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Technical Progress Report

SUPERSONIC METAL CLUSTER BEAMS

Department of Energy Contract No. DE-AS05-78ER06035

For Period 3-16-84 through 4-1-85

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DISCLAIMER

WILLIAM MARSH RICE UNIVERSITY
HOUSTON, TEXAS

7. R. E. Smalley, "Supersonic Cluster Beams: An Alternative Approach to Surface Science", to appear in Comparison of Ab Initio Quantum Chemistry with Experiment, R. J. Bartlett, et. al., eds.

8. L. S. Zheng, C. Pettiette, P. J. Brucat, S. Yang, and R. E. Smalley, "Production of Cold Metal Cluster Ion Beams" J. Chem. Phys., in preparation.

9. M. A. Alford, P. A. Williams, and R. E. Smalley "FTICR Spectroscopy of Metal Clusters Prepared in a Supersonic Beam", in preparation for a special FTICR issue of Int. J. Mass. Spec.

10. P. J. Brucat, L. -S. Zheng, C. L. Pettiette, S. Yang, "Metal Cluster Ion Photofragmentation Spectroscopy" J. Chem. Phys. , in preparation.

Metal Cluster Reactions Studies

By far the most highly visible activity of this group over the past year has been our work on chemical reactivity measurements for bare metal clusters. A copy of a short Communication on this subject is appended along with a short article featuring this work in the Jan 21 issue of Chemical Engineering News.

The key enabling technology for this work was a fast-flow pulsed reactor which fit directly on the supersonic metal cluster source developed in previous years of this DOE contract. This fast flow reactor was mentioned briefly in last year's proposal as being a part-time activity for which we were not at all assured of success. As is evident from this year's publications, the new fast flow reactor turned out to be a major success both in its performance and in the richness of the science it opened up.

As it became increasingly obvious during the year that these neutral metal cluster reaction studies were of major importance, a larger fraction of the group activities were concentrated in this area. As a result we did not place much emphasis on the small cluster spectroscopy originally planned for this year of the contract. As described in the proposal for next year, we do intend to pick up on this spectroscopy again -- particularly through the use of a new depletion spectroscopy approach in the case of the neutrals, and daughter ion appearance in the case of the bare metal cluster ions.

COLD CLUSTER ION BEAM PRODUCTION

Aside from the neutral cluster reaction studies, by far the most intense efforts related to this DOE contract have been associated with the study of metal cluster ions. The principal advantage here is, of course, that an initial mass selection of the clusters allows the properties of these clusters to be studied by sensitive techniques without worrying about interference from other cluster species originally produced in the laser-vaporization cluster source. It is critical, however, that these cluster ions be produced cold, and in high intensity.

Our original plan here was to produce the cluster ions by near-threshold direct one-photon ionization after the neutral clusters had been cooled in the supersonic expansion and skimmed to form a collisionless beam. Until a month ago, this was the procedure we actually used, and it worked rather well in the cases we tried. However, in principal we know that this direct photoionization technique is not a generally effective procedure for producing cold cluster ions. In some (perhaps even most) metal cluster species there will be a substantial difference in the geometry of the cluster ion as compared with the neutral, and in these cases the ionization cross-section is vanishingly small at the adiabatic threshold and direct (vertical) photoionization will produce a cluster ion with substantial vibrational excitation. In addition, even in the cases where the ionization threshold is sharp, the photoionization laser pulse must be kept weak enough to avoid absorption of a second photon which would

heat the cluster ions further. In practice this limits the maximum efficiency of cluster ion production to less than 10%.

Due to these restrictions of direct photoionization of the cold neutral clusters, we have examined the possibilities of producing the cluster ions directly in the supersonic nozzle -- allowing the supersonic expansion to cool the cluster ions prior to forming the cluster beam. Although this seems straightforward, this turns out to be not quite as trivial a problem as it initially appears.

