Cluster experiments in radio frequency Paul traps: Collisional relaxation and dissociation

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This paper presents techniques to store, manipulate, and detect cluster ions in an rf Paul trap as an approach to study the physics and chemical physics of clusters. The trap has been designed to be the primary experimental environment in the sense that experimental manipulation and ion detection are performed in situ within the trap. Specific design considerations for the trap and rf electronics relevant to metal cluster experiments are discussed. We present the application of these techniques to measurements of trapped C$_{60}^+$ in order to estimate their limitations for studying metal cluster ions. This paper demonstrates the capability to nondestructively detect small variations in the number of trapped C$_{60}^+$ ions with an ion noise level of $\approx$100 ions limited by thermal current fluctuations. Trapped ion lifetimes of $\tau_{\text{rel}}>30$ min are measured following the relaxation of C$_{60}^+$ translational energy to $\approx$300 K. Measurements of the collisional dissociation of trapped C$_{60}^+$ ions at rates $<100$ s$^{-1}$ by He at $\approx$10$^{-6}$ Torr have been performed and the products detected in situ by the mass distribution of the C$_{60}^+$ products. Several possibilities for metal cluster experiments in rf Paul traps are discussed.

I. INTRODUCTION

Most of our current understanding of cluster electronic properties has been derived from experiments relying on molecular beam techniques. Beam time-of-flight constraints limit the measurement time scale and preclude the possibility for many experiments of fundamental interest, such as associative collisions of neutral atoms with cluster ions which may have small cross sections and therefore proceed at slow rates relative to beam transit times. The ability to store cluster ions over extended periods of time offers two distinct advantages: (a) the opportunity for collisional relaxation of the clusters by a neutral background gas to establish a well-defined translational and internal energy distribution; and (b) the capability to accumulate and detect small numbers of cluster ions arising from slow rate processes.

It is well established that collisional relaxation of trapped cluster ions by a background pressure of He can significantly reduce the translational energy heating experienced by ions in rf traps. The possibility of removing excessive vibrational energy resulting from the cluster formation and ionization processes is of even greater importance for the study of metal clusters. Control of the internal energy of a trapped metal cluster ion would allow the spectroscopy of cluster electronic states and cluster reactivity to be studied as a function of vibrational excitation. Recent metal cluster research indicates a growing interest in the temperature dependence of chemical reactivity, the optical response, and structural transitions.

The capability to detect small numbers of clusters ($\approx$100) allows experiments to be performed on $\sim$10$^7$–10$^8$ trapped cluster ions which reduces the flux requirements of the cluster source. Measuring the accumulated products of slow rate collisional processes, such as the growth of cluster ions by single atom accretion, becomes a possibility with these experimental techniques.

This paper presents techniques to store, manipulate, and detect cluster ions in an rf trap as an approach to study the physics and chemical physics of clusters. Cluster ions produced in a supersonic beam source were first injected into an ion cyclotron resonance cell to study metal cluster reactions in 1986. The advantages of extending experiments performed on cluster beams to cluster ions stored in Penning traps were also discussed about the same time. Multipole ion traps have also been used in cluster ion beamlines to temporarily store ions within a high pressure ($10^{-3}$–$10^{-2}$ Torr) neutral gas for times $\approx$30 ms to reduce the cluster internal energy. More recently, rf traps have been used to store cluster ions$^{[1]}$ for time durations ($\approx$1 s) adequate to study dissociation patterns and develop techniques for heavy ion mass spectrometry. Our emphasis has been to develop techniques to study trapped cluster ions in experiments which depend on the unique advantage offered by longer storage times $\approx$1 min in a dilute rare gas background. An important issue is whether the low neutral background pressure ($10^{-6}$–$10^{-4}$ Torr) required to achieve these longer ion lifetimes is consistent with relaxing the ion translational and vibrational energies on a time scale reasonable for cluster experiments.

