

mation or the different channels making a certain fragment ion produce them with comparatively small kinetic energy release. Indeed, a small daughter ion resulting from more than one consecutive *thermal* fragmentation is expected to have a relatively small kinetic energy release. This is a result of the fact that, if one assumes that the maximum excess energy in the parent ion during the first photochemical fragmentation process is only 4.7 eV (see above), then the excess energy in consecutive fragmentations must be growing smaller and smaller in every sequential *thermal* fragmentation, due to the partitioning of the excess energy

during every fragmentation. This results in a smaller and smaller kinetic energy release and average kinetic energy of the final small ion produced.

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Dissociative Chemisorption of H₂ on Niobium Cluster Ions. A Supersonic Cluster Beam FT-ICR Experiment

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Positive cluster ions of niobium produced by laser vaporization and cooled by supersonic expansion have been injected into the ion trap of a Fourier transform ion cyclotron resonance spectrometer. By use of this new technique, the relative rates of H₂ dissociative chemisorption were measured for the clusters Nb₇⁺, Nb₈⁺, and Nb₉⁺. In striking agreement with earlier studies on the neutral clusters, Nb₇⁺ was found to be far more reactive than either Nb₈⁺ or Nb₉⁺. Such a close correspondence in reactivity patterns between the positive and neutral clusters is inconsistent with a simple electrostatic model of the dissociative chemisorption process.

Introduction

Fourier transform ion cyclotron resonance^{1,2} (FT-ICR) offers a tantalizingly powerful method for the study of chemical reactions on metal cluster surfaces—studies that could provide a vital connection to problems in surface science.³ For the very small metal clusters (two or three atoms) FT-ICR techniques have been available for some time. Freiser,⁴ Ridge,⁵ and their co-workers have done pioneering work along these lines, Freiser's group often using laser vaporization of metal targets within the ICR cell followed by ion/molecule reactions to build up an inventory of the desired clusters. More recently, a flurry of papers has appeared on semiconductor cluster FT-ICR where, again, laser vaporization in (or close to) the ICR cell is used to produce the clusters.⁶⁻⁹ While there is unquestionably much that can be done with these techniques, there is an intrinsic restriction in that only those clusters can be studied whose synthesis is compatible with the high vacuum and restricted access implicit in the design of all FT-ICR cells. For large clusters of any material and most metal clusters of any size range, this restriction forces one to resort to more elaborate techniques where the clusters are prepared in an external source.

As demonstrated last year,¹⁰ there is a straightforward means of efficiently coupling a supersonic cluster beam apparatus with an FT-ICR spectrometer. In general, it is difficult to inject ions from an external apparatus into an ICR cell since the ions must cross many field lines as they move into the high magnetic field of the ICR apparatus. However, this problem is minimized near the central axis of a solenoidal magnetic field. If the external ion beam is well collimated, a simple einzel lens system combined with a two-stage electrostatic decelerator is capable of efficiently performing the injection.

This Letter presents the first major application of this technique to a problem in metal cluster chemistry: dissociative chemisorption of H₂ on positive transition-metal clusters. Niobium has been used

because it has just a single stable isotope and because extensive measurements are available for the corresponding neutral clusters. The results show that there is a remarkable similarity in the reaction patterns of the positive cluster ions when compared with the neutrals.

Experimental Section

The metal cluster beam used in this experiment was generated in a pulsed supersonic beam apparatus similar to that described previously.¹¹ The niobium clusters were produced by laser va-

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porization in a supersonic nozzle, the cluster ions being enhanced by a 5–10-mJ pulse from an ArF excimer laser, fired 60 μ s after the vaporization laser pulse. This ArF excimer pulse produced a dense plasma composed of positive and negative niobium clusters which then experienced extensive cooling during subsequent flow through a 15° included angle, 10-cm-long exit cone and further cooling in the final intense supersonic free expansion in the helium carrier gas. After skimming and passage into a second vacuum chamber, the positive clusters were extracted from the supersonic beam by a high-voltage pulse applied as the clusters passed between a set of extraction grids. Time-of-arrival profiles of the supersonic cluster pulse as it passed between these extraction plates showed the clusters to have been accelerated without slippage to the terminal velocity expected of a helium beam from a static source at 400 ± 50 K. The measured translational temperature of the cluster beam was below 30 K, and given the expansion conditions, we expect the internal temperature of the clusters in the beam was less than 50 K.

The resultant cold positive cluster ion beam traveled at a right angle to the original supersonic beam and was generally run at an axial beam energy of 680 V with a 50-V energy spread. This beam was directed along the central axis of a 6-T superconducting magnet which housed the ICR cell. The critical focusing einzel lens was located 70 cm from the magnet center, its voltage adjusted so that the desired cluster ion would be focused to a point roughly 20 cm short of the magnet center. As discussed previously,⁹ this arrangement brings the ions in through the fringing field of the magnet so that their trajectories are nearly tangent to the field lines just at that point where the field first becomes strong enough to significantly affect the motion.

