

Mechanisms of CO ejection from ion bombarded single crystal surfaces

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We have calculated the response of a model Ni(001) microcrystallite to 600 eV Ar⁺ ion bombardment when it is covered with 0.5 monolayer of CO. Calculations were performed using a standard molecular dynamics treatment which employs pair potentials fit to the elastic constants of the solid to evaluate Hamilton's equations of motion. The model microcrystallite contained ~240 atoms. The CO was adsorbed in a $c(2 \times 2)$ coverage in both an atop or linear bonded and a twofold bridge bonded position with a binding energy to the surface of 1.3 eV. The results showed that most of the CO molecules eject molecularly, although a few (~10%–15%) eject dissociatively if they are hit directly with the primary ion or with other energetic solid atoms. We also found that NiCO as well as Ni₂CO and Ni₃CO formation probably occurs over the surface via interaction between Ni and CO species, and that the probability of NiC or NiO clusters ejected from a CO covered surface is extremely low.

I. INTRODUCTION

It is now well known that many small molecules like carbon monoxide can chemisorb on a variety of metal surfaces in a molecular state. This fact has induced a large number of investigations aimed toward elucidating the electronic and structural nature of the surface chemical bond. The use of 200–5000 eV ion beams has been of particular utility in describing both the orientation of the adsorbed CO molecule¹ and its adsorption site on a single crystal surface.^{2,3} With static secondary ion mass spectrometry (SIMS), for example, the ejection of the molecular cluster ion Ni₂CO⁺ was taken as evidence for a bridge bonded CO molecule, while the presence of NiCO⁺ was interpreted to represent a linearly bonded CO molecule.² In addition, the cluster ion yields have been shown to correlate empirically with known adsorption states on Mo surfaces.⁴ No firm theoretical base is yet available, however, for quantitatively understanding these observations.

The ejection of clusters from clean and oxygen covered metal single crystal surfaces has recently been examined theoretically using classical dynamics to model the ion impact event.^{5–8} The results show that it is possible to form clusters containing as many as seven atoms via a mechanism where ejected monomers experience attractive interactions above the surface plane rather than by direct ejection of a group of contiguous solid atoms.⁶ Thus, considerable rearrangement of atoms from their original sites on the surface could be expected during cluster formation. In contrast to this process, it has been experimentally observed that large organic molecules can eject from the surface retaining their molecular structure.^{9,10} It is highly improbable, then, that these species could completely break up and subsequently reform in the identical configuration. Obviously, there must be more than one mechanism of cluster formation.

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In this work, we present the first calculations of the ejection of molecularly adsorbed CO on a single crystal Ni surface by bombardment with 600 eV Ar⁺ ions at normal incidence. This system represents a natural extension of our calculations on clean metals^{5–7} and on oxygen covered surfaces^{8,11b} and provides mechanistic insight into the processes that lead to molecular ejection. Our objective is ultimately to define the relationships between the ejection yields and the surface structure for the CO system and to provide a model for the ejection mechanism for larger organic molecules. The results show that most of the CO molecules eject molecularly, although a few (~10%–15%) eject dissociatively if they are hit directly with the primary ion or with other energetic solid atoms. We also find that NiCO, Ni₂CO, and Ni₃CO formation probably occurs over the surface via interaction between Ni and CO species and that the probability of NiC or NiO cluster ejection from a CO covered surface is extremely low.

II. DESCRIPTION OF THE CALCULATION

The basic scheme for computing the dynamics of the bombarding ion and the metal substrate has been described in a recent series of articles.^{5–8} Briefly, the positions and momenta of all the particles in a microcrystallite consisting of four layers with 60 atoms/layer are determined in time by integrating Hamilton's equations of motion. The previous predictor corrector integration scheme based the time increment of each step on the fastest moving particle.^{5a} This scheme fails for the CO molecules that exhibit rapid vibrations. Thus, we now pick the time increment so that a given error criteria must be maintained between the predictor and corrector at each step.¹¹ To represent the interaction potential, we use a sum of pair potentials between all of the atoms where each pair potential is chosen to be as realistic as possible taking into account the known properties of the Ni/CO system. The general form of the potential for atoms in the bulk phase is composed of

three parts: a repulsive Born-Mayer function for small internuclear separations, an attractive Morse potential at long range, and a cubic spline to connect the two.