The trap has been specifically designed to be the primary experimental environment in the sense that measurements and experimental manipulation on metal clusters will be performed in situ within the trap. This is similar in approach to the atomic and molecular research which has followed the pioneering work of Dehmelt. Furthermore, active development of the rf trap as an analytical instrument by Cooks$^{[15]}$ has resulted in studies of ion–molecule reactions and collision-induced dissociation which are particularly relevant to the study of metal cluster chemistry. We have incorporated and extended trap technology derived from both these approaches to achieve the experimental capabilities demonstrated in this paper for trapped C$_{60}^+$ ions which include the

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nondestructive detection of the number of trapped \( C_{60} \) ions, with a detection sensitivity limited by thermal noise to \( \approx 100 \) ions; the measurement of trapped ion lifetimes \( \tau_{\text{ion}} > 30 \text{ min} \); relaxation of the \( C_{60} \) translational energy to \( \approx 300 \text{ K} \); and the collisional dissociation of trapped \( C_{60} \) ions at rates \( \approx 100 \text{ s}^{-1} \) by helium at \( \approx 10^{-6} \text{ Torr} \) and measurement of the mass distribution of the \( C_2 \) products.

We have chosen an effusive \( C_{60} \) source for these experiments for several reasons. First of all, it allows us to decouple trap technology issues, such as detection sensitivity and collisional processes, from issues related to a metal cluster source and injection of a supersonic beam into the trap. Although \( C_{60} \) was originally identified\(^1\) as a very unique cluster, it is now regarded as a molecule as a result of its synthesis\(^2\) in the form of a condensed powder of \( C_{60} \) units. Nevertheless, \( C_{60} \) retains certain physical properties which are an advantage to the experiments presented here and for estimating limitations of applying these techniques to metal cluster experiments. The mass of \( C_{60} \) is in the range of many smaller metal clusters of interest. Its spherical shape is comparable to the compact morphology of metal clusters and avoids the possibility of steric effects playing an important role in collisional processes. The activation energy for dissociation of \( C_{60} \) is larger than most metal clusters and, as a result, \( C_{60} \) dissociation provides an opportunity to observe the sensitivity of these techniques to detect slow rate processes.

This paper is intended primarily for those concentrating on experimental studies of cluster properties, however we do not attempt to provide a complete discussion of the operation of rf Paul traps. Many aspects of current trap technology applied in this work have been discussed in the references in great detail, in particular Refs. 18 and 19, but here we will reconsider these methods from the perspective of controlling translational and vibrational degrees of freedom of trapped clusters. This is the primary emphasis of this paper and the focus of our current research effort.

The paper is organized as follows: Sec. II discusses the experimental apparatus and trap design issues; Sec. III describes the measurement of ion line shapes and ion number; Sec. IV presents in situ detection measurements to identify conditions appropriate for long ion lifetimes, and experiments which study the translational relaxation and collisional dissociation of trapped \( C_{60} \) ions; and Sec. V summarizes the capabilities demonstrated by these trap techniques and considers areas of interest for trapped metal cluster experiments.

II. EXPERIMENTAL APPARATUS

A. Cluster ion storage

This section reviews those elements of rf trap operation essential for design considerations of cluster experiments. The reader is referred to a recent review of ion traps\(^3\) for additional details and references. The radio frequency trap configuration is shown in Fig. 1 in which the ring and endcap electrodes are conjugate hyperboloids of revolution about the \( z \) axis. This configuration is characterized by the endcap potential \( V(r, z; t) = V_{dc} + V_{rf} \cos \Omega t \), where

\[
\Phi(r, z; t) = \frac{V_{dc} + V_{rf} \cos \Omega t}{r_0^2 + 2z_0^2}(r^2 - 2z^2),
\]

where \( r_0^2 = 2z_0^2 \) for the trap used in these experiments. The resulting equations of motion for ion trajectories are Mathieu equations\(^4\) given by

\[
\frac{d^2 x_i}{d\tau^2} + (a_i - 2q_i \cos 2\tau)x_i = 0,
\]

where \( x_i = z, r \) and \( \tau = \Omega t/2 \). The single particle dynamics described by Eq. (2) ignores the presence of ion-ion interactions and ion-neutral collisions. Effects arising from these interactions will be considered in Sec. IV A. In addition, the potential in Eq. (2) neglects higher order field components introduced by deviations from cylindrical symmetry expected for an experimental trap. The impact of these nonlinearities will be discussed in Sec. III. The trap parameters \( a_i, q_i \) characterizing the ion trajectory are given by

\[
a_z = -2a_r = -\frac{16}{M} \left( \frac{V_{dc}}{r_0^2 + 2z_0^2} \right) \frac{1}{\Omega^2},
\]

