MECHANISMS OF EJECTION DUE TO ION BOMBARDMENT: c(4x4) OVERLAYER OF BENZENE
ON Ni(001)

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Abstract

A classical dynamics model has been used to examine mechanisms of molecular
ejection due to ion bombardment. The representative system studied is
benzene, C_6H_6, which forms an ordered c(4x4) overlayer on Ni(001). Intact
molecular ejection of the C_6H_6 is predicted from the calculations. Mecha-
nisms of ejection are discussed.

Bombarding a metal with keV ions causes a large variety of species to eject
from the solid. For adsorbates on clean metals these can be atomic species,
metal clusters M_n, adsorbates whether they are atomic or a large organic
molecule such as p-aminobenzoic acid, and mixed metal-adsorbate clusters.
The first question to ask is simply what are the mechanisms of ejection of
these clusters? Once it is understood how the clusters eject then it will
be possible to delve into the relationship of the cluster composition to the
orginal configuration of atoms on the surface.

Considerable theoretical effort has been expended investigating the forma-
tion of clusters of the type Cu_n, Cu_nO_m, CO, and Ni_nCO. Briefly, for clean
metals and metals with atomic adsorbates such as oxygen, a rearrangement
mechanism dominates. The constituent atoms eject individually and then
establish their identity as a cluster in the near surface region. Although
the atoms that eventually form the cluster originate from a localized region
or radius ∿5 Å on the surface, they were not necessarily from contiguous
sites {1-5}.

The ejection of CO which was originally adsorbed molecularly on a Ni surface
differs mechanistically from the above. Since the CO has a strong bond
(∿11 eV) compared to its adsorption energy on Ni of ∿1.3 eV, the CO can
adsorb excess energy from a hard collision and eject intact {6}. Extrapolat-
ing these concepts, however, to large organic systems such as p-aminobenzoic
acid seems difficult.

The purpose of this study is to examine in detail the important factors that
lead to molecular ejection of large organic molecules from ion bombarded
surfaces. The prototype system to be examined is benzene, C_6H_6, which forms
an ordered c(4x4) overlayer on Ni(001) {7,8}. The theoretical approach is
a classical dynamics model which has been used extensively to reproduce and
explain many observables of the ion bombardment process {1-6,9,10}.

Briefly the theoretical model consists of approximating the solid by a
finite microcrystallite. In this case the Ni(001) crystal has three layers
of 85 atoms per layer. Nine benzene molecules are then placed on the sur-
face in a c(4x4) configuration. Assuming a pairwise interaction potential
among all the atoms, Hamilton's equations of motion are integrated to yield
the positions and momenta of all particles - the primary Ar^+ ion, the sub-
strate Ni atoms, and adsorbate atoms in the benzene molecule - as a function

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of time during the collision cascade. The final positions and momenta can be used to determine such observables as total yield of ejected particles, energy distribution, angular distribution, and possible cluster formation. In addition to determining observables or macroscopic quantities, the classical dynamics procedure allows one to analyze microscopic mechanisms. It is the mechanisms of ejection that will be focussed on here.

The relative placement of the C_6H_6 molecule with respect to the Ni atoms is not precisely known but it is generally agreed upon that the ring is parallel to the surface {7,8,11}. The π-bonded site (C_6H_6 placed on top of a nickel atom) is consistent with current electron energy loss spectra (ELS) {7,8}. Using the geometry parameters from theoretical calculations of nickel-ethylene complexes {12} we arbitrarily place the benzene 1.96 Å above the nickel atom. The total binding energy of the molecule to the surface is 1.7 eV {13}, with the majority of the interaction in the Ni-C bond rather than the Ni-H bond. A more complete description of the calculational details will be published elsewhere {14}.

The primary ion was chosen to be Ar^+ with 600 eV of kinetic energy, bombarding at normal incidence to the surface. Since the purpose of this study is to examine mechanisms of ejection only 30 impacts of the Ar^+ ion were calculated. The motion that led to ejection of particles was carefully examined for each ion impact.

The trajectories show unequivocal evidence for intact molecular ejection of the C_6H_6 species. Although enough trajectories were not run to achieve reliable statistics, we did find molecular ejection at approximately half the impact points. In addition, fragments such as C_6H_5, C_5H_5, C_2H_2, and CH, along with atomic C and H were observed. Also predicted was an NiC_6H_6 cluster, similar to the cationized species detected in numerous ion bombardment experiments {15}.

There are three common traits in the mechanisms of intact benzene ejection. First, although the initial Ar^+ ion had 600 eV of energy, by the time the C_6H_6 is struck, the energy has dissipated considerably so that the collision energies are ~10-50 eV. Second, since the benzene has many internal degrees of freedom, it can adsorb excess energy from a hard collision. The ejected molecules are often quite distorted from their original planar configuration (see Figure). The final common trait is that the colliding particle, usually a Ni substrate atom, hits at least 2 of the carbon atoms in the ring. The collisions may be simultaneous or sequential and may involve 2-5 of the carbon atoms. This type of collision process causes several parts of the molecule to move in a concerted manner in one direction.
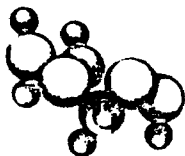
Distortion of the C_6H_6 as it ejects from the surface.

There are many variations to the above mechanism, most of which have direct analogs to the ejection of atomic adsorbates [4]. The particle that ejects the benzene may be a nickel atom either from directly below the benzene or from a neighboring site, the Ar^+ ion, or even a carbon-atom that has been fragmented from another C_6H_6. Exemplary collision cascades leading to the intact molecular ejection of benzene will be shown in a computer generated movie.

Naturally the fragments most generally originate from the C_6H_6 which is directly struck by the Ar^+ ion. The protruding H atom is most easily ripped off while head-on collisions cause more extensive fragmentation. Some of the fragments eventually implant into the solid and others reflect off the Ni substrate and eject.

Analogous to the formation of Ni_nCO clusters [6], the NiC_6H_6 is formed by a hybrid mechanism. The C_6H_6 ejected intact and combined with an ejecting Ni atom from a neighboring site to form the cluster. Since some recombination is involved, the experimental observations of species of the type NiC_6H_6 cannot be used as evidence that the organic molecule is directly bonded to the metal atom.

In conclusion, the classical dynamics procedure does predict the intact molecular ejection due to ion bombardment of large organic molecules from a metal substrate. Thus one can gain some knowledge about the original configuration of atoms. Care must be taken, however, because species such as NiC_6H_6 can form by a recombination mechanism. Based on the limited theoretical calculations performed to date, our general feeling is that species with a molecular identity in the solid sample, such as adsorbed C_6H_6 or CO, can eject intact. Recombination can occur when the species are independent units in the sample. This would include metal clusters, metal oxide clusters and metal-adsorbate clusters. Extrapolating these ideas to the observation of $(H_2O)_n$ from the ion bombardment of ice [16] would suggest that the H_2O units could eject intact while the cluster could show rearrangement. Mixtures of leucine (leu) mixed with LiCl adsorbed on silver have produced clusters such as $(leu-Li)^+$, $(leu + 2Li-H)^+$, $(leu + Ag)^+$ and $(leu + Ag + Li-H)^+$ [17]. The silver attached to the leucine we believe forms by a rearrangement mechanism. The attachment of the Li could either be part of the original molecule on the surface, in which case an intact ejection is possible, or be formed by rearrangement.

Acknowledgments

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