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FT-ICR STUDIES WITH LASER-GENERATED SUPERSONIC CLUSTER BEAMS

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ABSTRACT

By using a combination of einzel lenses and deceleration grids, it is possible to inject cold molecular ions from a supersonic beam apparatus directly into the superconducting magnetic trap of a Fourier Transform Ion Cyclotron Resonance (FT-ICR) spectrometer[1,2]. The injection cycle may be repeated many times until the trap is "filled" with an adequate number of ions. Since the ion source is completely independent of the FT-ICR apparatus, and since the injection is mass-specific and nearly 100% efficient, these techniques may find wide application in the analysis and study of complicated molecules and clusters. Examples are given for the application of this new technique to the study of dissociative chemisorption on the surface of metal and semiconductor clusters, and to the study of the "soccerball" molecule, C_{60}^+, and its metal-substituted complex, $C_{60}La^+$.

I. INTRODUCTION

To many observers, one of the most impressive advances in the field of mass spectrometry over the past 15 years has been the development of Fourier transform ion cyclotron resonance (FT-ICR) spectrometry[1,2]. Here the ion of interest is trapped in a high, uniform magnetic field, and the ions are excited by a radio frequency (RF) pulse of appropriate frequency and intensity. This ion excitation is readily monitored (nondestructively!) by measuring the weak image charges moving in the external circuit of the trap as the ion packet undergoes its coherent cyclotron motion. The Fourier transform of the resultant sinusoidal time-dependent signal shows a sharp spike at the cyclotron frequency of the trapped ion. Because the cyclotron frequency of even a 1000 amu ion is on the order of 100 kHz in the current generation of superconducting magnets, many periods of the cyclotron motion can be monitored. This permits extraordinarily high mass resolutions to be obtained for the trapped ions. Typical FT-ICR spectrometers routinely run at mass resolving powers in the 50,000 to 200,000 range, and mass spectra at over 10^6 resolving power are not uncommon.

For a wide range of applications, however, there are severe restraints in taking advantage of the powers of FT-ICR techniques. The requirements of extremely high vacuum quality (better than 10^{-8} torr) and extremely high and homogeneous magnetic field (1-8 Tesla, with better than 10^{-5} homogeneity over a 5 cm cubic sample volume) in the measurement zone often turn out to be prohibitive.

In this article, a solution to this problem of interfacing difficult ion production and sampling techniques to FT-ICR technology is described. It is a solution that was designed to permit metal and semiconductor clusters to be studied in the ICR trap, but the techniques used are expected to have a much wider applicability. Basically, what is described and illustrated below is a general means of injecting ions made in any external source into the analysis zone of a modern FT-ICR apparatus.

II. EXPERIMENTAL DETAILS

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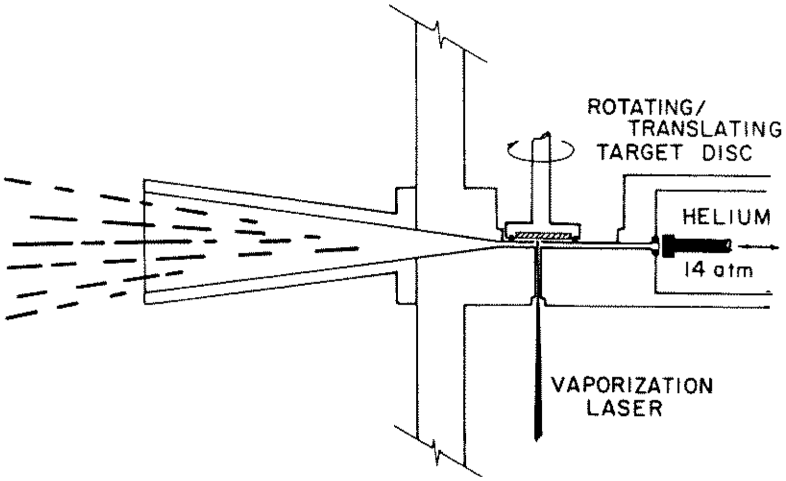

FIGURE 1.
Schematic of the laser-vaporization supersonic cluster beam source that were used in these studies.

several years ago[3], there has been increasing interest in developing powerful analytical tools to study the properties of these new cluster species. FT-ICR is one of these tools. The experimental discussion below starts first with the cluster ion source, then focuses on the means for coupling this source to the FT-ICR portion of the apparatus.