The composite pair potential V between the two atoms separated by a distance R is given by

$$V = A e^{-BR}, \quad R < R_a \quad (1)$$

$$V = C_0 + C_1 R + C_2 R^2 + C_3 R^3, \quad R_a < R < R_b \quad (2)$$

$$V = D_e e^{-\beta(R-R_e)}(e^{-\beta(R-R_e)} - 2), \quad R_b < R < R_c \quad (3)$$

$$V = 0, \quad R > R_c \quad (4)$$

The interaction of the Ar^+ ion with the other species is represented by a purely repulsive Born-Mayer function,

$$V = A e^{-BR}, \quad R < R_a \quad (5)$$

$$V = 0, \quad R > R_a \quad (6)$$

The construction of an appropriate pair potential to describe the metal-CO interaction is a difficult task due to the directionality of the C-O bond and to the fact that dissociated CO interacts strongly with Ni to form NiC and NiO. Our calculations for oxygen on Cu(001), however, clearly show that atomic placement, bond strength, and mass are the overriding factors in determining ejection mechanisms and relative yields for different configurations. The objectives here, then, are to examine in detail how the mass differences between the four components Ar^+ , Ni, C, and O influence the ejection mechanisms and to examine how different relative bond strengths affect the probability of molecular ejection. For example, for CO on Ni(100), the CO bond strength is 11.1 eV (Ref. 12), but the Ni(001) bond strength is only 1.3 eV.¹³ These factors can easily be cast into the pair potential framework.

The potential parameters for the Ni-Ni, Ar^+ -Ni, Ar^+ -O, and Ar^+ -C are scaled to those developed over the last 15 years for Cu-Cu and Ar^+ -Cu interactions.¹⁴ Those values have been used to determine a wide range of experimental observables on Cu and should provide a comparative base for similar calculations on Ni. Thus, to alter the A value in Eqs. (1) or (5), we have chosen the screened Bohr form of the potential, which adjusts A by scaling to the products of the atomic numbers of the two atoms. The B parameter has not been altered. We have scaled the Morse potential for Cu_2 to Ni_2 by using the D_e , β , and R_e values reported by Girafalco and Weizer for Ni_2 and Cu_2 .¹⁵

For the C=O interaction, we chose to use a Morse potential appropriate for gas phase CO at all values of R . The behavior of this potential surface in the repulsive region is not greatly different from that calculated by *ab initio* methods.¹⁶ For a $c(2 \times 2)$ coverage we find that using the same C=O potential for inter- and intramolecular interactions can lead to unrealistic attraction between CO pairs. To correct this problem, we employ a purely repulsive C-O potential for C and O atoms from different molecules, precluding the possibility of mixing. Likewise purely repulsive O-O and C-C interactions are used. Again, the A parameters are scaled by the products of atomic numbers, from the Cu-Cu interaction.

The Ni-C and Ni-O are chosen to yield an experimen-

tal binding energy of CO to the surface of 1.3 eV. Since the carbon is bonded to the surface, the majority (~1.2 eV) of the attractive interaction is assumed to be the Ni-C and the remainder Ni-O. For an assumed geometry, the pair potential well depth D_e can be determined. Ideally, one would like to choose the range parameter β to fit vibrational frequencies. This tends to make the potential too weak at small internuclear separations. Thus we chose β so that the value of the Morse potential at $R=0$ is the same as an exponential repulsion determined by the atomic number scaling procedure; that is,

$$A e^{-BR} \Big|_{R=0} \approx D_e e^{-2\beta(R-R_e)} \Big|_{R=0} \quad (7)$$

or

$$\beta = \frac{\ln(A/D_e)}{2R_e} \quad (8)$$

This procedure yields a reasonable pair potential that has the correct equilibrium geometry and binding energy. All the potential parameters are given in Table I.

