

THEORETICAL STUDIES OF THE ANGULAR DISTRIBUTIONS OF OXYGEN ATOMS EJECTED FROM AN ION BOMBARDED $c(2 \times 2)$ OVERLAYER OF OXYGEN ON Ni(001)

II. Effect of interaction potential

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A detailed molecular dynamics study has been performed in order to determine the influence of the interaction potential on the angles of ejection of oxygen atoms from an ion bombarded $c(2 \times 2)$ oxygen overlayer on Ni(001). The bonding site of the adsorbate appears to be the dominating factor which influences the angles of ejection. Changing the interaction potential affects the angular distribution similarly to varying the height of the adsorbate above the surface.

I. Introduction

The angular distributions of particles ejected due to the bombardment of solids by keV ions have been shown to be sensitive to the original geometry of the atoms on the surface [1-5]. In an earlier paper [6], the angular distributions of oxygen atoms ejected from a $c(2 \times 2)$ overlayer of oxygen on Ni(001), with the oxygen atoms in a variety of geometrical positions, were examined. The bonding site of the oxygen, either fourfold bridge, atop or twofold bridge, was reflected by distinctive characteristics in the angular distributions. In addition, the angular distributions were sensitive to the original height of the atom above the surface.

The theoretical model used to predict the angular distributions involves integrating the classical equations of motion for all the atoms in the system of interest. A necessary input for the model is the interaction potential from which the forces among the atoms are determined. Unfortunately, potentials for systems with large numbers of atoms are very difficult to obtain. Thus we are forced to use simple model potentials. In this case we have assumed the interaction to be pairwise addi-

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tive. Even with this simplification, choosing appropriate values of the parameters in the pair potentials is somewhat arbitrary. Thus, to determine how reliably the angular distributions of ejected atoms can be used as a way to measure bonding geometries, the sensitivity of these distributions to parameters in the potentials must be examined.

We have chosen to examine the effect of potential on a $c(2 \times 2)$ overlayer of oxygen on Ni(001), since previous studies examining height and site variations have been completed [6]. There are five pair potentials ($\text{Ar}^+ - \text{O}$, $\text{Ar}^+ - \text{Ni}$, $\text{Ni} - \text{O}$, $\text{Ni} - \text{Ni}$ and $\text{O} - \text{O}$) each with 2 or 3 parameters that could possibly be varied. Because the primary interest here is the angular distributions of ejected oxygen atoms, we have limited the potential variation to the $\text{Ni} - \text{O}$ and $\text{Ar}^+ - \text{O}$ potentials and have concentrated on the potential variations with the oxygen in the fourfold bridge site.

The results show that some characteristics of the distributions are controlled primarily by the placement of atoms rather than other features of the interaction potential. The bonding site of the oxygen atom continues to have a dominating influence on the ejection angles. Changing the effective size of the interaction induces effects on the distributions which are similar to those found for altering the height of the adsorbate above the surface. This observation indicates that experimental determination of atomic locations will be limited by our ability to theoretically describe the collision cross sections.

In section 2 is a brief discussion of the calculational procedure. The results of the potential variation are discussed in section 3.

2. Description of the calculation

Since a more detailed account of the method has been given earlier [6], only a brief description will be given here. In the classical dynamics procedure, Hamilton's equations of motion are integrated for all the particles of interest. The particles include the primary Ar^+ ion which bombards the crystal with 600 eV of energy at normal incidence, the substrate nickel atoms and the overlayer oxygen atoms. Since in this study we are only interested in the angular distributions of oxygen atoms with greater than 10 eV of kinetic energy, only a small microcrystallite of 2 layers with ~ 35 nickel atoms per layer and 9–12 adsorbate oxygen atoms is sufficient to describe the distributions accurately [6].

Only the $\text{Ni} - \text{O}$ and $\text{Ar}^+ - \text{O}$ pair potentials are varied. The $\text{Ni} - \text{O}$ interaction is assumed to be a Morse potential,

$$V = D_e \exp[-\beta(R - R_e)] \{ \exp[-\beta(R - R_e) - 2] \}, \quad R \leq R_c, \quad (1a)$$

$$V = 0, \quad R > R_c. \quad (1b)$$

The value of R_e is determined by the distance from the oxygen atom to its nearest neighbor nickel atom(s). The well depth, D_e , is adjusted to give a constant surface