\[
q_z = -2q_r = \frac{8}{M} \left( \frac{V_{rf}}{r_0^2 + 2z_0^2} \right) \frac{1}{\Omega^2},
\]

where the cluster ion has mass \( M \) and charge \( +e \). The ion motion is stable within the region shown in Fig. 2 determined by the parameters \( q_z \) and \( a_z \). In an ideal trap, the ion motion is a superposition of "secular" oscillations in both the axial \( z \) direction and the radial \( r \) direction having frequencies \( \omega_z \) and \( \omega_r \), respectively, and of a "micromotion"\(^5\) at the rf frequency, \( \Omega \). In particular, for \( q_z, a_z \ll 1 \), the ion...
The trap and associated electronics were designed considering planned experimental measurements of radiative and collisional interactions for trapped metal clusters. For example, the mass range of interest was given more consideration than the mass resolution. Since a metal cluster of $N$ atoms dissociates predominately by loss of a single unit, a resolution of $AN/N = \pm 1\%$ is adequate to cover the cluster range $N \leq 100$ of interest in an experiment which relies on unimolecular dissociation to monitor the radiative absorption of small clusters. It is clear that increased resolution will be necessary for experiments involving association processes of light atoms on metal clusters such as hydrogen–metal reactions; and for studying isotopic distributions or very high mass clusters. As discussed in Ref. 12, the resolution limit for rf traps has been extended to $M/AM > 10^6$, an accomplishment which suggests that rf trap technology will probably not be a limiting factor for cluster experiments requiring high resolution measurements. The mechanical design and overall design of trap electronics was constrained by the requirements for low noise to achieve the sensitive in situ detection of trapped ions. A particular experiment will require a unique sequence of ion manipulations which include loading the trap with ions, selecting a specific mass for study, and ion detection to establish initial ion number and final products; each being performed at a specific trap operating point determined by the parameters $q_z$, $a_z$. In addition there will be intermediate manipulations depending on the requirements of a particular experiment.

In the following discussion, we will refer to the stability diagram in Fig. 2 to review the design considerations introduced by experiments requiring

(a) heavy ion masses ($500 < M < 7500$ amu) trapped for long times ($t_{\text{ion}} > 1$ min),

(b) a translationally cold ion cloud ($T_i \approx 300$ K),

(c) in situ detection of small changes ($AN = 10^2$ ions) in the ion number.

Throughout the following discussion of trap parameters and ion manipulations, issues related to ion–ion interactions will arise. This coupling between ions is not significant for low ion number and densities ($N = 10^6$, $n = 10^6$ cm$^{-3}$) experienced for high temperature ion clouds ($\sim 5000$ K) of light ions ($M \approx 100$ amu). However for studies of metal cluster ions, masses will be in the range of 1000 amu and transla-
tional temperatures $\leq 300$ K. In this case, ion numbers $\sim 10^4$ can result in ion densities $\sim 10^6$ cm$^{-3}$ for which the effects of ion–ion interactions are significant and must be considered. In practice, these effects are minimized by loading the trap with an ion number in the range of $\sim 10^3 - 10^4$.

1. Trap loading

The rf trap can be loaded with ions either by first injecting a neutral beam which is then ionized within the trap, or by injecting ions directly. In the experiments on $C_{60}$, ions discussed in this paper, neutrals emitted by an effusive source were injected through an aperture in the ring electrode and then ionized by a crossed electron beam entering an endcap aperture. Ion injection techniques$^{21}$ have been developed which rely on collisions with a neutral background gas ($\sim 10^{-3}$ Torr) to enable ions to acquire stable trajectories by extracting excess kinetic energy. This technique has achieved trapping of ions up to $\sim 7 \times 10^6$ amu$^{13c}$ which are injected into the trap with kinetic energy less than the well depth. One of the important advantages of external ionization is the flexibility to choose an ionization method best suited for the specific ion to be studied. Radio frequency traps have been loaded with cesium iodide cluster ions$^{11}$ as well as $C_{60}$ ions$^{12}$ after external ionization by secondary-ion mass spectroscopy (SIMS) techniques.