A. The Supersonic Beam Cluster Ion Source

A schematic of the most current version of this laser-vaporization cluster beam source is shown in Figure 1. Although a number a examples will be discussed below, in order to be specific the following description deals with the production of niobium cluster ion beams. The methods, however, are quite general and only few changes need be made in order to generate intense cluster beams of any element.

This laser-vaporization source uses a focused beam (1-mm spot diameter) of second harmonic light (532 nm, 25 mJ/pulse, 5 ns pulse width) from a Quanta-Ray DCR1A Nd-YAG laser to vaporize material from a disk of the desired target material (niobium in this case). The disk is rotated and translated so as to maintain a smooth surface, by using a mechanism similar to that used in previous semiconductor cluster studies in this group[3d]. Metal vapor ejected from the niobium surface enters a near-sonic pulsed helium flow (0.5 torr liter/pulse, 200-300 microsecond pulse width), such that the helium pressure above the disk is about 0.7 atm during the laser pulse. Clustering and thermalization of the laser vaporized material then occurs as the metal vapor travels down a 0.2-cm diameter, 1.5-cm long channel connected to a 16-cm long cone, 15 degree included angle. The gas pulse then expands supersonically into a chamber pumped by three Varian VHS 400 diffusion pumps, which maintain the background pressure below $5x10^{-5}$ torr prior to each nozzle pulse at 10 pulses per second. The supersonic beam is skimmed from this expansion by a 55° included angle conical skimmer (Beam Dynamics Inc.), 0.5-cm diameter entrance aperture, 18 cm long; mounted so as to intercept the gas flow 28 cm downstream of the supersonic nozzle exit.

For these FT-ICR cluster experiments, the positive ion form of the niobium clusters needed to be produced in the supersonic beam. There are quite a few ways this can be done:

(1) the neutral cluster beam can be gently photoionized by an ArF excimer laser just before these ions are extracted from the beam;

(2) the laser vaporization and nozzle flow conditions can be adjusted to retain a portion of the clusters as a mixture of positive and negative ions, and the resulting plasma is cooled along with the neutral clusters in the subsequent supersonic expansion[4];

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(3) such a plasma can be recreated in the flowing gas just prior to expansion either by a pulse of ArF excimer laser light[5]; or

(4) an electron beam[6].

Certainly the simplest of these methods is (2), since it avoids the use of a separate ionization step. This technique works particularly well for refractory elements that have strongly bound dimers, trimers and small clusters. Such elements from clusters very rapidly in the hot laser-produced vapor. Electron attachment to the neutral clusters in such a hot vapor then slows the process of charge recombination, producing intense positive and negative cluster plasma beams. Carbon[4a], and many of the semiconductors[4b] are particularly successful in forming cluster ions this way. Metals are generally not quite so readily clustered. Nonetheless, in the particular case of niobium, this simple laser-vaporization production of cluster ions works well enough that a method no more elaborate method than this was necessary for these FT-ICR experiments.

Under the flow conditions that were used, it is estimated that each positive cluster ion receives between 10^3 and 10^4 thermalizing collisions with the helium carrier during the later stages of flow through the exit cone of the supersonic nozzle and the subsequent free expansion. The internal temperature of the cluster ions in the supersonic beam is therefore expected to be low, probably near 300 K.