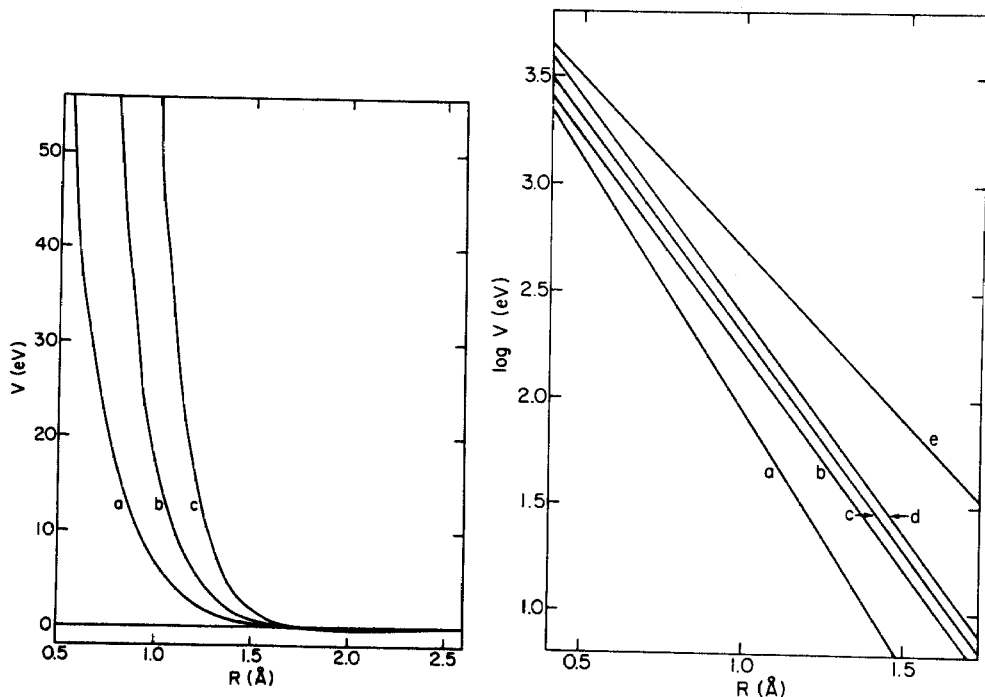


Fig. 1. Ni-O pair potentials for oxygen atoms in a fourfold bridge site 0.9 Å above the surface. In all cases $D_e = 0.18$ eV and $R_e = 2.0$ Å. Values of β (in Å^{-1}): (a) 2.0, (b) 2.45, (c) 3.0.

Fig. 2. Ar^+ -O pair potentials. Values of A (in keV) and B (in Å^{-1}) are: (a) 19.67 and 5.4; (b) 15.7 and 4.593; (c) 19.67 and 4.593; (d) 23.6 and 4.593; (e) 19.67 and 3.6.

binding energy. These parameters have been given previously [6]. The Morse parameter β is the only one we have varied in this study. Plotted in fig. 1 are the Morse potentials for three values of β . For this figure the oxygen is assumed to be in a fourfold bridge site, 0.9 Å above the surface, thus $R_e = 2.0$ Å.

For the Ar^+ -O pair potential we use an exponential repulsion

$$V = A \exp(-BR), \quad R \leq R_a, \quad (2a)$$

$$V = 0, \quad R > R_a. \quad (2b)$$

In the earlier studies values of $A = 19.67$ keV and $B = 4.593 \text{ Å}^{-1}$ were used [6]. Plotted in fig. 2 is this potential as well as four others where we have independently varied the A and B parameters.

3. Results and discussion

In order to examine the entire angular distributions of the ejected oxygen atoms, each ejecting oxygen atom's ultimate position is displayed on a flat plate collector at a large distance above the surface. Typical distributions are shown in fig. 3. The radial extent of a point is proportional to $\tan \theta$, where θ is the polar angle of ejection as measured from the surface normal. The azimuthal direction ϕ is aligned in the same manner as in fig. 4a. The vertical and horizontal directions correspond to the $\langle 100 \rangle$ directions or $\phi = 0^\circ$. Since only ion impacts in a reduced symmetry zone of the surface were calculated, the appropriate symmetry operations have been applied to each set of data [6].

3.1. Fourfold bridge site, Ni–O potential

The angular distributions of oxygen atoms which were ejected from fourfold bridge sites are shown in fig. 3. Plots for two heights, $z = 0.9$ and 1.0 \AA , and four values of the Morse parameter β are displayed in this figure. Figs. 3b and 3f are the same as shown earlier (figs. 2c and 2d of ref. [6]), except that in this potential variation study only half as many Ar^+ ion impacts were calculated. All these distributions have retained the fourfold bridge site characteristics. The outer envelope encompassing the points is oriented in the $\phi = 45^\circ$ directions with the most intense region at $\theta \simeq 55^\circ$ with $\phi \simeq 25^\circ$.