The potentials for the CO in the atop and twofold bridge configurations are slightly different. It is conceivable that during the course of an ion impact the CO may find itself in a site that is inappropriate for the chosen pair potential. We do not believe this difficulty is serious since the motion of the CO molecules is caused by highly directed collisions. The total collision time is so short (~200 fs) the molecules do not have enough time to thermally migrate. In addition, several of our studies have shown that the arrangement of atoms dominates the scattering and ejection processes. For example, with the same potential, the ejection yield from Cu(111) is ~1.5 times larger than that from Cu(001).^{5b} Likewise, the differences between the atop and twofold bridge configurations are due mainly to the original geometry.

For the studies presented in this work, the coordinates of the carbon and oxygen atoms are chosen to place the CO molecule in a $c(2 \times 2)$ coverage (0.5 monolayer) in an atop or linearly bonded site and in a twofold bridge site, structures that have been suggested from other experiments.^{17,18} For the atop site, the carbon is ~1.76 Å above the surface plane as determined by low-energy electron diffraction (LEED) calculations.¹⁷ We maintain the same Ni-C separation upon placing the CO in a twofold bridge site, making the height of the carbon atom above the plane 1.24 Å. In both cases the oxygen atom is placed 1.128 Å above the carbon.

The procedure we use for testing for cluster formation of the ejected species is the same as has been described elsewhere.⁶ The potential parameters, as shown in Table II, are chosen to represent, as closely as possible, the expected interactions of these species in the gas phase. The results are not intended to provide an absolute measure of the cluster yield, but rather to indicate whether the given species are close enough together in space and moving with low enough relative kinetic energies to experience binding interactions. The hopes of determining absolute cluster yields depends on knowing the correct interaction potential for the 300 atom system. For some systems, however, calculated relative yields [i.e., the number of dimers ejected from

TABLE I. Bulk potential parameters.

	A (keV)	B (\AA^{-1})	D_e (eV)	β (\AA^{-1})	R_p (\AA)	R_s (\AA)	R_b (\AA)	R_f (\AA)
Ni-Ni	21.04	5.088	0.58	1.47	2.55	1.46	1.94	4.22
Ni-O	6.01 ^a	...	b { 0.06 0.04	1.99	2.888	4.22
				2.15	2.680			
Ni-C	4.51 ^a	...	b { 0.82 0.50	2.45	1.760	4.22
				2.59	1.760			
C≡O	11.09	2.32	1.13	4.22
C-O	1.29	5.088	2.48
C-C	0.97	5.088	2.48
O-O	1.72	5.088	2.48
Ar ⁺ -Ni	68.84	4.595	2.48
Ar ⁺ -O	19.67	4.593	2.48
Ar ⁺ -C	14.75	4.593	2.48

^aThe A parameters used for determining β .

^bThe first set of values is for the CO in an atop site, while the second is for CO in a twofold bridge site.

Cu(111) is four times larger than the number ejected from Cu(001) (Ref. 7)] do appear to agree well with experimental observations.

III. RESULTS AND DISCUSSION

The results of the calculation of a typical trajectory sequence are shown in Fig. 1 for CO adsorbed in a $c(2 \times 2)$, twofold bridged configuration. In the figure, the size of the crystal has been truncated for graphical clarity, although all of the particles (~ 300) have been included in the calculation. The sequence shows the initial configuration of the surface region followed by the positions of all the atoms after the Ar⁺ ion momentum has dissipated throughout the crystallite and no more particles can eject. Note that virtually every Ni atom has moved from its initial position and that the CO molecules are no longer in their equilibrium, upright positions. In addition, at least one CO is considerably above the surface—it eventually ejects intact. A second one has been somehow dissociated with C and O ejecting atomically.

The processes that lead to the ejection of the various species are clearly very complex. On the other hand, the molecular dynamics procedure allows the individual trajectories to be examined at an atomistic level in order to define the most important events that contribute to the observables. In the rest of this section, then, we

examine the mechanisms that give rise to the processes illustrated in Fig. 1, and we attempt to provide insight into which factors control the molecular or dissociative ejection events.

