interaction parameters, including the electrostatic charge-charge repulsion components according to Allinger,[17] are added. Although not accurate, this indicates that in the gas phase 'prestraining' of the ligand would be caused by dipole-dipole repulsion. An attempt was made to 'solvate' cyclam by placing a hydrogen atom on each nitrogen in place of the dipole, so as to simulate hydogen-bonded water. This gave a *U* value similar to that obtained with dipoles present so that steric hindrance to solvation must occur as suggested.[4] How much this would decrease strain is not clear, however, since it would expose the dipoles, which might attract the remaining water of solvation more strongly, or else replace steric strain with dipole-dipole repulsion.

We initially[7] chose to neglect the electrostatic charge-charge repulsion component of the dipoles so as to minimize the influence of uncertain parameters on our calculations, but include other parameters relating to interactions with dipoles. This choice of parameters reproduces the macrocyclic enthalpy quite well (Table I), which probably relates to the quenching of purely electrostatic dipole-dipole interactions by solvation in aqueous solution. In summary, the main contributions to the macrocyclic enthalpy are (1) more secondary nitrogen-donor atoms unaccompanied by the usual large increase in *U* normally associated with changing a primary into a secondary nitrogen and (2) the high value of *U* for the free ligand, caused by dipole-dipole repulsion in the gas phase, which may be somewhat modified by steric hindrance to solvation in aqueous solution. The high LF strengths of the macrocycles are caused by the secondary nitrogens, and are highest in those into which the metal ion fits best; 13-aneN_4 (best-fit ionic radius 1.92 Å) for Co(III) (M-N ideal length 1.92-1.94 Å) and low-spin Ni(II) (M-N ideal length ~1.9 Å), and cyclam (best-fit M-N length 2.05 Å) with high-spin Ni(II) (M-N ideal distance 2.05-2.12 Å).

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Received March 17, 1980

Mechanism of Ejection of Organic Molecules from Surfaces by keV Ion Bombardment

Sir:

The application of secondary ion mass spectrometry (SIMS) to the analysis of nonvolatile, high molecular weight compounds is a rapidly evolving research field.[1-4] Of special interest is (i) that the observed fragmentation is similar to other methods of ionizing molecular solids,[5,6] (ii) that the parent ion (± one proton) is often the most intense peak,[1] and (iii) that large organic fragments have been observed to form complexes with a variety of metals,[2] both from the substrate holding the organic film and from metal salts mixed into the organic film. In this work, we examine for the first time the possible nuclear motion in the solid that can lead to the ejection of these fragments and illustrate how they can retain simple and direct structural information about the original surface.

The major question is this: if the primary ion has energy of ~500-10000 eV, how is it possible to eject molecular fragments with individual chemical bonds whose strength is on the order of 2-10 eV? This process should be contrasted to the formation of clusters from the ion bombardment of clean metals and metals with atomic adsorbates such as oxygen. Theoretical calculations have shown that these clusters, which can have from 2 to 12 constituent atoms, form from atoms which eject individually and establish their identity as a cluster in the near surface region.[7-10] As a consequence, the constituent atoms do not necessarily originate from neighboring sites on the surface. Extrapolating this concept to larger molecules seems statistically improbable, suggesting that another mechanism must dominate. From our theoretical calculations, three factors favor ejection of molecular fragments. First, a large molecule has many internal degrees of freedom and can absorb energy from an energetic collision without dissociating. Second, in the more massive framework of a large organic molecule, individual atoms will be small in size compared to a metal atom (Figure 1); thus, it is possible to strike several parts of the molecule in a concerted manner so that the entire molecule moves in one direction. Finally, by the time the organic molecule is struck, the energy of the primary ion has been dissipated so that the kinetic energies are tens of eVs rather than hundreds or thousands of eVs.

