detail elsewhere. The complete systematic assignment of the remaining sugar resonances is impeded thus far by strong overlap in the H4′, H5′, and H5″ regions, even in a 2-D spectrum. The remaining aromatic resonances (AH2) are part of another cross-relaxation network in double-stranded DNA, which also includes the exchangeable hydrogen-bridged imino protons. Systematic assignment of these resonances is also possible by using the nuclear Overhauser effect.[21,22]

The procedure presented here for DNA resonance assignments has the usual advantages over analogous one-dimensional approaches in that it avoids the necessity of selective irradiation of many resonances in crowded spectral regions[12] and is experimentally straightforward. Furthermore, it does not rely on the availability of numerous subfragments[23] or analogues[22] of the DNA duplex of interest, nor on assumptions about the exact solution structure as required for chemical-shift calculations,[24] nor on assumptions concerning the temperature dependence of the chemical shift such as are involved in the interpretation of melting behavior.[25]

(21) Johnston, P. D.; Redfield, A. G. *Biochemistry* **1981**, *20*, 1147.
(22) Patel, D. J.; Kozlowski, S. A.; Marky, L. A.; Broka, C.; Rice, J. A.; Itakura, K.; Breslauer, K. J. *Biochemistry* **1982**, *21*, 428.
(23) Borer, P. N.; Kan, L. S.; Ts'o, P. O. P. *Biochemistry* **1975**, *14*, 4847.
(24) Sanchez, V.; Redfield, A. G.; Johnston, P. D., Tropp, J. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5659.
(25) Several assignment strategies are discussed in the following: Jardetzky, O.; Roberts, G. C. K. "NMR in Molecular Biology"; Academic Press: New York, 1981.

Angle-Resolved SIMS Studies of Organic Monolayers on Ag(111)

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Organic molecules are desorbed and ionized directly from the solid state by using secondary ion mass spectrometry (SIMS).[1,2] The mechanism of molecular desorption has been open to discussion particularly with regard to species with molecular weights greater than several hundred daltons.[1-4] Of special concern is to explain how a >1000-eV Ar⁺ ion (or Ar atom) induces the desorption of a molecule whose bond strengths may be on the order of several electron volts. To address this question, the energy dissipation for a model system of benzene adsorbed into a c(4 × 4) overlayer on Ni(001) has been followed by using classical trajectory techniques.[5,6] In this work, we test several predictions of the classical dynamics model by measuring for the first time

(1) A. Benninghoven, *Surf. Sci.*, **53**, 596 (1975).
(2) B. J. Garrison and N. Winograd, *Science* (*Washington, D.C.*), **216**, 805 (1982).
(3) M. Barber, J. C. Vickerman, and J. Wolstenholme, *J. Chem. Soc., Faraday Trans. 1*, **76**, 549 (1980).
(4) R. D. Macfarlane, *Acc. Chem. Res.*, **15**, 268 (1982).
(5) B. J. Garrison, *J. Am. Chem. Soc.*, **102**, 6553 (1980).
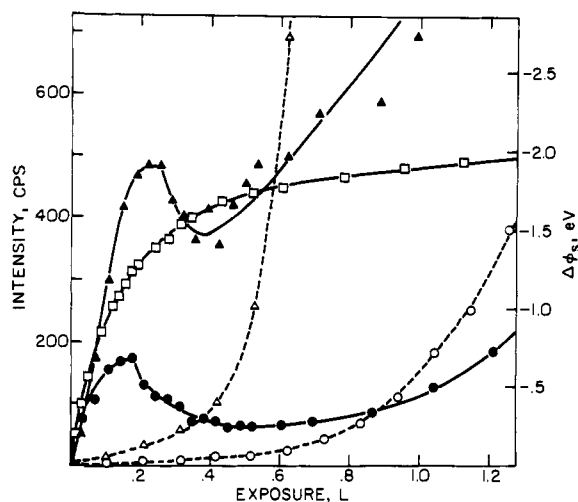(6) B. J. Garrison, *J. Am. Chem. Soc.*, **104**, 6211 (1982).

Figure 1. Ion yields of $C_6H_5^+$ (O) and $AgC_6H_6^+$ (△) from benzene on Ag(111) and ion yields of $C_5H_5NH^+$ (●) and $AgC_5H_5N^+$ (▲) from pyridine on Ag(111) as a function of exposure at 153 K. The Ar⁺ primary ion was incident perpendicular to the surface, and the polar collection angle θ was 45° relative to the surface normal; work function change (□) for pyridine on Ag(111) as a function of exposure at 153 K. Bombardment conditions: 1 keV, 2 nA, Ar⁺.

