions between neutral and ionized atoms. For example, the NiO⁺ ion should form by interactions between Ni⁺ ions and O atoms. The reaction between Ni atoms and O⁺ ions would not be important due to the low levels of O⁺ ions. Furthermore, if the number of ions above the surface is much less than the number of neutrals (which is the case for most materials except perhaps the alkali halides), the intensity of the resulting cluster ion will be controlled by the amount of the corresponding atomic ion.

This comparison is vividly illustrated in Fig. 3. In panel (a), we show how the yield of O₂⁺ and O⁺ ions change with oxygen exposure. Their intensities track each other quite closely, as predicted for a reaction between O⁺ ions and O atoms, maximizing at a value near 50 L exposure. In panel (c), however, note that the NiO⁺ and Ni⁺ yield show behavior toward oxygen exposures very different from O₂⁺ and O⁺ ions maximizing near 10 L. We believe this observation shows that NiO⁺ forms from collisions between Ni⁺ ions and O atoms. And finally, note in panel (b) that the NiO⁻ behavior is much different than NiO⁺, but that it follows closely the O⁻ ion yield. We conclude that NiO⁻ forms by collisions between Ni atoms and O⁻ ions.

This mechanism appears to be valid for the one case tested here. It remains to be evaluated for other systems, a necessary chore to confirm its general applicability. For Ni, however, the qualitative consistency of this model greatly helps to unravel some of the complexities inherent in the ion yield versus exposure curves.

These ideas do not include the influence of structural effects in the cluster formation process. The calculations, however,

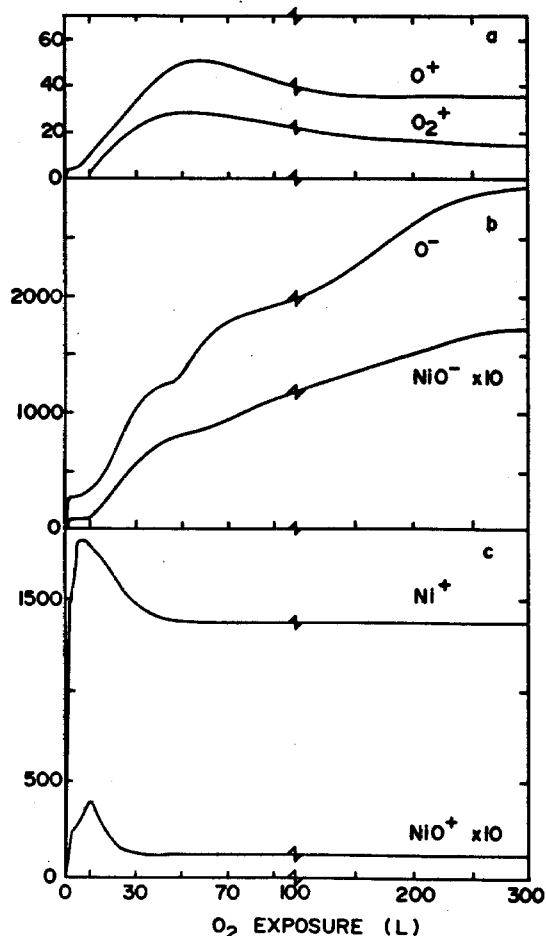


FIG. 3. Experimental ion yields vs oxygen exposure for Ni(100) bombarded by 2-keV Ar⁺ ions. The ordinate gives the number of ions/s detected.

clearly show that the coverage and adsorption site symmetry are major factors in determining which clusters are likely to form. The most spectacular example involves the effect of coverage on the O₂ formation probability. For a *p*(2 × 2) coverage (0.25 monolayer) the calculations show that the oxygen atoms are simply too far apart to have a significant opportunity to collide within interaction range of the solid. For a *c*(2 × 2) coverage (0.5 monolayer), however, the probability of O₂ formation is dramatically enhanced. The results of the calculations are shown in Table IV.

This effect is also observed experimentally on Ni(100). As shown in Fig. 4, the O₂⁻/O⁻ ratio increases to a value of 0.04 where LEED experiments indicate the *p*(2 × 2) structure predominates. This value rises to a maximum value of 0.16 at the *c*(2 × 2) coverage. Thus, the O₂⁻/O⁻ ratio increases by a factor of 4 as the coverage is doubled, similar to what is predicted by the calculations for oxygen in a bridged position

TABLE IV. Effect of coverage and site symmetry on the O₂/O ratio.

	<i>p</i> (2 × 2)	<i>c</i> (2 × 2)
A-top	0.008 (1/126) ^a	0.007 (2/274)
Fourfold bridge	0.008 (2/237)	0.037 (19/510)
Twofold bridge	0.007 (2/267)	0.040 (27/671)

^a The absolute number calculated for each species is given in the parenthesis.