A. Dissociative CO ejection

The yields of CO, C, and O ejected from Ni(001) with CO adsorbed in the two sites in the $c(2 \times 2)$ coverage are given in Table III. The vast majority of ejected particles consists of CO molecules that leave the surface intact. Approximately 10%–15%, however, are dissociated during the ion bombardment event. The dynamics show that dissociation often results from collisions with the incident Ar⁺ ion. As shown in Fig. 2(a), for example, the target CO molecular bond is broken the most frequently. These mechanisms produce many of the dissociated CO

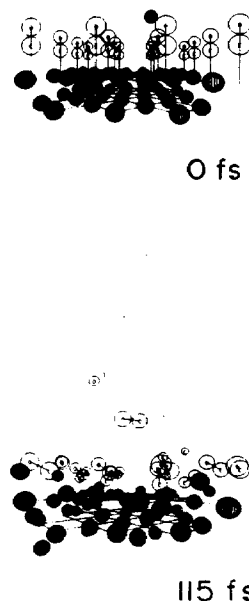


FIG. 1. Graphical depiction of a truncated version of the Ni microcrystallite used in our calculation. The Ar⁺ ion is shown in the initial frame above the CO layer. The sizes of the atoms are arbitrarily chosen for maximum graphical clarity. The grid lines are drawn between the original nearest-neighbor sites in each layer. The viewer is looking between the first layer of Ni atoms and the CO layer.

TABLE II. Gas phase Morse potential parameters.

	D_e (eV)	β (\AA^{-1})	R_p (\AA)
Ni ₂	2.368	1.48	2.15
Ni-C	1.30	2.45	1.84
Ni-O	0.50	1.99	2.97
C≡O	11.09	2.32	1.13

CO EJECTION FREQUENCY

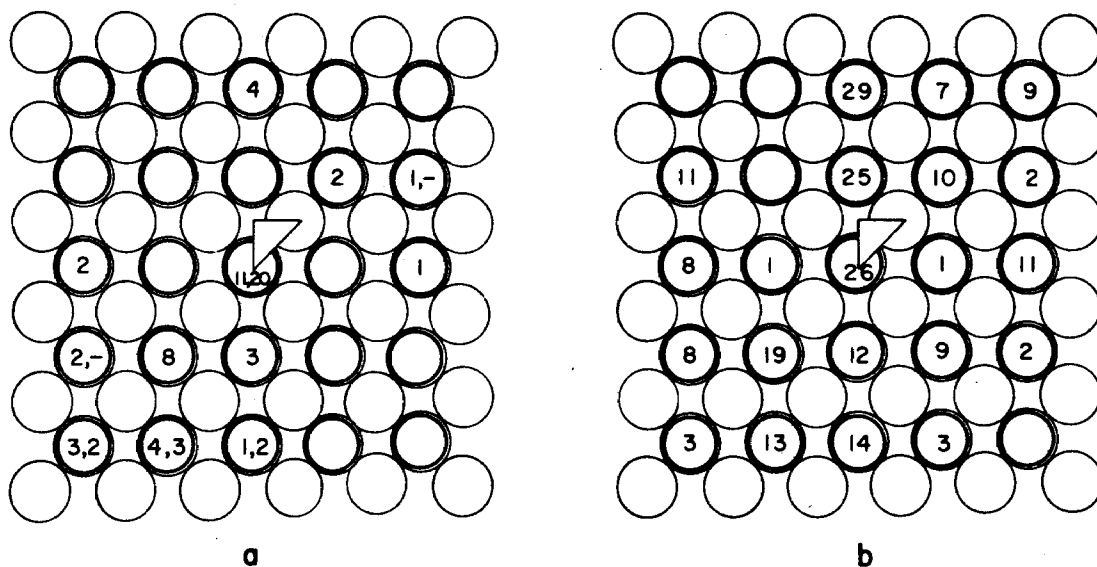


FIG. 2. (a) Percentage of time the CO is found to dissociatively eject when averaged over 118 different impact points selected in the triangular zone shown in the center of the crystallite. If two numbers are given, the first is for carbon and the second for oxygen. (b) Percentage of times the CO is found to eject molecularly. The dark circles represent CO molecules, while the other circles represent Ni atoms.

molecules and are shown schematically in Fig. 3(a).

