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## Site-Specific Studies of CH Bond Activation on Metal Oxide Clusters

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This project focuses on how the acid-base properties of individual sites on metal oxide clusters impacts their reactivity towards CH activation, and concurrently, how the presence of products of this reaction modify the acidity or basicity of nearby sites. This fundamental understanding is expected to facilitate the refinement of an intuitive framework for rationalizing reactivity of heterogeneous nanostructured catalysts towards transformations relevant to the petroleum industry in which CH activation is a critical elementary step. The successful execution of this work has required us to develop methods to address two key aspects of the overall goal: 1) initiating reactions on these clusters in temperature-controlled ion traps, and 2) the development of vibrational spectroscopic probes of CH bonds in mass-selected clusters under acidic or basic conditions (in this case, protonation or deprotonation). With the experience we have gained by carefully studying these test systems, we are now prepared to tackle the full complexity of hydrocarbon reactivity on metal oxide clusters.

### Evaluating the Reliability of Ion Trap Temperature as a Measure of the Temperature of a Complex

Typically, metal oxide clusters used in mass-selective experiments are produced by sputtering or laser vaporization of a metal target in a low-pressure atmosphere in the presence of a small amount of O<sub>2</sub>. Further reactions with hydrocarbons can be initiated by seeding hydrocarbon vapors into this mixture, or by clustering them in a subsequent ion guide or ion trap. We are using this second approach because it affords us more control over the conditions under which hydrocarbons react on the cluster, allowing us to more closely represent industrially-relevant conditions. However, this has required us to carry out a series of experiments to explore the level of control that we can achieve. To this end, we first characterized the uncertainty in temperature typical to our ion traps. Our test system for this work is the ammonium-water complex, an overall acidic cluster in which the ro-vibrational bands of the water asymmetric stretch may be analyzed to estimate the cluster temperature.

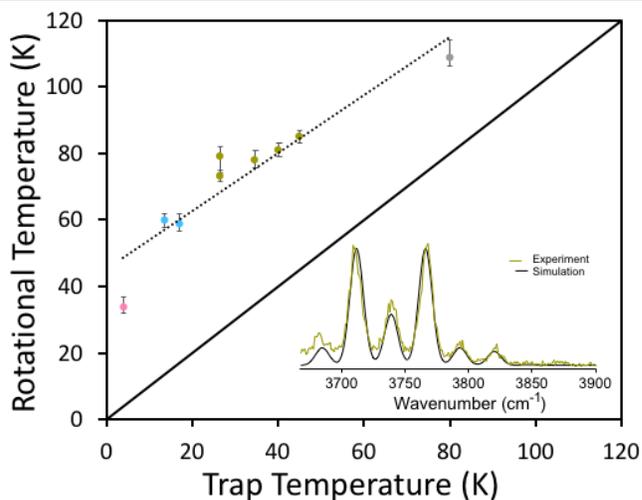


Figure 1. Derived ion rotational temperature vs. ion trap temperature for the ammonium-water complex with He (red), D<sub>2</sub> (blue), N<sub>2</sub> (brown), and CO<sub>2</sub> (gray). Ions are found to be consistently 30-40 K warmer than the trap. Inset is an example of a fit of temperature to the water asymmetric stretching band for N<sub>2</sub> tags.

We have complexed these clusters with weakly-interacting gases (He, D<sub>2</sub>, N<sub>2</sub>) and a more strongly-interacting one (CO<sub>2</sub>) and determined the temperature of the complex as a function of the temperature of the ion trap itself. A nearly linear relationship between trap temperature and complex temperature is seen

across all complexes, with a roughly constant offset from the nominal temperature by 30-40 K. Notably, however, for a given gas, the response to changes in trap temperature was substantially smaller, suggesting that the identity of the complexing gas (and thus its' binding affinity) plays a substantial role in the temperature. Therefore, we conclude that for weakly-interacting adsorbates, the temperature of the ion trap and the binding energy of the adsorbate compete to determine the overall cluster temperature, which typically will be substantially above the temperature of the ion trap. Given that covalent molecular ions are often found to be near the trap temperature, these results suggest that more care must be taken when determining the temperature of weakly-bound clusters.