One of the more important metal cluster sources which has been developed forms clusters by the laser vaporization$^{23}$ of atoms from a metal substrate followed by rapid condensation in high pressure He. The metal clusters leave the source as a collimated beam after expansion through a supersonic nozzle. This source is an excellent candidate to couple clusters into rf Paul traps since a large class of materials can be formed as clusters, and the intense cluster beam has a diameter $\sim 1$ mm comparable to a trap aperture. Since a supersonic beam source can yield either predominantly cluster ions or neutrals depending on source parameters, it is useful to consider both neutral and ion loading options. Smalley first demonstrated$^{8}$ that a supersonic beam of niobium cluster ions could be injected and stably trapped in an ion cyclotron resonance cell using electrostatic fields to reduce the ion kinetic energy. The efficiency of injecting ions from a supersonic beam source into Paul traps in the collision regime will first demonstrated$^{2}$ that a supersonic beam of niobium cluster ions could be injected and stably trapped in an ion cyclotron resonance cell using electrostatic fields to reduce the ion kinetic energy. The efficiency of injecting ions from a supersonic beam source into Paul traps in the collision regime will be examined experimentally. However, it is interesting to consider the issues involved in loading a trap with neutral clusters formed by a supersonic expansion$^{24,25}$ for which $v_{\text{neut}} = 1.2 \times 10^5$ cm/s (Ref. 24). If neutrals are injected along the axial direction through an aperture in the endcap electrode, the right-hand side of Eq. (7) is increased by $\sqrt{2}$ since $eD_{\perp}$ is $2eD_{\perp}$. Of course loading the trap in the presence of a background neutral gas will relax this constraint. The operating point at $q_z = 0.55$, $\alpha_z = 0.03$ has been shown$^{26}$ to be the optimum stable point resulting from a tradeoff of well depth and trajectory amplitude. Loading the trap with ions formed at this stable point provides a well depth energy of $eD_{\perp} = 30.1$ eV for an ion mass of $720$ amu and $V_{\text{rf}} = 735$ V. The trapped ion cloud can be maintained at this operating point during the time required to relax the translational and vibrational energy of the ions through ion-neutral collisions.

The requirement for efficient ion loading given by Eq. (7) determines an ion mass range which can be readily studied with a given trap geometry and electronics capability. This is of particular importance for metal cluster experiments in which the main interest is the variation of physical and chemical properties with cluster size. In a supersonic cluster beam we can assume we have a set of cluster masses which all have the same velocity. For $\alpha_z = 0$, we can rearrange Eq. (7) to obtain

$$q_z > \frac{4v_{\text{neut}}}{z_0 \Omega} = 0.48 \frac{z_0 \Omega}{z_0 \Omega}.$$  

Finally, an upper limit of the mass range can be obtained by substituting Eq. (3b) for $q_z$

$$M_{\text{load}} < \frac{eV_{\text{rf}}}{2v_{\text{neut}}(z_0 \Omega)} = 4.02 \frac{V_{\text{rf}}}{z_0 \Omega},$$

where $V_{\text{rf}} = 0$, $v_{\text{neut}} = 1.2 \times 10^5$ cm/s, and the units are $V_{\text{rf}}$ (V), $z_0 \Omega/2 \pi$ (cm MHz) and $M$ (amu). This upper limit can be increased in the presence of a background gas depending on the collisional relaxation rate of the kinetic energy.

Figure 3 shows the mass range accessed by varying the expansion.
product of rf drive frequency and trap dimension \((z_0 \Omega)\) for several values of \(V_{rf}\) amplitude. The mass range determined by Eq. (9) is shown by the solid curves and the restriction on \(q_z\) from Eq. (8) is shown by the dashed curve. The example drawn in Fig. 3 indicates that with the maximum voltage in our current design of \(V_{rf}=2\) kV and \((z_0 \Omega/2\pi)=0.15\) cm MHz, the largest mass which could be efficiently trapped is \(-8300\) amu as indicated by the arrows in the lower hand corner. The vertical line associated with \((z_0 \Omega/2\pi)=0.15\) cm MHz intersects the dashed curve at \(q_z=0.51\) as shown by the arrow on the right. This value of \(q_z\) ensures a well depth adequate to trap a cluster with kinetic energy \(1/2 M_{load}V_{load}^2=7.47 \times 10^{-3} M_{load} e\) V/amu. Since the number of ions trapped will become progressively less for \(q_z>0.55\), Fig. 3 indicates that the apparent increase in mass range at lower \((z_0 \Omega)\) will be constrained by increasing \(q_z\) values. The value of \((z_0 \Omega/2\pi)=0.15\) corresponds to a frequency of \(\Omega/2\pi=0.5\) MHz for the present trap design \(z_0=0.3\) cm. This constraint on ion mass loading would be an advantage in the case of trapping clusters formed in a supersonic expansion. Since the beam is composed of a distribution of cluster masses traveling at approximately the same speed, the choice of \(V_{rf}\) for a given \((z_0 \Omega)\) serves to truncate the distribution at the largest mass which can load into a stable orbit.