Bond breaking has also been observed to occur when energetic solid atoms experience direct collisions with the CO molecule as illustrated in Figs. 3(c) and 4. In the case shown in Fig. 4, the target atom is forced down into the crystal (see frames labeled 0–13 fs) while forcing its neighbor rapidly upward (16–33 fs). A carbon atom directly in the way is struck (39–115 fs) and the CO bond is ruptured.

The energy distributions of the ejected carbon and oxygen atoms are basically similar to those reported for oxygen adsorbates.¹⁹ However, in this case the energy distribution is broader because atomic C and O ejection is dominated by high energy collisions. Approximately 70% of the atomically ejected C and O have kinetic energy greater than 8 eV. This is in contrast to the atomic oxygen adsorption where only ~25% of the ejected species have kinetic energy greater than 8 eV.^{8,19}

TABLE III. Molecular and dissociative CO ejection from Ni(001).

	Species	Number ejected	Yield
Atop	CO	273 ^a	2.31 ^b
	C	50	0.42 ^b
	O	55	0.47 ^b
Twofold bridge	CO	398 ^a	3.62 ^c
	C	39	0.36 ^c
	O	43	0.39 ^c

^aIncludes CO's in clusters.

^bBased on 118 trajectories.

^cBased on 110 trajectories.

B. Molecular CO ejection

In all our previous descriptions of cluster formation, the calculations have shown that the clusters are formed

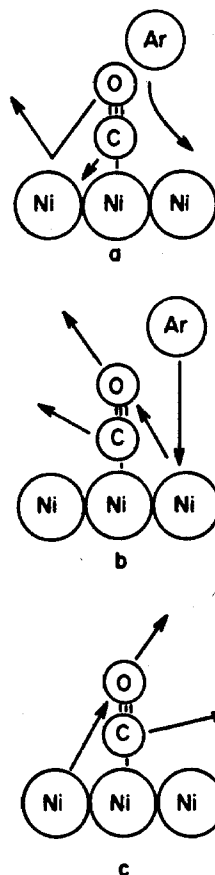


FIG. 3. Mechanisms for dissociative CO ejection. (a) bond breaking induced by direct collision with the primary ion, (b) bond breaking induced by the primary ion after it has reflected from the Ni surface, and (c) bond breaking induced by energetic ejecting Ni atoms. The drawings are schematic with the CO placed in an atop site.