The cluster ions were slowed to the 0–45-eV range in two stages with a pulsed electrostatic decelerator similar to the design published previously. The first stage was located at 25 cm from the magnet center, where the ions were slowed to 10–60 eV; the final deceleration stage was located at 12.5 cm.

Since our original ICR experiments,¹⁰ extensive changes have been made in the vacuum system design, the ICR cell design, and the computerization of the detection system. The ICR cell for this new experiment was of cylindrical design (4.8-cm i.d., 15 cm long). The cylindrical side electrodes were divided longitudinally into four sectors. One opposing pair of 60° sectors served as the excitation plates of the ICR cell. The other pair, the detection plates, were each 120° sectors. The end plates (the front and rear "doors" to the ICR cell) were flat copper disks 5 cm in diameter with 2.5-cm-diameter central apertures, covered with molybdenum mesh.

All components of the ICR cell and decelerator were baked to 600–700 K, the ICR cell also being provided with liquid nitrogen cooling capability to operate at roughly 100 K, although the experiments described below were done with the cell at room temperature.

The coherent excitation and detection electronics were essentially as described earlier,¹⁰ except that a far more substantial computer system (MicroVAX II with CSPI array processor) was used to handle the huge data processing requirements that are one of the hallmarks of this FT-ICR technique. A separate computer system (IBM-AT) controlled the supersonic cluster beam apparatus, with its associated lasers, detectors, and beam-guiding electronics. The cluster source operated at a repetition rate of 10 Hz, the ICR cell dump, inject, and excite cycles being controlled by the small AT computer.

Multiple Injection Cycle Filling of the ICR Cell. Since our original publication, improvements in the cold cluster ion generation technique have enabled a dramatic increase in the metal cluster ion beam intensity available for injection into the ICR cell. Even so, for the larger clusters we still need to work hard for acceptable signal levels from a single injection shot. The long ICR

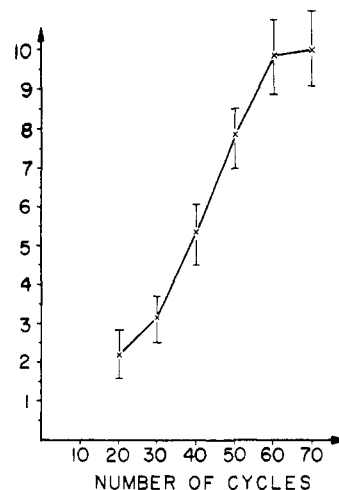


Figure 1. Magnitude of the Nb₇⁺ cluster signal from the FT-ICR cell as a function of the number of successive injection cycles from the cluster ion beam apparatus. The apparent positive curvature of this trace in the 0–20 injection cycle region is an artifact due to the 1–2-s warm-up period of the vaporization laser during the injection period.

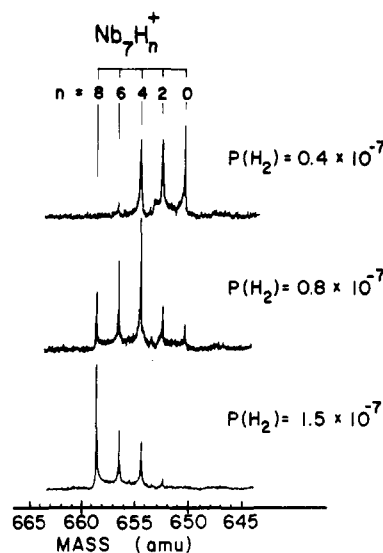


Figure 2. FT-ICR mass spectra of Nb₇⁺ clusters as they dissociatively chemisorb H₂ while being trapped in the magnetic field of the ICR cell with increasing partial pressures of hydrogen gas. Note the absence of any reaction beyond Nb₇H₈⁺. Alongside each trace is the approximate partial pressure (Torr) of H₂ in the ICR cell.

cell geometry does allow, however, an effective integration of the trapped cluster ions over many injection cycles. In the simplest mode, the front door of the ICR cell is pulsed to 0.0 V for a few microseconds as each new metal cluster ion packet arrives from the source and then is returned to the normal trapping potential, which is typically 12 V in these experiments. Figure 1 gives an example of success of this injection technique in the case of Nb₇⁺, showing the strength of the ICR signal as a function of the number of injection cycles prior to excitation and detection. As is evident in the figure, over 50 successive injection cycles can be performed before there is significant reduction in the signal rise per cycle.