### 2. Mass selection

Although the initial cluster mass distribution can be narrowed by the choice of cluster source operating conditions and operating point at which ions are loaded, the trapped ion distribution will require mass selection to isolate a single cluster ion for study. Mass selection can be accomplished in the trap either by the mass dependence of the stability boundary\(^{27,28}\) or by resonance ejection.\(^{29}\) In either case the choice of operating point at which selection takes place will be influenced by the \(V_{rf}\) amplitude required.

First, consider mass selection at the stability boundary in the upper cusp shown in Fig. 2 at \(q_\ast=0.78\), \(a_\ast=0.15\). If the ion mass \(M_0\) is positioned at \(q_\ast=0.78\) by rf amplitude \(V_{rf}=V_0\), then for each value of \(a_\ast=a_\ast\) there will be a range of ion masses which will remain stable for this rf voltage. As the value of \(a_\ast\) increases, this mass range decreases until ideally only the desired mass remains stable. An estimate of the mass resolution \((M_0/\Delta M)\) as a function of \(a_\ast\) can be obtained from a linearization of the cusp boundary equations which yields \(\Delta M/M_0=4.57(a_\ast-a_\ast)\) over the range 0.12 \(\leq a_\ast \leq 0.15\). This suggests that a mass resolution of \(-100\) can be achieved assuming a voltage stability for \(V_{rf}\) of \(-0.05\) ms for a rf frequency \(\Omega/2\pi=1\) MHz. This selection time scale is significantly less than the collision times \(t_{\ast} \sim 5\) ms and \(t_{\ast} \sim 30\) ms estimated in Sec. IV B for a \(C_{60}\) ion cloud at \(-300\) K in a He background gas at \(2\times10^{-5}\) Torr. A minimal selection duration will also reduce cluster ion loss through evaporation of the cloud or vibrational heating\(^{31}\) which will occur if the cloud is excessively heated at the cusp operating point.

Resonance ejection is a technique which sweeps the ion frequencies \(\omega_\ast(n)\) of unwanted masses \(M_\ast\) into resonance with an external rf excitation field. As each ion absorbs energy from the field, the trajectory amplitude increases until \(z_\ast \geq z_0\) driving those ion masses from the trap. This technique has been used to achieve mass selection\(^{32}\) of high mass ions by applying forward and reverse sweeps of the ion frequencies. An optimum choice of operating point for ion ejection will probably be determined by the trapped mass distribution. However, resonance excitation in the vicinity of smaller \(q_z\) clearly can provide a significant reduction in rf amplitude \(V_{rf}\) over that required to select at the cusp (a factor of \(-2\) at \(q_z=0.4\)). Although smaller \(q_z\) values are closer to the stability boundaries, the reduced well depths require lower rf excitation amplitudes (<10 \(V_{0,p}\)) to efficiently eject heavy ions.\(^{33}\) It is important to note that resonance ejection introduces the possibility of heating adjacent masses by excitation in the wings of the ion resonance linewidth; an effect which becomes more important at smaller \(q_z\) values. For smaller metal clusters composed of <100 atoms, mass selection requires a resolution of only \((M_0/\Delta M)=100\), so that the issues related to adjacent ions will probably not be important considerations. For our purposes then, the choice of mass selection technique will probably depend on the degree of ion heating rather than mass resolution requirements.