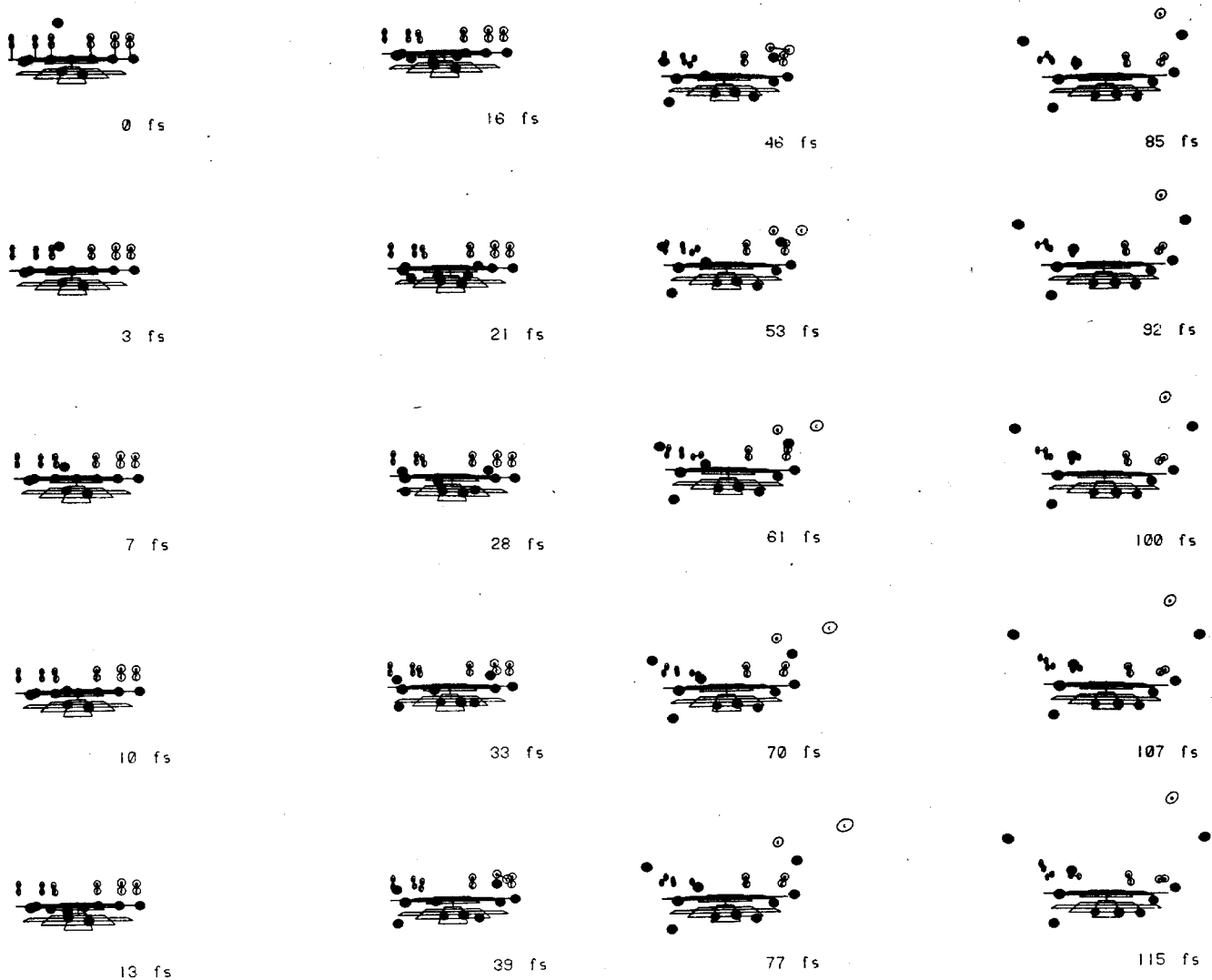


FIG. 4. Sequence of motion leading to dissociative CO ejection in a sample trajectory. The Ar^+ ion is shown in the first frame above the CO layer. For graphical clarity only the atoms of interest to the discussion are shown. See Fig. 1.

from atoms ejected more or less independently from the surface. Their composition, therefore, does not directly reflect the surface structural order. For CO, however, the calculations show that ~85%–90% of the CO molecules eject intact (Table III). Apparently, the strong bond of 11.1 eV is sufficient to keep the molecule together unless it undergoes very energetic collisions.

The frequency of ejection for CO molecules over the crystallite is shown in Fig. 2(b). This pattern is virtually identical to that obtained for oxygen adsorbed in an atop position and indicates that the ejection mechanisms for CO are very similar to that for O atoms.⁸ We find, for example, that all the mechanisms that occur for oxygen ejection also occur for CO ejection.

The energy distribution of the ejected molecules is shown in Fig. 5. The distribution has a shape similar to that reported for atomic adsorbates in that it exhibits measurable intensity at rather large kinetic energies. This feature is in contrast to the energy distribution curve for clusters that form over the surface where the high energy tail is absent.¹⁹ However, the CO mole-