### Manifestations of CH Bond Reactivity in Vibrational Spectra

Simultaneously, we have investigated the reactivity of adipic acid under acid conditions in confined geometries. We have determined that, when protonated (to an overall cation), adipic acid undergoes sequential losses of water. Given that protonated adipic acid has only three OH groups, one of these four hydrogens must come from a CH bond. We

have confirmed this with the use of isotopically-labeled collision-induced dissociation experiments, which reveal that the first water originates from OH groups, while the second involves either one or two aliphatic hydrogens. This reactivity occurs in very mild collisions, more typically associated with dissociation of hydrogen-bonded clusters than the breaking of covalent bonds, indicating that the acidic nature of this complex drastically changes its reactivity in isolation.

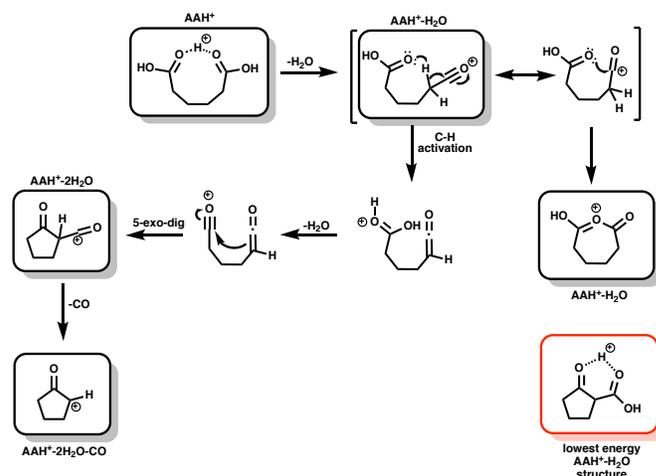


Figure 2: Proposed mechanism for acid-induced CH bond cleavage in adipic acid. The lowest energy isomer for the product of the first water loss is not seen, implying a substantial barrier to formation. Evidence is seen in the spectra for all structures in black boxes.

Using vibrational spectroscopy to determine the functional groups present in the products of these water losses, we have proposed a mechanism by which this reactivity may occur. Critically, the step involving CH bond breaking is revealed to be attack of a particularly electrophilic methylene group by a carboxylic acid, yielding  $[\text{HOCOH}]^+$  which eliminates water. This intramolecular reaction is made possible by the fact that in the gas phase, much like on a cluster surface, the adipic acid molecule takes on a U-shape, a motif significantly less likely in solution. This reactivity is apparent for a range of dicarboxylic acids that we have studied. This work not only gives an example of the unique reactivity possible in acidic clusters, but also provides us with much-needed experience in evaluating CH reactivity in the gas phase by vibrational spectroscopy.

### New Metal Oxide Cluster Preparation Techniques

We are also investigating alternative ways to produce metal oxide clusters of interest for these studies. While laser vaporization sources, which involve the ablation of a metal target by a high-energy pulsed laser, or magnetron sputtering sources, are commonly employed for this purpose, they require extensive modification of instrumentation to implement and are thus limited in their applicability. Furthermore, some metals are not amenable to cluster formation using these sources. Thus, we are developing approaches to obtaining these clusters from common electrospray ionization sources using solution-phase chemistry. Of particular interest are polyoxometallates, which we have observed to produce interesting and potentially useful fragments upon introduction to the mass spectrometer, likely due to Coulomb explosion of the highly-charged solution-phase ion. If we are able to harness this fragmentation in a controllable way, we can develop methods for generating clusters that can be employed by any researchers with commercial electrospray mass spectrometers, potentially opening up new avenues for the study of these catalytically-relevant systems.

### Impacts on the PI and Supported Students

The student supported by this funding has gained a proficiency in using ion traps and custom-built mass spectrometry instrumentation to characterize ionic clusters and their reactivity. She has presented this work at the 2018 ACS Spring National Meeting in New Orleans, where she also had the opportunity to broaden her scientific interests and participate in ACS-organized career development events such as interview training and a discussion of careers for chemists beyond academia. She is on track to graduate in Spring 2019 with her Ph.D. thesis almost entirely discussing PRF-funded work. In the course of these investigations, we have initiated a collaboration with a radiochemist in our department that uses the same experimental approaches described here to evaluate the binding energies of water to lanthanide-based organometallic magnetic resonance imaging (MRI) contrast agents. This unanticipated side project arose from the work on ammonium-water cluster temperatures and will form the basis of a collaborative proposal to rapidly develop and evaluate improved imaging agents.