Independent of which selection technique is used, the maximum mass which can be selected or isolated after loading the trap with ions is determined by the value of \(q_z\) at the operating point chosen for selection. The mass constraint is then given by Eq. (3b) as

\[
M_{select} \leq \frac{2eV_{rf}}{q_z(z_0 \Omega)^2} = 1.93 \frac{V_{rf}}{q_z(z_0 \Omega)^2} \tag{10}
\]

in which the units are the same as in Eq. (8). In the current trap, \((z_0 \Omega/2\pi)=0.3\) cm MHz which yields \(M_{select} \leq 1400\) amu for \(V_{rf}=2\) kV\(_{0,p}\) at the select operating point \(q_z=0.78\) corresponding to selection at the cusp instability \(q_\ast=0.78\). The rf drive electronics can extend this limit to \(5600\) amu by switching the drive frequency to \((\Omega/2\pi)=0.5\) MHz. However it is more flexible to extend the mass range to \(-7300\) amu by using resonance ejection at \(q_z=0.15\).
3. Detection

Ions can be detected both within the trap through currents induced by the ion motion, or by ejection from the trap into an electron multiplier. This paper concentrates on *in situ* electronic detection.

The ion cloud will be detected electronically within the trap at the operating point \( q_z=0.3, a_z=0 \). Ion trajectories at this point are accurately given by the secular motion approximation for a pure quadrupole field and yield near harmonic resonance signals at \( \omega_q \) under appropriate detection conditions demonstrated below in Sec. III C. This operating point provides an adequate well depth to ensure strong trapping and is far enough from the stability boundary to allow a mass range to be detected without ion loss. Finally, the ion resonance at this operating point is near \( \omega_r/2\pi = 100 \) kHz for a drive frequency of \( \Omega/2\pi=1.0 \) MHz. Narrow band detection can be accomplished at this frequency by resonant LC circuitry with a sufficiently narrow bandwidth \((\omega_r/\Delta \omega_r)\sim 200\) to achieve low noise in the presence of large background signals at frequency \( \Omega \).

*In situ* electronic detection imposes yet another condition on the maximum mass which can be detected by this technique. In this case, the detection frequency is fixed by electronic design of the resonance inductance to a frequency \( \omega_0 \). In addition, we require that the ratio \( \omega_0/\Omega \approx 0.1 \) in order to ensure that the detected ion trajectories satisfy the secular approximation. The detection signal amplitudes derived from these nearly harmonic trajectories are more simply interpreted. The detection operating point is determined by this frequency ratio and Eq. (4), \( q_z=2^{3/2} \omega_0/\Omega=0.283 \) for \( V_{de}=0 \). Then the detectable mass range determined by Eq. (3b) is given by

\[
M_{\text{detect}} \leq \frac{e V_{rf}}{\omega_0 \sqrt{2(\epsilon_0 \Omega)}} \frac{7.1}{(z_0 \Omega)^2} V_{rf}^2
\]

with the same units as above. In the current trap, \((z_0 \Omega/2\pi) = 0.3\) cM Hz which yields \( M_{\text{detect}}=4000\) amu for \( V_{rf}=2\) kV per \( p \) at the detect operating point \( q_z=0.283 \). Although the detected mass range can be extended by using a detector resonance at lower frequency or higher \( V_{rf} \) drive amplitude, this would probably result in a lower detector sensitivity.

An operating point for ion detection based on ejecting ions into an electron multiplier is not constrained by a resonance detection requirement and this flexibility can be used to advantage. For example, the operating point for ejection can be placed at the optimum stable point, \( q_z=0.55 \), for the detection of a cluster ion formed during an experiment with excessive kinetic energy. Rapid ion ejection may also be useful in an experiment in which helium collisions would be detrimental, such as identifying the formation of clusters with weakly adsorbed atoms. Although this paper concentrates on *in situ* ion detection, ejection is clearly an important complementary technique.

B. Trap design

Figure 4 displays the cylindrically symmetric trap assembly to scale with the symmetry axis shown along the \( z \) direction. The trap electrodes are composed of two endcaps and a ring machined from oxygen-free high-conductivity (OFHC) copper in the shape of hyperboloids of revolution to within a tolerance of \( 10^{-4} \) in. Using numerically controlled machine tools. Electrode shapes which are simpler to machine and probably adequate for most experiments are described in Ref. 34. As shown in Fig. 4, these electrodes are mounted with the endcaps separated from the ring by Macor spacers which maintain the overall cylindrical symmetry to within \( 1-2 \times 10^{-3}\) in. The separation between endcaps is \( 2z_0=0.60\) cm and the inner diameter of the ring electrode is \( 2r_0=0.6/2\) cm; the dimension in Fig. 4 indicates the overall scale. An aperture is positioned in each of the endcaps and three apertures in the ring electrode each having 1 mm diam at the entry point. The ionizing electron beam enters the trap through the endcap on the left and the opposite endcap has been machined to enable ion ejection. The axes indicated in Fig. 4 will be used for reference to the trap axials (\( z \)) and radial (\( x,y \)) directions. The electrodes are held together within the mounting bracket by pressure exerted on one of the Macor insulators with stainless spring plungers. The trap is assembled after degreasing and cleaning ordinarily applied to ultrahigh vacuum (UHV) components and no additional treatment of the electrode surfaces was performed.

