The increased reactivity of **2** in the metal-exchange step appears to be associated with internal tin–nitrogen coordination in the transition state.[1,2] At least two pathways are conceivable, both of which would benefit from the unusual bonding that is available in **2**. A simple four-center exchange process between Sn–C and the Pd–X bond (X = Br or I) of L_2ArPdX would be facilitated because the exocyclic bond of **2** is unusually long[1] and, therefore, more reactive. Alternatively, metal exchange might involve electron transfer from tin bonds to L_2ArPdX. In this case, an electron-deficient tin center could be stabilized by nitrogen coordination, resulting in partially positive nitrogen and a tricyclic organotin transition structure. Tzschach et al. have presented evidence for bonding interactions of this type in **1**, and they have also suggested at least some Sn- - -N bonding in **2a** based on the X-ray structure.[1] Since the ring C–Sn bonds of **2** are constrained to occupy pseudoequatorial sites in trigonal bipyramidal derivatives, only the apical alkyl group is activated by internal coordination, and selective transfer is thereby assured. The mechanistic details cannot be specified with confidence, but there are other indications that **2a** is unusually reactive toward electrophiles.[13] We are exploring related systems where geometric constraints may provide selective activation of carbon–heteroelement bonds.

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[13] **2a** is more reactive than is Me_4Sn toward iodinolysis. Thus, a 1:1:1 mixture of **2a**:Me_4Sn:I_2 in $CDCl_3$ afforded **1c** (80%) with <5% of Me_3SnI or ring cleavage.

Structure Dependence of Ammonia Adsorption on Alkali Halide Clusters

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Molecular adsorption on solid surfaces is a process of great technological importance that has also been used as a means of studying surface structure.[1] From systematic exploration of initial adsorption rates on crystalline surfaces[2] combined with intensive theoretical investigation, important rules have been established about the role of specific structural and electronic features of the surface in controlling adsorption. A similar approach can also be used to characterize the nanocrystalline surfaces of larger clusters. This is in contrast to approaches that use either the number of adsorbed molecules[3] or the initial reactivity[4] to help determine the (unknown) structures of transition metal or silicon clusters. In this communication we describe a clear correlation between the adsorption reactivity of alkali halide clusters and the structures previously established by other experiments and theory,[5-10] leading to the identification of a certain active site.

Alkali halide clusters (AHCs) are ionic systems $M_n^+X_m^-$, the most stable of which have ions arranged in a rock salt structure of cuboidal morphology.[5] They serve as good theoretical and experimental models for microscopic aspects of ionic crystals, their surfaces,[6] and even defect states.[7] Here we use pulsed flow reactor methods and time-of-flight mass spectrometry to investigate, for the first time,[11] the adsorption reactions of a number of alkali halide systems in ±-charge states. Neutral and charged clusters are formed and equilibrated in helium in a laser-ablation source using previously described methods.[12] A dilute NH_3/He mixture is introduced downstream from the cluster formation region. The flow of reactants and products expands into vacuum at the end of the reactor channel, and charged products are measured mass spectrometrically without further ionization.

The initial reaction of sodium fluoride clusters toward ammonia at ambient temperature is the elementary process:

$$Na_nF_{n-1}^+ + NH_3 \rightarrow Na_nF_{n-1}^+\cdot NH_3 \qquad (1)$$

Figure 1 plots the relative reactivity[13] of process 1 at ambient temperature, as extracted from a number of experiments at different NH_3/He concentrations (0.1–10%). The reactivity is strongly dependent on cluster size, with certain sizes (n = 14, 23, 32, 38, 53) showing no definite evidence of reactivity at even the highest concentration, whereas other sizes, n = 13 and 22, can be reacted completely by process 1 at moderate concentration. Smaller clusters in particular tend to show secondary adsorption at higher concentrations. The pattern shown in Figure 1 for ammonia adsorption is also found for other $M_nX_{n-1}^+$ clusters, MX = KF and NaCl, with precisely the same values of n for reactivity maxima and minima. However, negatively charged clusters, $Na_{n-1}F_n^-$, are found to be much less reactive.

The reactivity pattern can be associated very well with the structures established previously for AHCs.[5-10] Relaxed structures[10] calculated for the most important of these are shown in Figure 1. The clusters that are nonreactive toward ammonia adsorption at ambient temperature (n = 14, 23, 32, 38, and 53) are the cuboidal nanocrystals with lattice dimensions 3 × 3 × 3, 3 × 3 × 5, 3 × 3 × 7, 3 × 5 × 5, and 3 × 5 × 7. The least reactive smaller cluster (n = 5) is a single sheet (3 × 3). The lowest energy structures for other less-reactive clusters, n = 10 and 17, also have entirely convex surfaces, unlike those of more reactive clusters which have various lattice defects. The most reactive clusters, n = 13, 22 and 31, 57, 52 (not shown), have several closely related, low-lying isomers based on removal of a contiguous MX unit from the cuboid structure. However, the lowest in energy is the basketlike structure shown, and the others are weakly stable with respect to collapse to this structure.[8,10] We therefore associate high reactivity with this defect.