the ion yield as a function of the polar angle of ejection and coverage for benzene and pyridine adsorbed on Ag(111) at 153 K. These model systems are of interest for a number of reasons. (i) The molecules are similar in size and shape and should behave in a closely related fashion under the influence of ion bombardment. (ii) Classical dynamics calculations have been performed on these molecules adsorbed on Ni(001) where dramatic differences in the molecule yield are predicted to occur with molecular orientation.[6] (iii) Electron energy loss spectroscopy indicates that pyridine on Ag(111) initially adsorbs in a π-bonded configuration but undergoes a compressional phase transition to a σ-bonded configuration as the coverage is increased.[7,8] Benzene, on the other hand, is believed to remain in the π-bonded configuration at all coverages.[9-12]

The details of the angle-resolved SIMS apparatus have been described elsewhere.[13] The Ag(111) surface was cleaned by cycles of heating at 700 K and ion bombardment. After a final annealing at 620 K for 5 min, the crystal exhibited sharp 6-fold symmetric LEED spots. Exposure values in langmuir units were corrected by a guage factor of 5.8. The SIMS spectra of a Ag(111) surface exposed to pyridine or benzene at 153 K are characterized by a series of cluster ions including the molecular ion M⁺, (M + H)⁺, Ag⁺, (Ag + M)⁺, and (Ag + 2M)⁺. For benzene, all positive ion yields begin to increase after 0.6 langmuir of exposure and reach a plateau at monolayer coverage after 2.5 langmuirs of exposure. Exposure to benzene beyond 2.5 langmuirs results in a decrease in the intensities and an increase in the relative fragment yields as has been reported to occur using the Ni(001) surface.[14] For pyridine on Ag(111), however, the ion yields exhibit a distinct maximum at 0.2 langmuir of exposure before increasing to a second maximum after 4.5 langmuirs of exposure. We do not believe this first structure arises from any anomolous electronic effects since the surface work function change measured simul-

(7) J. E. Demuth, K. Christmann, and P. N. Sanda, *Chem. Phys. Lett.*, **76**, 201 (1980).
(8) J. E. Demuth, P. N. Sanda, J. M. Warlaumont, J. C. Tsang, and K. Christmann, in "Proceedings of the Surface Vibrations Conference", Belgium, Sept 1980. –
(9) T. E. Fisher, S. R. Kelemen, and H. P. Bonzel, *Surf. Sci.*, **64**, 157 (1977).
(10) S. Lehwald, H. Ibach, and J. E. Demuth, *Surf. Sci.*, **78**, 577 (1978).
(11) J. C. Bertolini and J. Rousseau, *Surf. Sci.*, **89**, 467 (1979).
(12) C. M. Friend and E. L. Muetterties, *J. Am. Chem. Soc.*, **103**, 773 (1981).
(13) R. A. Gibbs and N. Winograd, *Rev. Sci. Instrum.*, **52**, 1148 (1981).
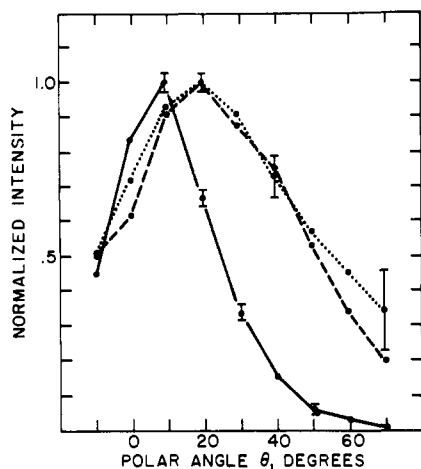(14) E. J. Karwacki and N. Winograd, *Anal. Chem.*, in press.

Figure 2. Normalized polar angle distribution of molecular ion yields for 4.5-langmuirs pyridine (—, $(M + H)^+$), 0.15-langmuirs pyridine (——, $(M + H)^+$), and 2.5-langmuirs benzene (···, $(M - H)^+$) on Ag(111) at 153 K.

taneously by the electron-beam-retarding field method exhibits a continuous decrease through this exposure region. The details of this behavior are illustrated in Figure 1 for the $AgC_5H_5N^+$ and $C_5H_5NH^+$ positive ions during pyridine adsorption. Related ions exhibit parallel trends. Similar curves for the $C_6H_5^+$ and $AgC_6H_6^+$ ions obtained during benzene adsorption are shown for comparison. The drop in the molecular ion signals after the maximum at 0.2 langmuir for the pyridine case is consistent with classical dynamics calculations, which predict that a shift in orientation of the molecule from parallel to perpendicular to the surface should decrease the probability of molecular emission.[6]

To further substantiate the link between the ion ejection process and molecular orientation, we have measured the polar angle distribution of various ejected ions for three systems—2.5-langmuirs benzene (monolayer), 4.5-langmuirs pyridine (monolayer, σ bonded) and 0.15-langmuir pyridine (π bonded) on Ag(111). The results of these distribution measurements are illustrated in Figure 2. For monolayer benzene and for π-bonded pyridine where the molecules are believed to lie flat on Ag(111),[7] the polar angle distribution of $(M - H)^+$ (benzene) and $(M + H)^+$ (pyridine) are broad with a peak at $\theta = 20°$.[15] At the onset of the compressional phase transition, however, the polar angle distribution of the $C_5H_5NH^+$ ion sharpens dramatically, and the peak moves to $\theta = 10°$.