Extraction of the cluster ions is accomplished by a pulsed electric field generated by a voltage pulse to a pair of flat grids on either side of the skimmed supersonic beam as shown in Figure 2. Once extracted, the ions are accelerated through another flat grid to a total translational energy in the range of 660 to 710 eV. As shown in the figure, the resultant cluster ion beam is then aimed toward the FT-ICR part of the apparatus by

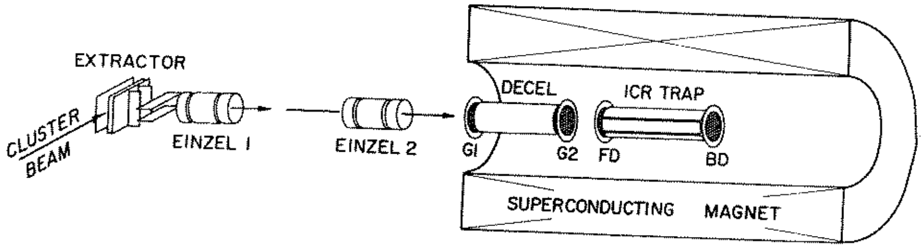
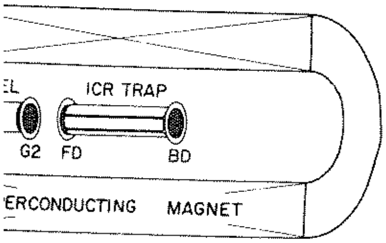


FIGURE 2.
Schematic of ion-injection optics for the supersonic beam/FT-ICR apparatus, showing the extraction stack, deflectors, and first einzel lens (EINZEL 1) that were used to extract the cluster ions from the supersonic beam and to prepare a parallel ion beam suitable for injection. After a 1.3-m flight tube, these cluster ions are directed by EINZEL 2 through the fringing field of the 6 Tesla superconducting magnet. The cluster ions are slowed in two stages (G1 and G2) by the pulsed decelerator (DECEL), then admitted into the cylindrical FT-ICR TRAP by momentarily lowering the potential of the "front door", FD.

using with a pair of horizontal and vertical deflectors, and mildly focused by an initial 3-tube einzel lens, E1, so as to produce a nearly parallel beam suitable for injection into the magnet.

B. Injection and Trapping in the FT-ICR Magnet

As we have discussed in detail in our original publication on this technique[7], the key problem to overcome in injecting the cluster ions into an FT-ICR cell is the magnetic mirror effect. In our case, the magnetic field of the FT-ICR trap is produced by a 6 Tesla superconducting magnet, (50 cm long, 15-cm ID, 30-cm OD) with a 9-cm diameter room temperature bore. As the ions enter this strong magnetic field, most begin to cross field lines in



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the strongly convergent portion of the magnetic field. The vxB component of the Lorentz force in such a convergent field has a component that pushes against the on-coming ion, causing it to slow as its axial energy is converted into cyclotron motion around the local field line. This is the origin of the magnetic mirror: for most incoming trajectories all forward motion is ultimately reversed.

However, there is a set of trajectories for which this magnetic mirror effect is minimal. It is those that are nearly parallel to the local magnetic field lines in that region of the fringing field where the ion motion is first strongly affected by the magnet. For such trajectories, the ion simply follows the local field line into the center of the magnet, with only a few percent of its translational energy being converted into cyclotron motion. Once in the strong magnetic field, the axial component of the ion's translational energy can be readily removed by a simple electrostatic field, and the ion can then be easily trapped in the ICR cell.

Figure 2. shows the arrangement of lenses and grids used to achieve this efficient trapping. The nearly parallel cluster ion beam extracted from the supersonic source was focused into the fringing field of the magnet by the second einzel lens, E2 (composed of three copper tubes, 4.5-cm ID). This critical focusing component is located 75 cm from the center of the ICR cell, which, of course, is centered in the magnetic field.

Soon after the converging ions enter the critical region of the magnetic field where they "hop on" the local field lines, they are slowed in the first of two deceleration stages by the pulsed decelerator marked "DECEL" in Figure 2. This is a 12 cm long, 4.0-cm ID copper cylinder with flat molybdenum grids on either end. It is isolated from the rest of the apparatus by two grounded grids, G1 and G2 (spaced 0.35 cm from the end grids of the cylinder). While the ion packet of the desired cluster passes through the first grid, G1, the decelerator cylinder is held at 600 volts, thereby slowing the 660-710 eV ions to 60-110 eV. As these cluster ions then pass through the decelerator cylinder, its voltage is dropped to -60 volts. Cluster ions emerging from grid G2 are thereby decelerated to 0-50 eV without any net change in the overall potential of their surroundings.