The qualitative types of changes in the angular distributions that occur when β is changed are comparable to those from varying the height of the adsorbate [6]. Ten percent changes in β (figs. 3b and 3c) are similar in magnitude to the same percentage change in height (figs. 3b and 3f). In one case almost identical distributions were obtained by varying either β or the height.

The details of the influence of the parameter β can be traced in the ejection of oxygen atom O6 of fig. 4a. Oxygen atom O6 ejects due to the Ar^+ ion striking Ni1 which then hits Ni2 which pushes O6 upward. Depending on the value of β , O6 may also collide with Ni3 and Ni4 upon ejecting from the solid. The net effect of changing β on the ejection angles of O6 is shown in fig. 4. As β increases the azimuthal angles of ejection rotate counterclockwise and the polar ejection angles become more towards the surface normal. In addition, the number of oxygen atoms ejected in this energy range increases. This trend is consistent for all heights (0.0, 0.8, 0.9, 1.0, 1.1 and 1.3 \AA) that were investigated.

3.2. Fourfold bridge site, Ar^+ –O potential

The effect of changing the Ar^+ –O potential on the angular distributions of the ejected oxygen atoms is shown in fig. 5. Even with these relatively large changes in the Ar^+ –O potential the angular distributions continue to reflect the original fourfold bonding geometry. For the potentials a–c, oxygen atom O6 is the major con-

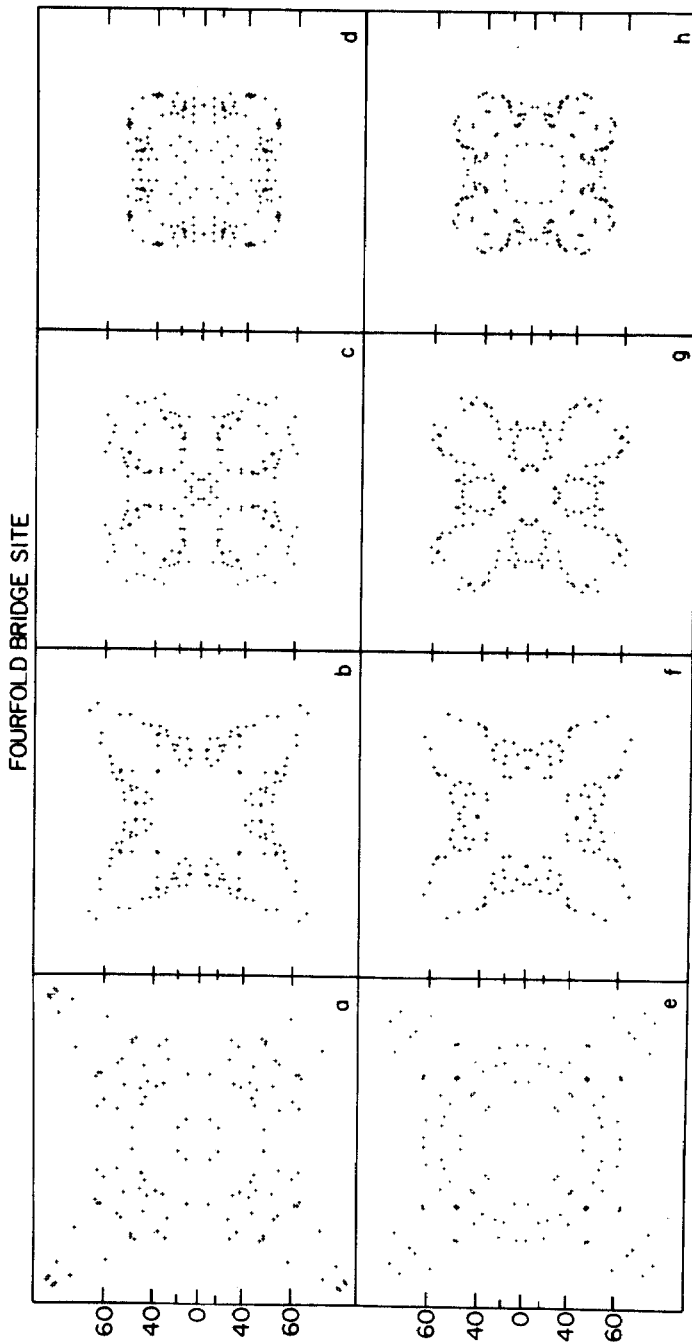


Fig. 3. Angular distributions of oxygen atoms ejected from fourfold bridge sites. The numbers on the ordinate are the polar deflection angles given in degrees. Only the atoms with between 10 and 20 eV of kinetic energy are shown. Two heights, z , above the surface and four values of the Morse parameter, β , are used. The Morse parameter, β . Values of z (in \AA) and β (in \AA^{-1}) are: (a) 0.9 and 2.0; (b) 0.9 and 2.45; (c) 0.9 and 2.63; (d) 0.9 and 3.0; (e) 1.0 and 2.0; (f) 1.0 and 2.57; (g) 1.0 and 3.0.