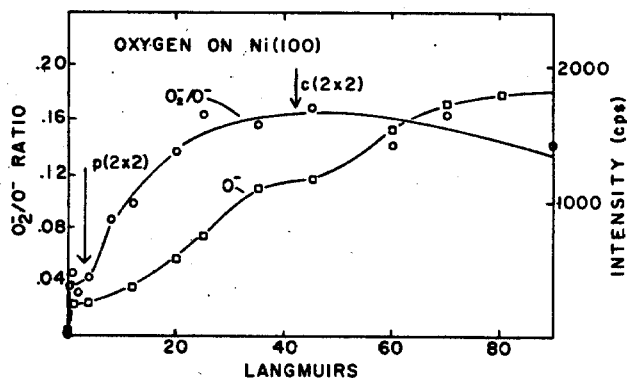


FIG. 4. Experimental ion yields vs oxygen exposure for O⁻ and the O₂⁻/O⁻ ratio from Ni(100).

as shown in Table IV. Similar structural effects have been noted in the calculations for many of the other clusters although a quantitative comparison to experiment is not yet possible due to low statistics.

B. Molecular adsorbates

The response of a surface to ion bombardment covered with a molecularly adsorbed species is mechanistically distinct from the atomic adsorbate case. For CO on Ni(100), for example, the strong C–O bond of 11.1 eV and the weak Ni–CO bond of 1.3 eV help to keep the molecule together during ejection. In the experimental studies, the main peaks in the SIMS spectra for a Ni(100) surface exposed to a saturation coverage of CO are Ni⁺, Ni₂⁺, Ni₃⁺, NiCO⁺, Ni₂CO⁺, and Ni₃CO⁺.¹² All ions show a smooth increase in intensity with CO adsorption and reach saturation after 2-L CO exposure (0.5 monolayer coverage). The yields of C⁺, O⁺, Ni₂C⁺, Ni₂O⁺, Ni₃C⁺, and Ni₃O⁺ are all less than 0.01 of the Ni⁺ intensity.

The classical dynamics treatment for CO on Ni(100) yields results which are in qualitative agreement with these findings. Approximately 80% of the CO molecules that eject are found to eject intact, without rearrangement.¹² The formation of NiCO and Ni₂CO clusters have been observed to form over the surface via reactions of Ni atoms and CO molecules. No evidence has been found for NiC or NiO clusters in the calculations. The ion bombardment approach, then, is a very sensitive probe for distinguishing between molecular and dissociative adsorption processes.

Several workers have now observed that the Ni₂CO⁺/NiCO⁺ ratio is sensitive to the coverage of CO in that it drops from a value of 0.35 at 0.5 L to 0.15 at saturation.^{12,21,23} Early attempts to explain these results were based on the idea that a bridge bonded CO species would eject as Ni₂CO⁺ while a linear-bonded CO species would eject as NiCO⁺. The ratio then would indicate which fraction of each state is occupied. Our calculations clearly show that the mechanism of Ni₂CO and NiCO formation is not consistent with this picture since the clusters form over the surface via atomic collisions. On the other hand, the adsorption site position has been shown to be a sensitive factor in controlling the yield of the clusters. For example, for oxygen on Cu(100), the CuO yield is three times higher for the twofold bridged adsorbate than for the A-top adsorbate. The reason for this effect is that the tighter packing

in the bridged structures allows more effective momentum dissipation through the crystal surface region. Although the calculations for CO adsorbed on Ni(100) are only in a preliminary state, similar conclusions appear to hold for this system as well. It is possible, therefore, that the high $\text{Ni}_2\text{CO}^+/\text{NiCO}^+$ ratio at very low coverages suggests that at least part of the CO adsorbate is positioned in a bridged configuration. We emphasize however, that the appearance of Ni_2CO^+ ions is only an indirect manifestation of bridged-bonded CO because the metal-CO molecular cluster ions do not leave the surface intact, but form in the near surface gas phase.

IV. CONCLUSIONS

In this paper, we have made a detailed comparison between experimental results obtained by Ar^+ ion bombardment of single-crystal Cu and Ni surfaces to recent classical dynamical calculations which describe the ion impact event. The range of agreement between experiment and theory is gratifying; relative yields, angular distributions, energy distributions, multimer yields, and dependence of multimer yields on adsorbate coverages are all in good agreement with experiment using a model with no adjustable parameters.

Of most importance to surface characterization studies is that the clusters are found to form over the surface and that some rearrangement can be expected as the atoms leave the solid. A consequence of this mechanism is that the cluster ions observed in SIMS probably form from ion-atom collisions over the surface. By ratioing appropriate cluster ion yields, good agreement between the calculated neutral yields can be obtained. Finally, the cluster yields show a strong dependence on coverage and adsorption site position. Although there are so far a limited number of quantitative comparisons between experiment and theory to confirm this point, it seems clear that more intensive work in this direction can bring a complete understanding of SIMS spectra.

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