Extensive optimization of the parameters of this two-stage decelerator scheme via computer simulations[7] led to the positioning of the grids G1 and G2 at 25.5 and 12.8 cm from the magnet center, respectively.

The ICR cell that was used for these experiments[7-10] was cylindrical, 15 cm long, 4.8 cm inside diameter. The sides of the cylinders were split longitudinally into four sectors: one opposing set of two 60° sectors was used to apply RF power to excite the cyclotron motion, the second opposing set of sectors being larger (each 120° of the cylinder) so as to pick up the maximum possible image charge signal to detect the coherent ion cyclotron motion. These cylindrical sectors were fabricated from oxygen-free high conductivity (OFHC) copper, polished and silver plated with a final surface "flash" of rhodium in order to provide a clean corrosion-free surface with uniform surface potential.

In such an ICR cell, the ions are trapped along the magnetic field axis by two end plates held at a small positive potential. These are marked in Fig. 2 as "FD" and "BD", which we shall refer to hereafter as the "front door" and the "back door" of the ICR cell. These end plates were made of 5.0-cm OD copper disks with central 2.5-cm ID access holes covered with molybdenum mesh (75 /inch). They were polished, Ag/Rh plated, and mounted together with the cylindrical sectors on machineable ceramic (Macor) forms. The entire ICR cell with its associated electrical connections was mounted on a copper tray, which could be baked to 600-700 K by in-

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Between injection pulses, the front and rear doors of the ICR cell are kept at +12 V. When injecting a new ion packet, the front door potential is lowered to 0 V for a period just short enough to allow most of the ion packet to enter the cell. For a typical cluster ion, Nb_{10}^+ for example, this open-door time is 30 microseconds. In this short interval, those ions with translational energy between 1 and 12 eV are efficiently trapped in the cell, ie. roughly 20% of the injected 0-50 eV cluster beam. This lack of perfect trapping efficiency comes entirely from the energy spread in the original cluster ion beam. One can envisage pulsed extraction techniques that would greatly reduce this energy spread 11.

Since the arrival time of the cluster ions at the front door of the FT-ICR cell depends on the mass of the cluster, only a narrow range of cluster ion masses is trapped in any particular experiment. With the proceedure described above, the effective mass selectivity on injection is roughly 20 to 1. In those cases where this selectivity is insufficient for the experiment desired, the unwanted cluster ions can be selectively ejected from the ICR cell by resonant RF excitation of the cyclotron motion of the unwanted clusters. After extended excitation these clusters are effectively swept from the cell since they follow such large cyclotron orbits that eventually result in them striking the side walls of the cell.

The ICR cell and pulsed decelerator devices are mounted on independent copper trays, which can be smoothly inserted into the 7.4-cm ID, 100 cm long magnet bore tube. This tube is connected on both ends to 30-cm cubic UHV chambers, each evacuated by a LN2 cryropumped Varian VHS-6 diffusion pump. After bakeout with internal 500 watt infrared lamps (Phillips) Typical background pressures in these end chambers are in the 1-3 x 10^{-9} torr range.

C. Multiple Injections and Thermalization with Neon

In order to build up a sufficient number of ions in the ICR trap of the desired cluster, it is necessary to repeat this injection process 10 to 1000 times, depending on the size of the cluster and the degree of optimization of the supersonic beam source. The trick, of course, is to be able to pulse open the "front door" to let the new ions in without the previously trapped ions leaking out.

With the long ICR trap design used here, this injection-without-leakage problem is not quite as severe as one might initially expect. Even if there were no net loss of kinetic energy in the ion motion, after the thousands of bounces each ion makes back and forth in the cell in the 0.1 second interval between injections, only one-third of the energy will remain in the axial direction, the other two-thirds is partitioned into the two cyclotron degrees of freedom. Furthermore, the ions spend most of their time near the turning points of their near-harmonic motion back and forth in the cell, during which time their axial velocity is quite low. A short injection period with the front door down therefore gives little chance for the trapped ions to escape.