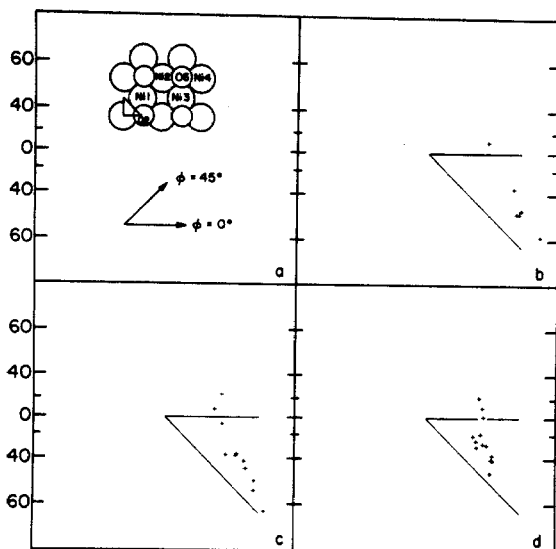


Fig. 4. Unsymmetrized angular distributions of oxygen atom O6 versus Morse parameter, β . The oxygen atom was originally in a fourfold bridge site 0.9 Å above the surface. (a) Placement and labeling of atoms. The triangular region is the impact zone for the Ar^+ ion bombardments. The larger circles are nickel atoms while the smaller ones are oxygen atoms. The atom labels are consistent with those in ref. [6]. (b) $\beta = 2.0 \text{ \AA}^{-1}$ (c) $\beta = 2.45 \text{ \AA}^{-1}$ (d) $\beta = 3.0 \text{ \AA}^{-1}$.

tributor to the pattern. Since the Ar^+ ion only glances off oxygen atom O2 before striking Ni1 which initiates the ejection of O6, changing the $\text{Ar}^+ - \text{O}$ potential has minimal effect on these angular distributions.

As the effective size of the Ar^+ ion increases (potentials d, e), oxygen atom O2 begins ejecting with 10 to 20 eV of kinetic energy. It is the introduction of this new mechanism that causes the large change in appearance of the angular distributions in going from potential c to d.

3.3. Atop site, Ni-O potential

The angular distributions of oxygen atoms ejected from atop sites probably contain the most characteristic feature. Because the oxygen atoms in this site are directly in line of the ejecting substrate nickel atoms, the oxygen atoms tend to eject in the $\phi = 0^\circ$ or $\langle 100 \rangle$ azimuth, the same as the nickel atoms. This is shown in figs. 6a–6c, where the angular distributions of the oxygen atoms are given as a function of the Morse parameter, β . As β increases, the polar angles of ejection tend to decrease or become more normal to the surface. The unsymmetrized distributions of the oxygen atom (O8 of ref. [6]) that ejects in the $\phi = 0^\circ$ direction are presented in figs. 6d–6f. The polar angle also decreases upon increasing the height of the adsorbate [6].