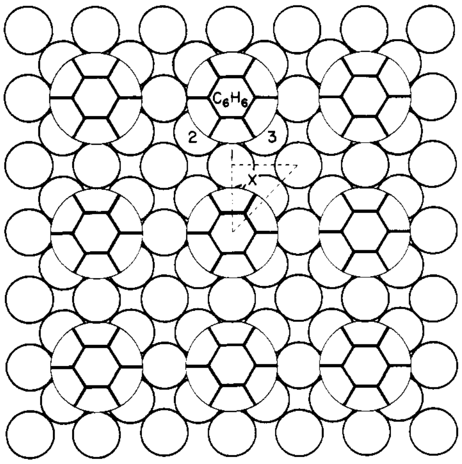

Figure 1. Ni(001) with a *c*(4 × 4) overlayer of benzene. The dashed triangle is the impact zone for normal incidence ion bombardment. The numbered atoms correspond to the atoms shown in Figure 2. The X is the impact point for the Ar^+ ion which leads to the motion depicted in Figure 2. The circle around each C_6H_6 is the radial extent of the hydrogen position, 2.5 Å.

We choose to examine the ejection mechanisms with a classical dynamics procedure developed in order to study in detail the ion bombardment process and subsequent ejection of particles.[7-12] The model system to be studied is benzene, which forms an ordered *c*(4 × 4) overlayer on the (001) face of nickel.[13,14] 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 surface in a *c*(4 × 4) configuration. With the assumption of a pairwise interaction potential among all the atoms,[15] Ham-

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ilton's equations of motion are integrated to yield the positions and momenta of all particles—the primary Ar^+ ion, the substrate Ni atoms, and adsorbate atoms in the benzene molecule—as a function 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.[7-9,12] In addition to the determination of observables or macroscopic quantities, the classical dynamics procedure allows one to analyze microscopic mechanisms. It is the mechanisms of ejection that will be the focus of this work.

The Ni(001) surface with a $c(4 \times 4)$ coverage of benzene molecules is shown in Figure 1. The placement of the C_6H_6 molecule with respect to the Ni atom is not precisely known, but it is generally agreed that the ring is parallel to the surface.[13,14,16] The π-bonded site (C_6H_6 placed on top of a nickel atom) is consistent with current electron energy loss spectra (ELS).[13,14] Using the geometry parameters from theoretical calculations of nickel–ethylene complexes,[17] 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,[18] 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.[19]

The primary ion must bombard at all unique points on the surface to properly reproduce experimental results. The appropriate impact zone for normal incidence bombardment is shown in Figure 1, assuming the benzene to be a circular adsorbate rather than having sixfold symmetry. This zone is already eight times larger than the one for the clean metal, and assuming the proper symmetry of the benzene would make it even larger. Since the purpose of this study is to examine mechanisms of ejection, only 30 impacts of the 600-eV Ar^+ ions were calculated. The collision cascades for many more impact points would need to be determined to obtain statistically averaged data.

Upon analysis of the detailed atomic trajectories based on these procedures, there is unequivocal evidence that the benzene molecule can eject intact. In addition, fragments such as C_6H_5, C_5H_5, C_2H_2, and CH, along with atomic C and H, were observed. Since the goal of this study is to examine mechanisms of ejection, it is impossible at this time to make predictions as to the relative abundances of these fragments and the possible identity of other fragments. We found molecular ejection at approximately half of the impact points. In addition to the benzene molecule and fragments, we also observed an NiC_6H_6 cluster. Species of this type with a metal atom attached have been detected in numerous SIMS experiments.[2,4]

SIMS experiments have been published detailing the chemical composition of cluster ions ejected from solid benzene, although the analogous experiment for an ordered monolayer of benzene on a metal has not been performed. For solid benzene, large ions such as $C_{12}H_8^+$, which originated from more than one benzene molecule, have been observed.[3] The lack of observation of species such as $C_{12}H_8^+$ in the calculations is probably due to having only one layer of benzene, rather than multilayers as in a solid. At this time, it is not possible to make quantitative comparisons to experiments of cluster yields. Theoretically, one must know the stability and geometry of each fragment in order to determine its yield. In addition, the molecules and large clusters are highly vibrationally excited. Undoubtedly, some of these will dissociate into smaller fragments on the way to the detector.