First there is the problem of space charge. In order to produce a cluster ion beam of sufficient intensity after the supersonic expansion, it is necessary to produce greater than 10^6 cluster ions per cm^3 back in the nozzle. Without some counteracting negative ions, the space charge of such a dense array of positive ions would push most cluster ions off axis far before the end of the supersonic expansion, and collisions of these space-charge accelerated ions with the helium in the jet would actually heat the clusters, not cool them.

Second, there is the problem of stray electrostatic and magnetic fields in the apparatus. Even if the cold positive cluster ions beam could be produced, it would only be moving at the terminal velocity of a helium supersonic expansion : 1.9×10^5 cm/sec. For cluster ions in the 100-1000 amu range, this corresponds to an ion beam of only a few eV translational energy, and such low energy ion beams are terribly sensitive to small stray fields along the beam path. Stray electric fields of only a couple volts/cm would be sufficient to produce extensive beam deflection, and such small fields are extremely difficult to

eliminate in any practical apparatus. The production of intense cold cluster ion beams, therefore, is no easy trick.

Nonetheless, this problem has now been solved -- and solved in a general way that actually will allow us to study negative cluster ions as well!

Only a few weeks ago we found that our new developments in intense pulsed nozzle operation permit sufficient helium density in the beginning of the expansion to thermalize not only the positive ions produced by excimer exitation in the nozzle, but the associated photoelectrons as well. The result is the production of a dense, cold plasma. Since this plasma is neutral over-all, the cluster ions experience the full cooling of the supersonic helium expansion just as efficiently as a neutral cluster. There is no net charge imbalance so there is no space charge; even extremely high cluster ion densities remain stable. Finally, since the Debye screening length in such dense plasmas is so short (less than .01 cm in our case), stray electric and magnetic fields have little effect on the cold plasma beam. Even very slow cluster ion beams can then be routed through various differential pumping chambers and electrode assemblies without beam loss from stray fields.

This new technique does wonders for our positive cluster ion experiments, and the entire cluster ion apparatus has been rearranged to take advantage of this new development. More exciting, however, is the fact that this new ion-production scheme also allows us to study negative cluster ions as well. It turns out that an intense shower of slow photoelectrons is

ejected when the excimer laser strikes the aluminum end of the pulsed supersonic nozzle (and a preskimmer located several cm downstream). These slow electrons then undergo an extremely efficient attachment process to form negative metal cluster ions in the supersonic jet. This attachment process is so efficient that we presume the dominant mechanism is dissociative electron attachment accompanied by the loss of a metal atom from the cluster. At the same time, positive clusters are produced by direct photoionization, and the net effect is again to produce a neutral cold plasma which now contains both positive and negative cluster ions, all of which feel the full cooling of the supersonic expansion. A figure showing negative niobium cluster ions is attached.

We are quite excited as to the long range impact of this cold ion beam technology -- it should be quite generally applicable to a wide range of species, not just small metal clusters.

ION CYCLOTRON RESONANCE OF METAL CLUSTERS

Another major push during this past year has been in the development of our ICR experiments with metal cluster ions. Throughout the year this has been almost solely the responsibility of a few Rice physics undergraduate majors who have done a superb job. Last month this work broke through to the observation of our first strong FTICR signals from a metal cluster injected from the supersonic beam. A figure showing the FTICR spectrum of Nb_3^+ is attached showing a mass resolution of over 50,000.

The most important aspect of this result is that it is a proof of principal. It was done before our development of the cold cluster ion beam source, and at several orders of magnitude less cluster density than we expect to achieve within the next year. Nevertheless, it did show that our injection procedure into the ICR cell from the skimmed cluster beam was basically sound. We are still in the process of measuring the beam injection efficiency directly, but our initial results indicate that at least 10% of the cluster ions produced in the supersonic beam are being successfully trapped in the ICR cell and produce coherent ICR transients.