Results and Discussion

Figure 2 displays the FT-ICR mass spectrum in the region of the seventh cluster of niobium when exposed in the ICR cell to increasing partial pressures of H₂. The H₂ reactant was simply bled into the entire ICR vacuum system to maintain the indicated pressure throughout the experiment. Each trace is the coherent average of five experiments, each consisting of 50 injection cycles (5 s at 10 Hz), a 1-s additional reaction time, followed by excitation and detection of the coherent ICR transient. Without the H₂ reactant, the FT-ICR mass spectrum showed only the Nb₇⁺ cluster to be present.

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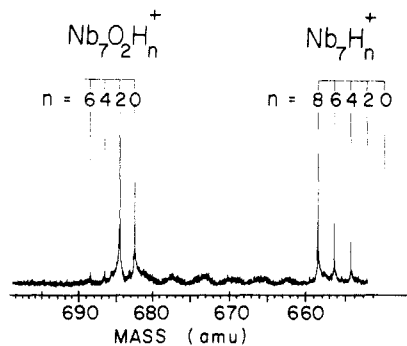


Figure 3. Broader view of the FT-ICR mass spectrum taken under the conditions used to obtain the bottom trace of Figure 2 (1.5×10^{-7} Torr of H_2). Residual O_2 contamination in the vacuum system has produced $Nb_7O_2^+$ and $Nb_7O_2H_2^+$ in the ICR cell, but there is little reaction to higher H_2 chemisorption products.

Figure 2 clearly shows the effective chemisorption of H_2 on the Nb_7^+ cluster. At higher H_2 concentrations, this chemisorption achieves successively higher coverages of the cluster but stops abruptly with the adsorption of the fourth H_2 molecule. Similar results were obtained when a constant H_2 pressure was maintained, and the extra reaction time was increased in increments to 5 s.

As in our earlier experiments with the reaction of D_2 on neutral transition-metal clusters,¹² this chemisorption is almost certainly dissociative (molecularly adsorbed H_2 is far too weakly bound to allow the product to survive under these conditions).^{12,13} Whatever the nature of the active site on the surface of Nb_7^+ , such sites apparently continue to exist on the cluster until $Nb_7H_8^+$ is reached. At this point the cluster either is coordinatively saturated or has lost the type of surface site necessary to catalyze the dissociative addition of another H_2 .

Trace oxygen contamination of the ICR apparatus is readily apparent with transition-metal clusters. Niobium clusters are extremely reactive toward O_2 , and this can be seen easily in Figure 3 where the mass axis has been extended to include the first O_2 reaction product. As was noted for the neutral niobium clusters, the chemisorption of oxygen drastically affects the activity of the cluster toward hydrogen chemisorption. Even though in this experiment we have no way of telling which reaction occurred first, the $Nb_7O_2^+$ and $Nb_7O_2H_2^+$ clusters are clearly much less reactive toward H_2 than any of the nonoxidized $Nb_7H_x^+$ clusters except $Nb_7H_8^+$.

By far the most significant result, however, is seen in Figure 4. Here the Nb_8^+ cluster has been injected into the ICR cell and

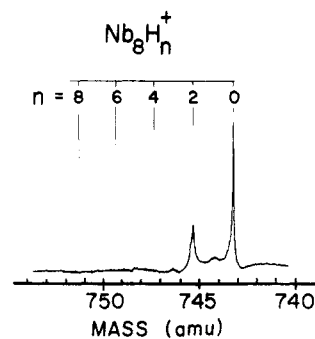


Figure 4. FT-ICR mass spectrum of Nb_8^+ clusters as they chemisorb H_2 under the same conditions as used in the bottom trace of Figure 2 (1.5×10^{-7} Torr of H_2). Note the far lower reactivity of this eight-atom cluster compared to that of Nb_7^+ . This is particularly remarkable since the same reactivity pattern has been found for the corresponding neutral clusters.

exposed to the same H_2 pressures for the same length of time as Nb_7^+ in the bottom trace of Figure 2. Although the mass axis scale is a bit different, it is clear that Nb_8^+ is far less reactive than Nb_7^+ . Under the same conditions Nb_8^+ is a bit more reactive, but still far less than shown in Figure 2 for Nb_7^+ .

This is a key result because this pattern of reactivity toward H_2 chemisorption is exactly the same as measured in earlier experiments for the *neutral* niobium clusters in this size range. Clearly, there is some vital aspect of the surface of the Nb_7 cluster that activates H_2 chemisorption. Whatever this aspect is, it is largely missing in Nb_8 and is missing somewhat in Nb_9 as well.

Now, together with the neutral results, these new high mass resolution experiments with the cluster ions suggest that what is special in this chemisorption process on niobium has more to do with the numbers 7, 8, and 9 than it does with the total electron count or the net charge.¹⁴ Even though there seems to be a correlation between the ionization potentials of the neutral clusters and their reactivities,¹⁵ it is now hard to rationalize any purely electronic theory of chemisorption with the fact that the neutral clusters and positive cluster ions are so similar.

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