The most effective way of ensuring that virtually no ions escape, however, is to remove most of their translational energy by collisions with an inert gas. Since we are usually interested in studying the cluster chemistry at moderate temperatures, this thermalizing gas exposure is necessary in any event. In the experiments discussed below, neon gas was pulsed into the ICR cell for 10-30 milliseconds during and immediately following each injection pulse (a Veeco PV-10 pulsed valve was used, the neon being directed into the bore of the magnet toward the ICR cell by a 30

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cm long, 4-mm ID stainless steel tube). We estimate the average neon density in the ICR cell between injections to have been 5x10^{5-} torr. Assuming a (Langevin) collision rate of 5x10^{-10}cm^{3}-sec^{-1}, the average ion in the cell is expected to have received roughly 100 collisions with this neon gas over the 0.1 s interval between injections.

With such thermalization gas pulses during the injection process, it is found that the ICR signal for typical cluster ions increases linearly with the number of injection pulses up to over 1000 cycles -- or until the total ion inventory in the cell becomes so large as to broaden the ICR transients unacceptably. In other words, the multiple injection cycle processes works well until the cell is too "full".

For the typical experiment discussed below, 100 injection cycles were used to fill the cell. After the 10 seconds necessary for this injection process, a subsequent thermalization period of 1-5 s was spent while the neon pulses were maintained. The ICR cell was cooled with liquid nitrogen throughout this time; the measured cell temperature being roughly 100 K. Both through collisions with the neon and by infrared radiation to the walls of the cell, it is expected that the niobium cluster temperatures prior to reaction were low: probably below 300 K, though as yet, we have no direct measure to verify this prediction.

D. Reactant Gas Addition

Frequently in cluster FT-ICR studies, it is desired to study the reactivity of the trapped cluster with a particular reactant gas. When desired, it is added directly to the final 30 cm cubic vacuum chamber, so that its pressure could be monitored without concerns about possible directional effects to the ICR cell. After the cluster ions are trapped and thermalized, the reactant valve (another Veeco PV-10) is opened and held open for the entire reaction time (1-10 s). This ability to add the reactant after the injection/thermalization cycle eliminates potentially convoluted kinetics from energetic ion-molecule reactions.

All pressures (reactant and thermalizing) quoted below were measured by a nude ionization gauge mounted in the 30 cm cubic chamber adjacent to the ICR. In all cases, this pressure was corrected for the ion gauge's sensitivity to the gas, and for the pressure differential between the two chambers, but errors in this measurement may yet be present. The fastest reactions examined thus far with this apparatus (for $Ta_{13}^+ + H_2$)[9] appear with this pressure calibration to proceed at very close to the Langevin collision rate. It is expected that the absolute reaction rates reported by this method will be accurate within a factor of three.

E. Experiment Control and FT-ICR Detection

During typical experiments the ICR cell is allowed an extra 5 s to pump-out between the closing of the reactant valve and the start of the excitation/detection cycle. This dramatically improves transient length by reducing the background pressure and therefore the number of collisions during the detection cycle. This also reduces the possibility of energetic ion/molecule reactions confounding the results. In addition, as mentioned above, the ICR cell is typically cooled to roughly 100 K. This provides cryopumping of reactive background gases, thereby increasing the period for which particularly reactive cluster ions can be trapped and also provides a lower ultimate pressure (typically 2×10^{-9} torr).

Also during this 5 s pump-out period, the trapping potential on the end plates of the ICR cell was smoothly ramped down to the range of 0.5-1.0 V. As a result of the thermalization period, this smaller voltage was sufficient to hold the cluster ions in the cell. The lower trapping potential reduced the importance of magnetron motion of the excited cluster ions in the ICR trap, and markedly increased the effective resolution and sensitivity of the FT-ICR detection.