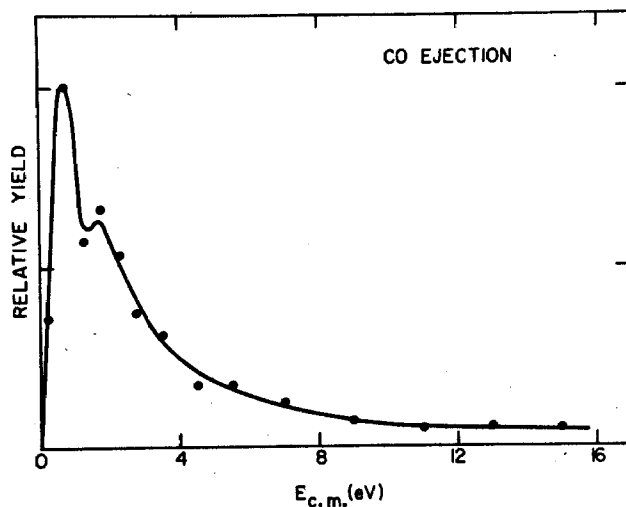


FIG. 5. Center-of-mass energy distribution of the ejected CO molecules. Results from both the atop and twofold bridge sites are added. Approximately 12% of the ejected molecules have center-of-mass kinetic energy, $E_{c.m.} > 16$ eV. The line is drawn as a guide to the eye and has no physical significance.

VIBRATIONAL STATE DISTRIBUTION

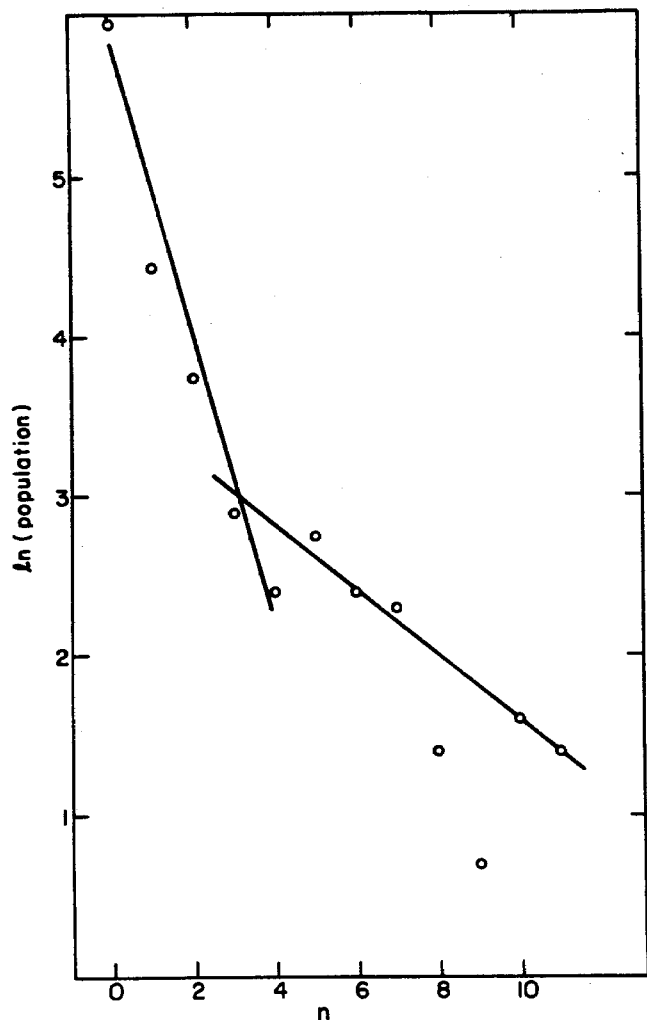


FIG. 6. Vibrational state distribution for the molecular ejected CO species. The temperature corresponding to the line of steepest slope is 3450 K, while the temperature corresponding to the other line is 15 400 K.

cules do not eject with high kinetic energies nearly as often as the dissociated carbon and oxygen atoms discussed in Sec. III A.