There are many variations in the mechanisms for molecular ejection of C_6H_6. However, there are three common traits. First, since the benzene has many internal degrees of freedom, it can absorb excess energy from an energetic collision. The ejected molecules are often quite distorted from their original planar configuration (see Figure 2c). The second common trait in the ejection process is that the colliding particle, usually a Ni substrate atom, hits at least two of the carbon atoms in the ring. The collisions may be simultaneous or sequential and may involve 2–6 of the carbon atoms. This type of collision process causes several parts of the molecule to move in a concerted manner in one direction. Finally, since the initial motion of this colliding nickel atom is the result of other collisions, the energy with which the benzene is struck is often much less than the energy of the initial Ar^+ ion.

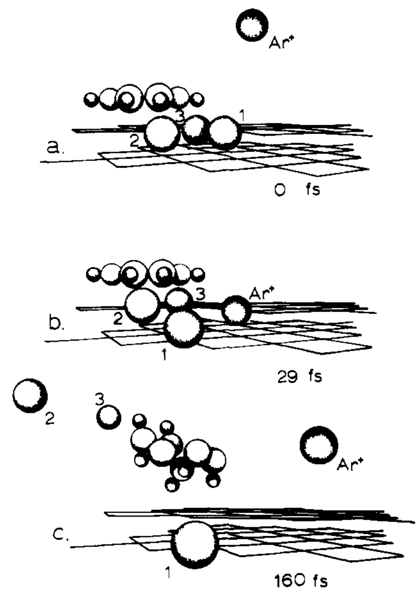

Figure 2. Ejection of a C_6H_6 molecule by the simultaneous collision with two Ni atoms. Only the species (one Ar^+ ion, three Ni atoms, and one C_6H_6 molecule) directly involved in the collision are shown. The grid lines are drawn between nearest neighbors in each plane; thus, a Ni atom is initially situated at each intersection of lines. The sizes of the atoms are arbitrary. The elapsed time during the collision is shown in the lower right corner in fs (10^{-15} s). (a) Initial positions of the atoms. The benzene is being viewed from the side. (b) Positions as the two Ni atoms are about to collide with the benzene. (c) Distortion of the ejected benzene.

Most of the variations to the above mechanism have direct analogues in the mechanisms of ejection of atomic adsorbates.[9] 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 hydrocarbon fragment from another C_6H_6. One benzene molecule even ejected due to two nickel atoms ejecting in parallel and concertedly striking the C_6H_6 molecule. This particular collision process is depicted in Figure 2, with the original placement of atoms also shown in Figure 1. The Ar^+ ion strikes atom 1, which moves under 2 and 3, ejecting both up toward the neighboring benzene (Figure 2a). In Figure 2b, the two Ni atoms are just about to strike the C_6H_6. By this time in the collision cascade, the original 600 eV of energy has been divided among many atoms. Atoms 2 and 3 only have 28 and 40 eV of kinetic energy, respectively, as they begin to strike the benzene molecule. Several of the carbons are struck in a concerted manner, pushing the molecule in one direction. The two Ni atoms and the distorted but intact C_6H_6 eject and are shown in Figure 2c. Note that the entire ejection process is over in $\sim 2 \times 10^{-13}$ s.

The fragments most generally originate from the molecule nearest the impact region and result from collisions with the Ar^+ ion. The protruding H atom can be easily ripped off without damaging the remainder of the molecule. More head-on collisions of the Ar^+ ion with the target benzene result in more extensive fragmentation. Some of the fragments implant into the solid while some reflect off the nickel atoms in the substrate and eject. In addition, energetic substrate atoms or hydrocarbon fragments have been observed to cause fragmentation of some benzene molecules.

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J. Am. Chem. Soc. **1980**, *102*, 6555–6556

The cationization of the molecular species has been shown to stabilize the parent molecule.[2] We found one NiC_6H_6 species in the calculations. The Ni involved was a neighboring atom, not the atom under the benzene. Since some recombination is involved, the experimental observations of the cationized species cannot be used as evidence that the organic molecule is directly bonded to the metal atom. This is completely analogous to the recombination mechanism of cluster formation of atomic adsorbates with metal atoms.[9,10]

The factors leading to the ejection of molecular fragments from ion-bombarded solids are then clear, at least in a mechanistic sense. These include the facts that (i) the energy of the primary ions is rapidly dissipated to energies of the order of chemical bond strengths by multiple collisions in the solid, (ii) the molecular fragments can eject intact since there are many internal vibrational modes which can absorb energy from an energetic collision, and (iii) multiple atoms can be struck by a larger substrate atom, forcing them to move in a concerted fashion. Although the classical dynamics calculations neglect the ionization process and the possible fragmentation of molecules on the way to the detector, the predicted nuclear motion giving rise to the ejection of stable molecules appears physically reasonable. The results provide the basis, then, for interpreting SIMS spectra in terms of the molecular structure of the original sample.