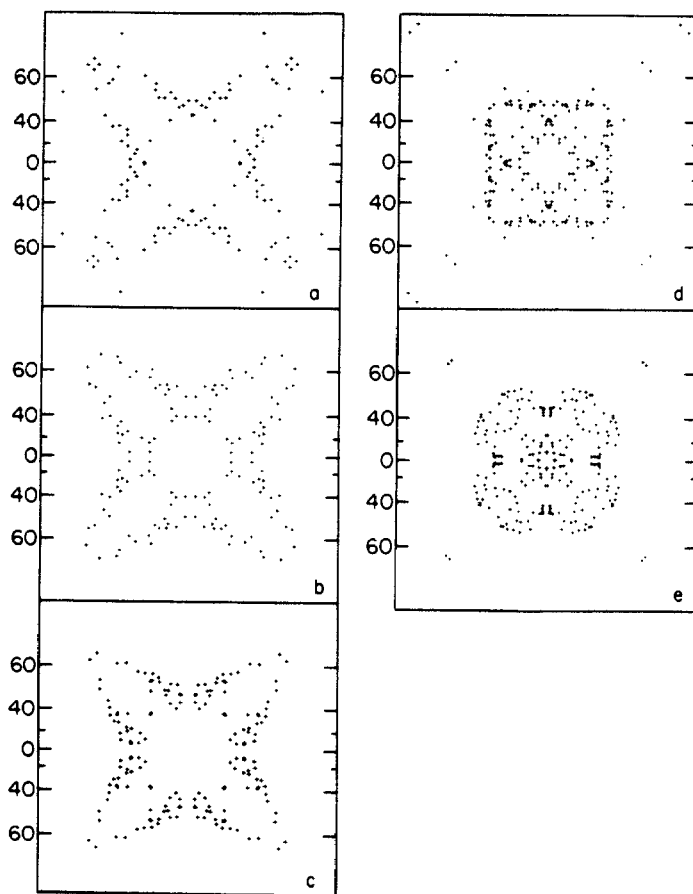


Fig. 5. Angular distributions of oxygen atoms ejected from fourfold bridge sites. Only the atoms with between 10 and 20 eV of kinetic energy are shown. The oxygen atoms were originally 0.9 Å above the surface. The five frames correspond to using the five Ar⁺-O potentials given in fig. 2. Frame c is identical to fig. 3b.

4. Summary and prospects

The angular distributions of oxygen atoms ejected from an ion bombarded $c(2 \times 2)$ overlayer of oxygen on Ni(001) are sensitive to the interaction potential as well as the bonding geometry. The bonding site, such as fourfold bridge or atop, appears, however, to be the dominating factor controlling the ejection angles. Changing the Ni-O or Ar⁺-O interaction potentials influences the ejection angles in a manner similar to changing the adsorbate height.

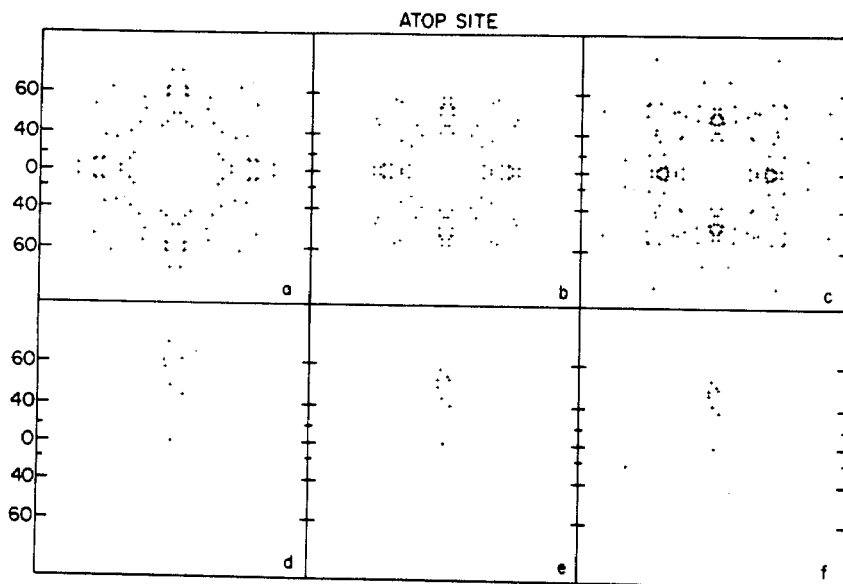


Fig. 6. Angular distributions of oxygen atoms ejected from atop sites. Only the oxygen atoms with between 10 and 20 eV of kinetic energy are shown. The oxygen atoms were originally 2.0 Å above the surface. Frames a–c are for $\beta = 2.0, 2.45$ and 3.0 \AA^{-1} , respectively. Frames d–f are the corresponding unsymmetrized distributions of oxygen O8 of ref. [6].

It is a little premature to make any definite conclusions regarding the ability of ion bombardment to measure adsorbate geometries. Based on this study and the current lack of known interaction potentials, it appears most promising that bonding sites can be determined from well-defined ion bombardment experiments. Possibly, bounds can be placed on adsorbate heights, but determining the height to better than $\pm 0.1 \text{ \AA}$ does not currently appear feasible. If this premise continues to be valid, this approach would be complementary to low energy electron diffraction (LEED), as the adsorbate height rather than the bonding site can be more reliably determined from LEED. Optimistically, though, we can hope for high resolution data [5] on systems where the bonding geometry is known, so that we can calibrate the model including the interaction potentials; thus more accurate geometry determinations can eventually be made.

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