This injection procedure involves pulsing the cluster ions out of the supersonic beam at a right angle, collimating with an initial einzel lens, mass-selecting with a pulsed mass gate, focussing into the superconducting magnet with a second einzel lens, pulsed decelleration in two steps down to a few eV translational energy, and final trapping in the ICR cell. It sounds complicated -- and it is. But once set up with full

computer control it turns out to be quite a reasonable technology which is quite general, and (apparently) quite efficient. In fact, the only other group we know of that has succeeded in injecting ions from outside the superconducting magnet is the McIver group. They use an rf quadrupole guide to overcome the magnetic mirror effect, but we hear that their injection efficiency is less than one part in ten thousand. We do far better because our initial ion beam comes from a very cold and well-collimated supersonic beam. We have very little off-axis energy in the initial ion beam, and a simple einzel lens is all that is needed to direct the cluster ions smoothly down the axis of the magnet where the magnetic mirror effect is a minimum.

Although we now have our first strong FTICR signals for a range of cluster ions (we've currently been able to get out to Nb_6^+ there is still quite a bit of development to be done on this very ambitious experiment. Just seeing a mass spectrum at high resolution is only the first step. We must get another one to two orders of magnitude of trapped ion density for the large clusters, and do extensive software development before the actual ion-molecule reaction and photodissociation experiments we have in mind will really be able to pour out of the machine. But I am now confident this will all happen.

CLUSTER ION PHOTODISSOCIATION EXPERIMENTS

A final area of extensive activity over the past year was the design and construction of a tandem double time-of-flight mass-spectrometer for photodissociation studies of supersonic

ions. The bulk of this effort was funded by the NSF in preparation for our studies of photochemical and photophysical processes occurring with chemisorbed species on the surface of cluster ions. But the apparatus is quite general, and will be superb for the study of bare metal cluster ions as well. In accord with our operating understanding, any research on this new apparatus devoted to the study of bare metal clusters will be considered to be part of the DOE contract research, and we will make an attempt to keep this work as separated as reasonable from the NSF-supported research on chemisorbed adducts of metal clusters.

Initial experiments have been completed with this apparatus and a manuscript will shortly be submitted. The key feature is the use of a long drift tube to separate the various cold cluster ions by mass, all clusters other than that desired being deflected away by a computer-controlled pulsed "mass gate" consisting of a pair of electrodes isolated by grids. This turns out to be an exceedingly clean and effective means of providing mass selection at high transmission -- we achieve a mass resolution of 500 to 1 with nearly 100% transmission for a 1 cm diameter ion beam. The mass selected set of cold cluster ions is then decellerated to roughly 30 eV as it enters a high vaccuum chamber. As it enters the chamber it is irradiated by a coaxial, counter-propagating dye laser beam pulse, and allowed to drift for 10 cm before the ions are pulsed out at a right angle and directed down a second time-of-flight tube. This second mass analysis allows us to determine if the original mass-selected clusters fragmented as a result of laser irradiation, and, if so, what daughter ions were formed. The over-all experiment is

extremely elaborate, involving in its simplest form three separate lasers and 18 independently synchronized timed events. Luckily, this is the age of microcomputers in the laboratory and such experiments are realistic even with the realitively unexperienced current generation of students in the lab.

In addition to being able to bracket the dissociation thresholds of a variety of iron and niobium clusters, we have been able to establish the following general rule of thumb: for bare metal clusters, by far the dominant fragmentation mechanism is the loss of a single metal atom -- regardless of the size of the cluster. Metal clusters do not appear to decay by a fission mechanism. This turns out to be drastically different than the behavior of semiconductor clusters such as silicon and germanium, which we have found (in the ARO - supported project) to have a strong propensity to decay by fission into large chunks in the 6 to 11 atom size range. We believe the reason for this lies in the relatively smooth evolution of bonding in metal systems, as opposed to a relatively abrupt switch in bonding in the semiconductor systems from closest-packed, icosohedral-type geometries for the small clusters to the more open, tetrahedral form preferred by the bulk silicon or germanium lattice.

Extensive spectral studies of small bare metal cluster ions are now readily accessible in this new apparatus -- involving both the detailed high resolution spectroscopy of these metal clusters, and the routine measurement of binding energies as a function of cluster size.

APPENDICES

1) Copy of J. Chem. Phys. Communication on hydrogen chemisorption on transition metal clusters.