Acknowledgment. We acknowledge support from the Camille and Henry Dreyfus Foundation for a grant for Newly Appointed Young Faculty, the Alfred P. Sloan Foundation for a Research Fellowship, and the Research Corporation for a Cottrell grant. Portions of the computations were supported by the National Resource for Computation in Chemistry under a grant from the National Science Foundation and the Department of Energy (Contract W-7405-Eng-48). We also thank N. Winograd, E. Karwacki, and K. Foley for helpful discussions.

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Received May 19, 1980

An Efficient Photocathode for Semiconductor Liquid Junction Cells: 9.4% Solar Conversion Efficiency with p-InP/VCl_3-VCl_2-HCl/C

Sir:

The first efficient semiconductor–liquid junction solar cell based on a p-type semiconductor is reported. At an insolation of 110 mW/cm^2, the output of the photoelectrochemical p-InP/VCl_3–VCl_2–HCl/C cell is 10.4 mW/cm^2 for a solar-to-electrical conversion efficiency of 9.4%. The output power remains stable upon passage of 13 000 C/cm^2 near the maximum power point (0.52 V, 20 mA/cm^2), and there is no measurable weight loss. The results contradict suggestions of a fundamental limitation to the efficiencies of p-type cells from surface states and fermi-level pinning.

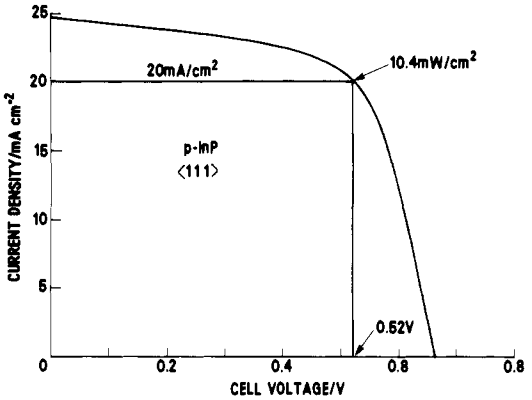

Figure 1. Current voltage characteristics of the cell p-InP/VCl_3–VCl_2–$ZnCl_2$–HCl/C at 110 mW cm^{-2} sunlight.

Although both n- and p-type regenerative liquid junction solar cells have been investigated, conversion efficiencies above 5% for sunlight have hitherto been obtained only with n-type photoanodes.[1-10] The present benchmarks of 12% and 7.8% for single-crystal and polycrystalline chemically vapor deposited electrodes, respectively, were reached with n-GaAs/selenide–polyselenide/carbon cells.[5,6,10] These achievements required counteracting the effects of surface states and grain boundaries on cell behavior.[5-10] Surface and/or interface states can lead to high electron-hole recombination rates which are manifested as a deficit in maximum power output and may even pin the semiconductor fermi level at the surface, thus limiting the open-circuit voltage. Interface modification by chemisorbed ions such as Ru(III) and Pb(II) was used in the case of n-GaAs, thereby reducing recombination losses so that the theoretical cell output could be more closely approached.[5-10]

The use of photocathodes instead of photoanodes is intriguing because illumination tends to cathodically protect the semiconductor against the key obstacle to stability, namely, surface oxidation. The reductive degradation of the semiconductor must, however, be slow, and the rate of electron transport to the redox couple dominant. In this respect, we are not aware of photoelectrochemical cell failures traceable to reductive photocorrosion.

These attractions of p-type materials stimulated investigations on a variety of photocathodes such as p-GaP,[11-18] p-GaAs,[11,19-21] p-Si,[22] p-Ge,[23] p-CdTe,[15,24] and p-InP.[15,25-28] None of the resulting

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