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The coherent excitation and detection electronics used for the ICR experiment were described previously[1,7]. Briefly, the ions are excited into large orbits by applying an RF field (typically 0.5 V p-p, swept over the frequency region of interest by a computer-controlled Rockland Wavetek Model 5100 digital frequency synthesizer) to the excitation plates of the ICR cell for several milliseconds. The image current induced by the coherent cyclotron motion of the cluster ions between the detection plates is amplified, heterodyned, filtered, and digitized at 5 MHz with a 12-bit transient digitizer. The resultant 64-K word digitized transient ICR signal is then transferred to a microcomputer for calculation of the fast Fourier transform and subsequent data processing. Although the apparatus is designed to permit the digitized transients of many repeated ICR experiments to be added together coherently, the single-shot transients for the experiments reported below were quite adequate, and no averaging was done.

The overall experiment is controlled by two computers. The first is a CAMAC-interfaced IBM-AT running as the master. It handles all aspects of the laser-vaporization supersonic cluster beam source, as well as the various control pulses that extract the cluster ions from the supersonic beam, turns on and off the pulsed decelerator, opens and shuts the front door of the ICR cell, triggers the thermalizing and reaction gas pulses, starts an ICR excitation/detection cycle, and dumps the cell's ion contents in preparation for the next experiment. With small modifications, this is the same computer control system (and software) that is used on the other supersonic cluster beam apparatuses in the group, and it takes advantage of all the extensive diagnostic facilities that were developed for these other machines. The second computer (a CAMAC-interfaced DEC MicrovaxII with a CSPI miniMAP array processor) handles all aspects of performing the ICR excitation/detection cycle once this cycle has been triggered by the IBM-AT. Information transfer between the two computers is achieved through a pair of fast serial data buffers (BiRa 032) located in the respective CAMAC crates.

III. EXEMPLARY RESULTS

Since the intention of this paper is simply to present a demonstration of the supersonic beam/FT-ICR technique, only a few examples will be presented of its application.

The first example is the study of dissociative chemisorption of molecules such as H_2 on the surface of transition metal cluster positive ions prepared in a supersonic beam. Figure 3 shows results obtained in one such study. Here the 7th cluster of niobium was extracted from the supersonic cluster beam, and injected into the FT-ICR cell. A total of 100 injection cycles were used over a period of 10 seconds in order to fill the cell. The H_2 reaction gas nozzle was then opened so as to maintain a pressure of 5 x 10^{7-} torr for 2 seconds. After a 5 second pump out time, the ICR transient was excited, the time-dependent cyclotron image current was recorded, heterodyned, and Fourier transformed to produce the FT-ICR mass spectrum shown in Fig. 3. Note that much of the Nb_7^+ has reacted under these conditions to chemisorb one or more H_2 molecules.

Experiments of this sort with transition metal clusters have revealed that drastic variation in reactivity occur as the size of the metal cluster increases[8,10]. Some clusters (such as Nb_{10}^+ for instance) are found to be completely inert, while others (like Nb_{13}^+) are found to react with nearly 100% efficiency even on the first collision. In some cases (such a Nb_{19}^+) these experiments have revealed that two distinct isomeric forms of the cluster is present in the ICR cell: one which reacts readily, and one which doesn't[10]. Systematic analysis of such transition metal cluster surface chemistry may lead to a clear understanding of the nature

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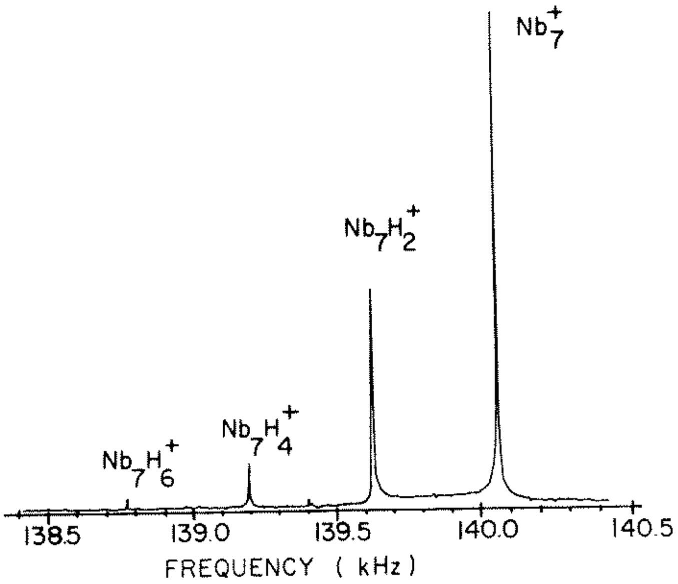

FIGURE 3.