The arrangement of atoms and molecules on surfaces has been shown to influence the angular distributions of ejected atomic and molecular species.[2,16] The reason for this dependence is that there is a surface channeling mechanism that forces atoms to eject along open crystallographic directions where atom–atom repulsions are at a minimum. The anisotropies have previously only been found in azimuthal angle distributions. For the case of an ordered array of molecules stacked at an inclined angle relative to the surface, however, recent computer simulations[17] indicate that channeling effects are more clearly observable in polar angle distributions rather than in the azimuthal angle distributions as is indicated by our experiments. If this explanation is correct, our experimental results suggest that the tilt angle of the σ-bonded pyridine molecule is somewhat smaller than proposed previously.[7] Calculations currently in progress are aimed toward determining how precisely the polar angle distribution can be related to the tilt angle of the σ-bonded pyridine. We find that the polar angle distribution of

σ-bonded pyridine is unusually sharp and 1.5 times wider at high kinetic energies (6–10 eV) than at low kinetic energies (3–7 eV). Presumably, the faster moving molecules can more easily deform the channel walls during desorption.[18]

In conclusion, we have measured the SIMS spectra of a number of organic monolayers adsorbed on Ag(111) with the goal of obtaining a detailed understanding of the basic mechanism of ejection of the molecular clusters. The experiments were suggested by molecular dynamics calculations, which predict that the yield and angular distribution of the desorbed species should be sensitive to the orientation of the surface molecule relative to the substrate. The experimental verification of these concepts establishes a new approach for the study of the orientation of molecular systems where molecular channels influence the desorbing particle's trajectory. More important, perhaps, these results provide striking confirmation of the basic application of the classical dynamics model to the understanding of organic SIMS spectra. This confirmation is particularly satisfying in view of the approximations inherent in the classical calculations and the overall complexity of the momentum dissipation process.

(18) This trend toward wider polar angle distributions for faster moving particles is counter to that found for atom ejection. The surface channels on single-crystal metals should be more rigid than those formed by organic molecules and are less subject to deformation.

Redox Properties of $(CN)_8PcZn$, a New Charge-Transfer Complex

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According to simple Hückel theory, the lowest unoccupied molecular orbital (LUMO) of phthalocyanines has doubly degenerate e_g symmetry and can therefore accept up to four electrons in an electroreduction of the π ring system.[2,3] This reversible addition of four electrons, which has been shown experimentally,[4] does not occur for metalloporphyrins. Although metalloporphyrins may undergo four ring reductions in nonaqueous media, the latter two reactions at more negative potentials involve irreversible two-electron transfers with concomitant protonation.[5,6]

In this communication we report the formation of a stable zinc phthalocyanine tetraanion that is electrochemically generated in nonaqueous media. The starting compound is octacyano-substituted zinc phthalocyanine, $(CN)_8PcZn$ (Figure 1), whose synthesis has been reported in the literature.[7–9] As seen in Figure

(15) The M^+ ion signal is experimentally too small to obtain angular distributions. However, the $(M + H)^+$ or $(M - H)^+$ ion trajectories are expected to be similar to the M^+ ion trajectory due to the small mass influence of hydrogen.

(16) S. P. Holland, B. J. Garrison, and N. Winograd, *Phys. Rev. Lett.*, **43**, 220 (1979).

(17) This effect has been seen in our recent computer simulations of ion-bombarded pyridine on Ni(001) and is discussed in detail in a paper in preparation.

(1) (a) Université Louis Pasteur. (b) Centre de Recherches sur les Macromolecules. (c) University of Houston.

(2) Linder, R. E.; Rowlands, J. R.; Hush, N. S. *Mol. Phys.* **1971**, *21*, 417.

(3) Schaffer, A. M.; Gouterman, M.; Davidson, E. R. *Theor. Chim. Acta* **1973**, *30*, 9.

(4) Clack, D. N.; Yandle, J. R. *Inorg. Chem.* **1972**, *11*, 1738.

(5) Lanese, J. G.; Wilson, G. S. *J. Electrochem. Soc.* **1972**, *119*, 1039.

(6) Peychal-Heiling, G.; Wilson, G. S. *Anal. Chem.* **1971**, *43*, 550.

(7) Wöhrle, D.; Wahl, B. *Tetrahedron Lett.* **1979**, 227.