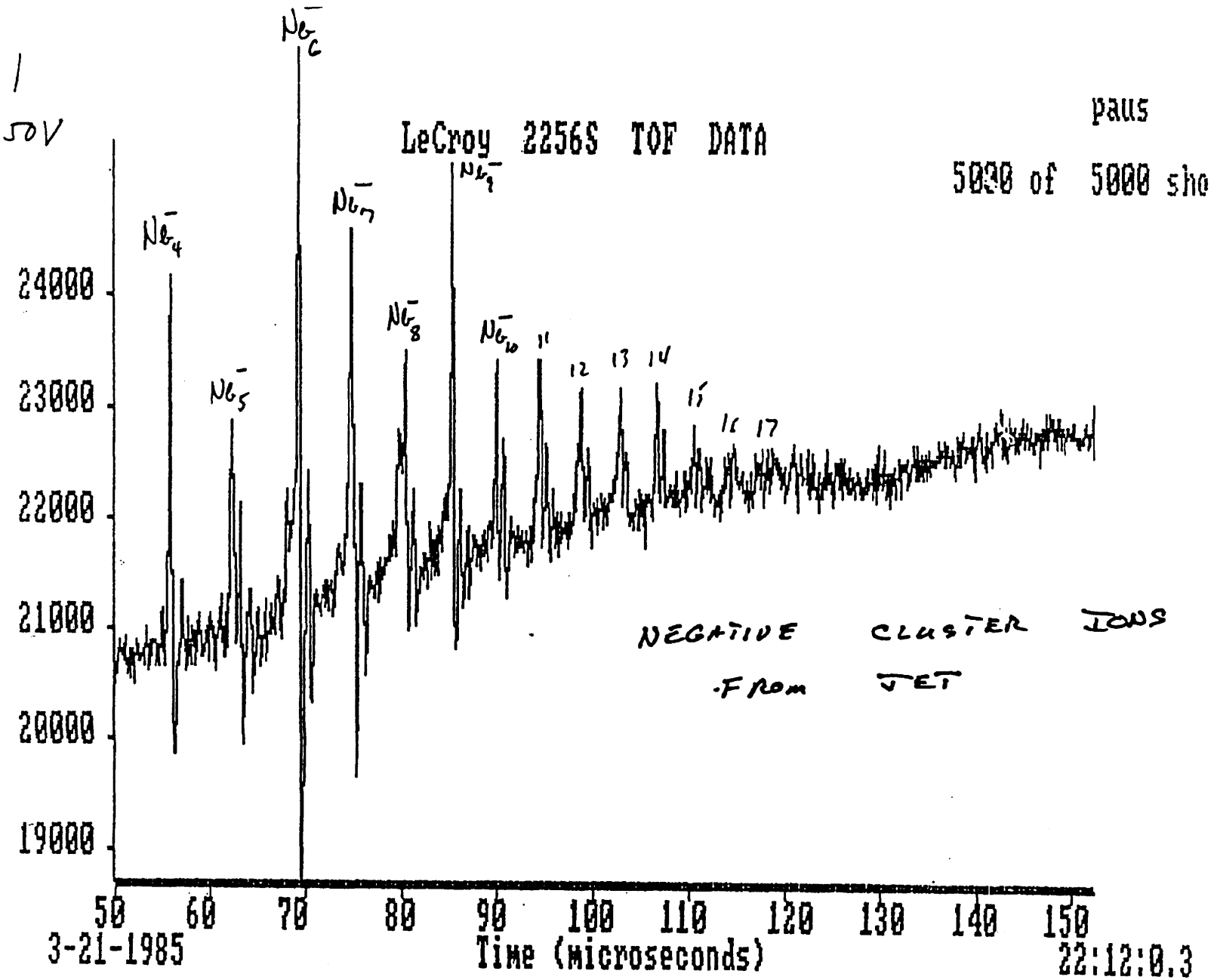
2) Copy of Chemical Engineering News article from Jan 21 issue.

3) Figure showing first observation of cold NEGATIVE metal cluster ions in a supersonic beam.