An FT-ICR study of dissociative chemisorption of H_2 on Nb_7^+ prepared in a laser-vaporization supersonic cluster beam source, and injected into the ICR cell via the ion optics shown in Fig. 2.

of the surface site leading to dissociative chemisorption on metal surfaces.

Figure 4 demonstrates the application of this new technique to semiconductor clusters. Here the FT-ICR mass spectrum of a particular cluster of silicon, Si_{60}^+, is shown with its extensive isotopic fine structure arising from the ^{29}Si isotope at 1% terrestrial abundance. By using the laser-vaporization supersonic beam cluster source, it is now routine to inject silicon clusters made up of over 100 atoms into the ICR apparatus for detailed study. An initial survey of the reactivity of these small reconstructed pieces of silicon has shown that some reactants

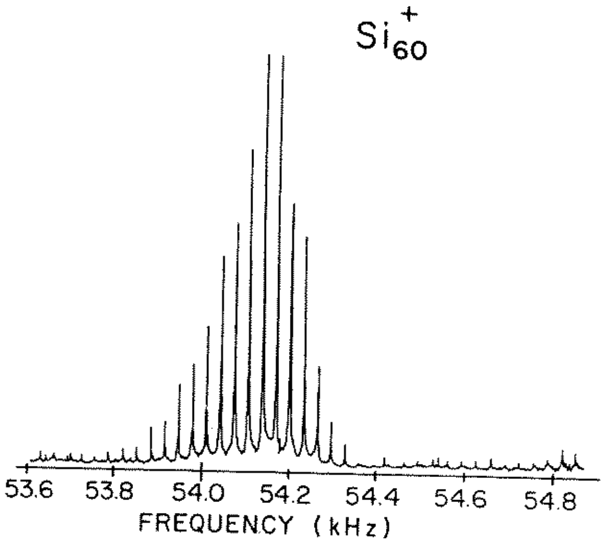

FIGURE 4.
An FT-ICR mass spectrum of Si_{60}^+ injected from a supersonic cluster beam, showing resolution of the various isotopic forms.

(like NH_3 and CH_3OH) display an extreme sensitivity toward the exact cluster size. Again, as in the transition metals, these highly-structured reactivity patterns are expected to provide vital clues as to the nature of the chemical sites responsible for chemisorption.

Although Si_{60}^+ turns out to be nothing particularly special, Figure 5 shows that C_{60}^+ is a totally different story[12]. Here the FT-ICR spectrum of carbon clusters injected from the supersonic beam reveals that only the even-numbered clusters are present, and one of these, C_{60}^+, is by far the most abundant. Results obtained a few years ago similar to these, led to the suggestion that C_{60} (in all its charge states) may be so stable because it alone can close to form a perfectly symmetric spherical shell: the truncated icosahedron, composed of 12 pentagons and 20 hexagons[13]. This

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clusters are present, and
undant. Results obtained
the suggestion that C_{60}
able because it alone can
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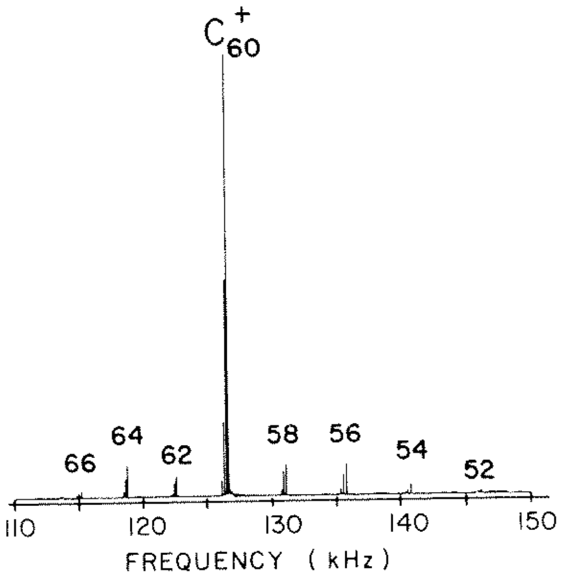


FIGURE 5.