The adsorption activity of alkali halide crystal surfaces toward ammonia is not known, but it is known for the related MgO ionic crystal surface.[14] We find no adsorption of NH_3 on cuboidal nanocrystals, so that our results might indicate that (100) faces, edges, and corners, might be nonadsorbing at ambient temperature. In contrast, the AHCs with a basket defect are extremely reactive, suggesting that such defects are well suited to adsorption. Seeking a structural explanation, we have examined models and favor one in which the NH_3 molecule fills the basket with the nitrogen end

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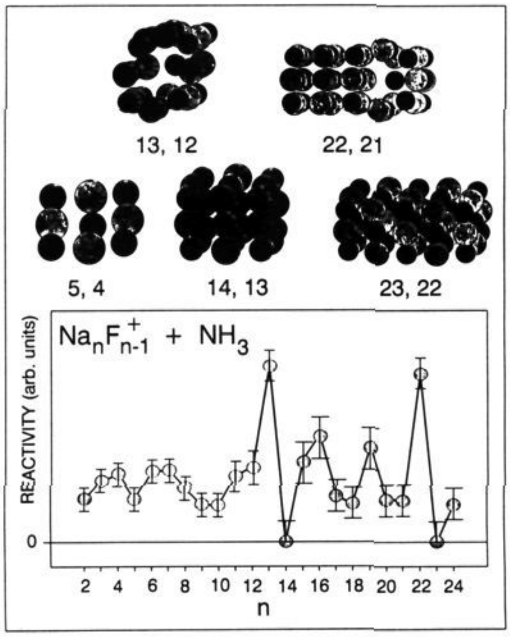

Figure 1. Relative rates for process 1 plotted vs cluster size, n = 2–24 (bottom) and calculated minimum energy structures for the most reactive (n = 13, 22) and the least reactive (n = 5, 14, 23) clusters (top). Small, dark spheres represent Na^+ ions and large, light spheres represent F^- ions. The upper structures are oriented to show the basketlike defect obtained by removing a single NaF unit from the n = 14 and 23 clusters. Point group symmetries are as follows: 5, C_{4v}; 13, C_{4v}; 14, O_h; 22, C_s; 23, D_{4h}.

near the cluster center where a halide ion X^- would have been.[15] *The hydrogen atoms would lie in the interstices between the middle* and outermost layers. For the case of $Na_{13}F_{12}^+$, the Na–F nearest-neighbor distance is near 2.2 Å. This is very close to the computed bond distance in the linear $Na^+\cdot NH_3$ complex (2.25 Å);[16] which has a measured binding energy of 1.26 eV,[17] as compared to the computed energy gain of 3.3 eV by adding NaF to this site.[10] While this type of lock-and-key arrangement could neatly explain the high reactivity, and also the nonreactivity of the negatively charged analogs like $Na_{12}F_{13}^-$, the electronic character of the sites may also be important. The greatly lowered reactivity of the negatively charged clusters suggests that an important factor is the ability of NH_3 to act as a Lewis base, which could explain the results of $Si_n^{\pm}$ reactivity toward NH_3.[4]

In conclusion, the relative reactivity of charged alkali halide clusters $M_nX_{n-1}^+$ (M = Na, K; X = F, Cl) toward NH_3 has been measured under isothermal conditions using pulsed flow reactor and mass spectrometric techniques. By comparing relative reactivities to computed cluster structures, the reaction process is interpreted as molecular adsorption at favorable sites of cluster structures. Clusters with closed structural shells (n = 14, 23, 32, 38, and 53) are nonreactive at ambient temperature, whereas a specific structural defect (a "basket" or diatomic hole, present for n = 13, 22, 31, 37, and 52) greatly enhances initial adsorption. Negatively charged clusters ($Na_{n-1}F_n^-$) are much less reactive. In this approach, one can use clusters of known structures to obtain difficult-to-measure elementary reaction rates for other molecules (e.g., H_2O, CO_2, and NO_2), activation energies, and equilibrium quantities for real surfaces by extrapolating from larger clusters to the infinite.

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(15) Previous experiments on AHCs have shown that it is possible to integrate different species (e.g., an electron (ref 7) or F_2^- (ref 9)) into a cluster lattice site while still maintaining the integrity of the lattice.

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Mass Spectrometric Detection of the Noncovalent GDP-Bound Conformational State of the Human H-*ras* Protein

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In recent years, the development of several new ionization methods[1-4] has allowed the direct analysis and sequencing of biomolecules previously not amenable to mass spectrometry (MS).[5-9] However, it is only recently that noncovalent receptor–ligand,[10] enzyme–substrate,[11] and enzyme–inhibitor[11,12] complexes have been detected via direct infusion ion-spray MS.[13]

Sample solutions analyzed by ion-spray MS generate a series of multiply protonated ions which, under normal operating conditions, do not undergo molecular fragmentation. Experiments can be performed in aqueous solutions without the addition of organic solvents or acidic modifiers, thus making the detection of noncovalent association complexes feasible. In this report, we describe the use of ion-spray MS for the study of the noncovalent complex of human *ras* protein with GDP, as well as the effect of pH and cosolvent on the stability of the *ras*:GDP complex system.

The *ras* proteins are regulatory guanine nucleotide binding proteins which, only in the GTP-bound active form, serve as signal transducers controlling cell proliferation or differentiation.[14] Malignacies in many different tissue types are in part brought on by mutations in the *ras* oncogene. For our studies, C-terminally truncated human H-*ras* (1–166) (Figure 1) was expressed in *Escherichia coli* from a synthetic *ras* gene under the control of both the *lpp* and *taq* promoters,[15] while *ras*:GDP (1–166) was purified from fermentor-grown, IPTG-induced cells.[16] The ac-

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