4) Figure showing first FTICR observation of a bare transition metal cluster injected into the ICR cell from an external supersonic cluster beam. The displayed spectrum has been heterodyned, this limited region of the mass spectrum shows only the Nb_3 cluster at a mass resolution greater than 50000 to 1. FTICR spectra were observed out thru the sixth cluster.

* Reprints removed. JSW

APPENDIX 3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NEGATIVE CLUSTER IONS
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80
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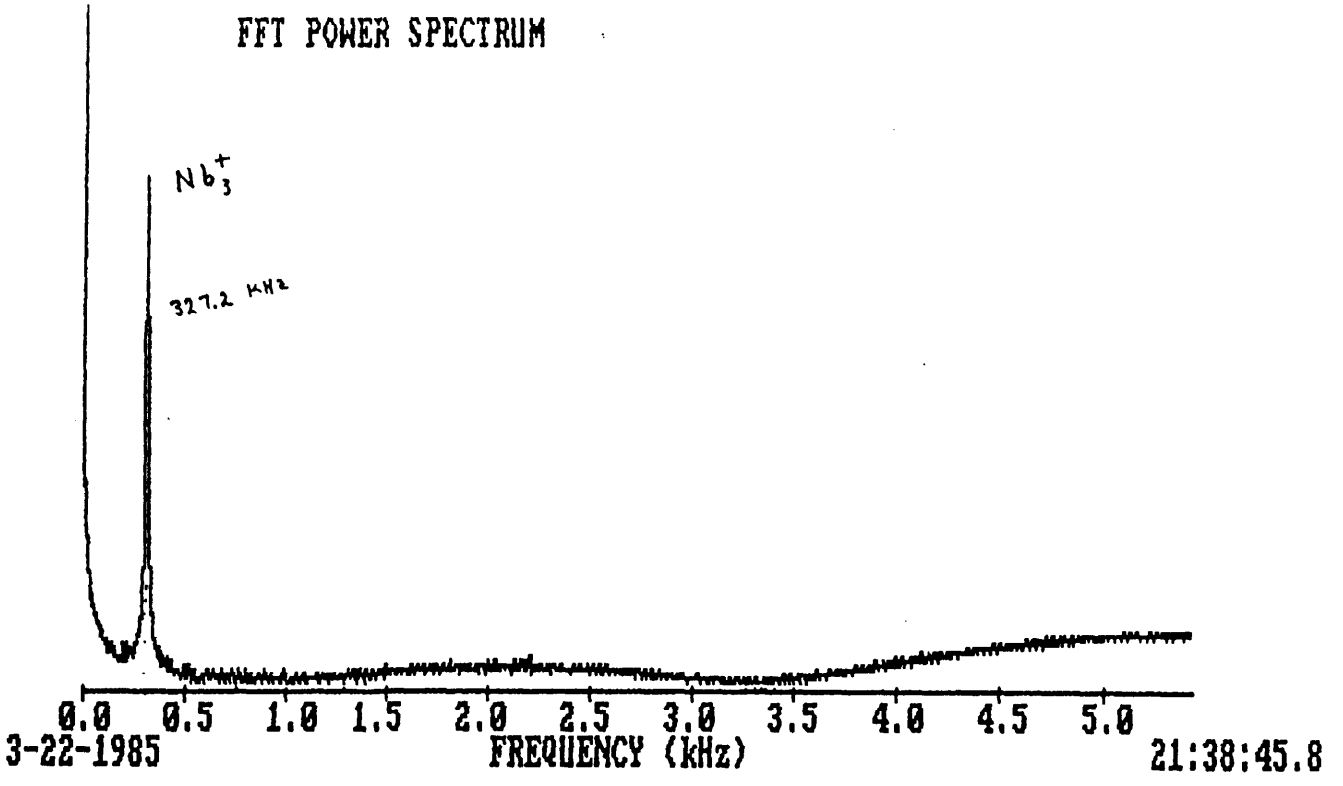

1530 shots

mix = 326.9 KHz

$y = 1.5 \times 10^{-5}$