The FT-ICR mass spectrum of C_{60}^+ and neighboring carbon cluster ions produced by laser-vaporization of a graphite disc and expanded in a supersonic beam. Note the pre-eminence of the 60th cluster. It is thought to have the structure of a soccer ball.

structure is most commonly known encountered in the form of a soccerball.

Since this soccerball structure is hollow, one might expect it may be possible to trap an atom inside. Indeed, evidence for the formation of metal-containing carbon cages was soon published[14]. Figure 6 shows the result of a recent FT-ICR experiment designed to test this hypothesis. Here, on the top panel one can see clearly that both bare carbon clusters and clusters of the formula C_nLa^+ are present in the ICR cell. These were made by laser-vaporization of a graphite disc impregnated with $LaCl_3$ in the supersonic cluster beam apparatus.

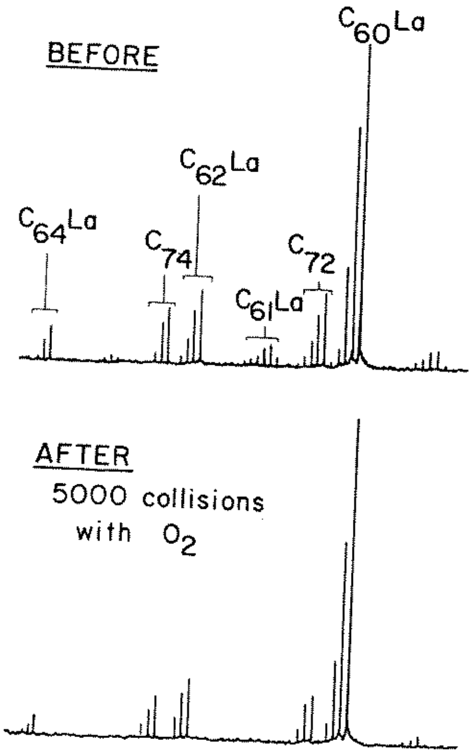
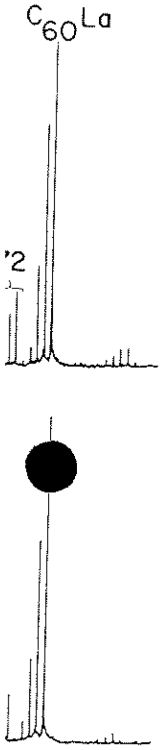


FIGURE 6.
An FT-ICR study of the reactivity of positive carbon cluster ions and their La-substituted forms with oxygen. The unreactivity of the even-numbered metal-containing clusters is evidence that the La atom resides inside the closed spheroidal carbon cages.

The bottom trace of Figure 6 shows the resultant FT-ICR spectrum after the clusters were exposed to about 5000 collisions (on average) with O_2. Note that the odd-numbered carbon-lanthanum cluster $C_{61}La^+$ has reacted away completely under these conditions, but neither the bare C_n^+, nor the even-numbered C_nLa^+ clusters have shown any sign of reacting. This is further evidence that (as originally suggested[14]) the lanthanum atom in these even clusters is, in fact, surrounded by a closed carbon shell.



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IV. CONCLUSIONS AND OUTLOOK

This marriage of supersonic ion beams with the technology of FT-ICR may seem forbiddingly difficult at first glance. But our experience with it has been uniformly pleasant. It is one of those cases where the natural physics of the apparatus seems to work in one's favor. Once set up, the ion injection electronics is perfectly stable and reproducible over many days. Fundamentally its is no more complex than many modern analytical instruments.

Because of the concentration in this research group with refractory clusters, these have been the only examples of the technique. It should be clear, though, that a huge variety of ionic species can be prepared in such a supersonic beam and then submitted to the FT-ICR analysis. One of the more intriguing possibilities would be to laser-vaporize biomolecules off a rotating disc source similar to that used here to make laser-vaporized transition metal cluster beams. There are many possibilities!

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