It is of interest to analyze the internal state distribution of the ejected CO molecules. As is clear from Figs. 1 and 4, highly excited rotational motion dominates the CO trajectories. The molecule is generally struck on one end causing it to spin quite rapidly. Using the standard techniques of small molecule classical scattering,²⁰ we can partition the available internal energy into rotational and vibrational energy. As is shown in Fig. 6, a significant fraction of the ejected CO molecules are vibrationally excited. A force-fit of the results to a Boltzmann distribution produces a vibrational temperature of 3400–15 000 K. It should be noted, however, that the results of the calculation are very poorly described by this type of distribution, indicating that the system is far from thermodynamic equilibrium. The calculations also show that the rotational states are highly excited, with an almost random population of states

to J values as high as 100. The effective rotational and vibrational temperatures, then, are vastly different.

C. NiCO ejection

From an analysis of the final positions of the CO molecules and Ni atoms after the trajectory has been completed, we find a number of cases where the Ni and CO species are moving with near zero relative kinetic energy and are spatially within interaction range. Using the potential parameters given in Table II and the prescription for determining cluster stability, several NiCO clusters are found. The formation of NiCO, then, proceeds via the interaction of Ni and CO over the surface in a fashion completely analogous to that proposed for metal and metal–oxygen clusters.^{6–8} There are also a few clusters of the types Ni_2CO , Ni_3CO , Ni_4CO , and $\text{Ni}(\text{CO})_2$ that are calculated to form in a similar manner.

The constituent atoms in these clusters need not originate from contiguous points on the surface. In our calculations, for example, only about 60% of the NiCO clusters that eject involve an Ni and CO that were originally nearest neighbors.

The primary goal of this study is to analyze the mechanisms of molecular CO ejection; this consequently influenced our choice of potentials (Sec. II). In particular, the Ni–O and Ni–C bond strengths are weaker than those expected for a NiO or NiC surface species. Previous studies of atomic oxygen on copper have shown that by increasing the adsorbate–metal bond strength the adsorbate ejection yield decreases.⁸ In the present case, this approximation, then, results in an overestimation of the atomic carbon and oxygen ejection yields. The values we do obtain are already considerably less than one atom per incident ion and are given in Table III. Since the atomic C and O yields are low and since the kinetic energies of these particles are large, the formation of clusters such as NiC, NiO, and a recombined CO is improbable when compared to the molecular CO ejection.

IV. CONCLUSIONS

In this work we have examined the mechanisms of ejection from ion bombarded surfaces covered with a molecularly adsorbed species. The dynamical calculations have shown that for CO adsorbates on Ni(001) most of the CO ejection occurs molecularly and without rearrangement. In addition, Ni_mCO cluster formation is found to occur above the surface in a fashion analogous to that reported for metals and metal–oxides. The model provides a reasonable picture of the ejection mechanisms that can, hopefully, be employed to interpret ongoing experimental studies.

The results of the calculations are so far consistent with the qualitative features of the experimental results. For example, the main components in the SIMS spectra are Ni^+ , Ni_2^+ , Ni_3^+ , NiCO^+ , and Ni_mCO^+ with virtually no C^+ , O^+ , CO^+ , NiC^+ , or NiO^+ observable.^{2,3} It is interesting that our calculations predict that the yield of CO will be quite large, and yet the presence of CO^+ is undetectable in SIMS.^{2,3} Apparently, the high ionization

potential of CO (~ 14 eV) results in an extremely low ion/neutral ratio. The lack of C^+ and O^+ in the experimental spectra could be due to their high ionization potentials or to the fact that the atoms are not formed during the bombardment. It is relevant, however, that measurable quantities of O^+ and NiO^+ have been observed from Ni(001) surfaces reacted with O_2 .²¹ For the CO case, then, the small amount of O^+ species probably arises because there are only small numbers of O atoms formed during the bombardment.

With this model, it is now possible to quantitatively examine the effects of the adsorption site and the coverage on the yields of Ni, Ni_2 , CO, NiCO, and Ni_2CO . These calculations should be directly comparable to recent SIMS measurements if ratios of ion yields, e.g., $NiCO^+/Ni^+$ and Ni_2CO^+/Ni_2^+ , are proportional to ratios of the neutral species. The strong sensitivity of the oxygen yields to the nature of the adsorption site found in previous calculations indicates that this sensitivity should also be present for CO adsorbates.

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