C. Vacuum system

It is essential for long trapped ion lifetimes that the vacuum system maintain a background impurity partial pressure in the range of \( 10^{-10} \) Torr to avoid ion–neutral reactive collisions with residual atmospheric gases. The trap is positioned within the UHV chamber as shown in Fig. 5 so that the electrode apertures can be accessed simultaneously by an electron beam for ionization, an electron multiplier for detecting ejected ions, a cluster neutral beam source, and an atomic beam or radiative source. After bakeout, the UHV chamber is evacuated to a base pressure of \( <2 \times 10^{-10} \) Torr by a 500 l/s turbomolecular pump (Balzers TPU 510). The trap mounting is connected to a manipulator which provides...
FIG. 5. The UHV chamber is configured with gate valve, vacuum pumps, and ion gauge positioned below the trap detection electronics. The trap is mounted on a translation-rotation feedthrough to allow alignment of rf trap apertures with an electron beam, cluster source flux, experimental irradiation by particle or photon flux and an electron multiplier.

D. Trap electronics

The electronics schematic shown in Fig. 6 depicts the components for trap drive, ion excitation and detection, and computer control and data acquisition. The frequency synthesizers (Sciteq Corp. VDS-3A) generate the primary rf voltages ($-0.75 V_{0,p}$) from a common master oscillator at the four frequencies indicated and these outputs are phase locked. The rf amplifiers provide a voltage controlled gain up to $\sim 7 V_{0,p}$ for outputs at frequencies $\omega_0$, $\omega_0$, and $\Omega$. The trap rf drive $V_{rf}(\Omega)$ is further amplified by a broad band power amplifier (75 W) with a gain of 10 and a 2 $\Omega$ output impedance. The rf drive is finally increased to a maximum of $\sim 800 V_{0,p}$ by a high voltage transformer having a $50 \times$ turns ratio. A second generation power amplifier is currently being designed to extend $V_{rf}$ to 2 $kV_{0,p}$. The rf detection voltage $V_{det}(\Omega+\omega_0)$ and excitation voltage $V_{exc}(\omega)$ are directly coupled to a common endcap electrode providing the capability to either detect or eject ions by resonant excitation. All rf voltages are measured with active voltage dividers and a Fluke 8920A true rms voltmeter. Each of these amplifiers is fitted with null filters at the detection frequency $\omega_0$ to minimize the noise level at this frequency. The ring dc bias, $V_{dc}$, is computer controlled so that the ion resonance can be slowly swept across the narrow-band detector and also rapidly switched to high voltages (250 V) for ion selection or flushing the trap. The bias voltage is summed with the rf drive at the transformer secondary.

The ion detection electronics was designed to reach noise levels set by Nyquist limits of the resonant impedance in the preamplifier which translates to a detection sensitivity of $\sim 100$ ions. As shown in Fig. 7, the trap endcap electrode is directly coupled to the detection circuit which has a high $Q$ parallel LC resonance at $\omega_0/2\pi=1$ kHz having a resonant impedance of $\sim 2.5 \text{ M} \Omega$. This circuit also includes a series resonance which provides a low impedance of $\sim 50 \text{ }\Omega$ at $\Omega/2\pi=1$ MHz increasing slightly to $\sim 500 \text{ }\Omega$ at $(\Omega+\omega_0)/2\pi$. The LC resonance circuitry is coupled to a field-effect transistor amplifier and both are mounted within a small vacuum tight cell at atmospheric pressure. This cell is fitted with...
FIG. 7. The ion-induced current in the endcap electrode directly drives the detection circuit impedance as shown. The detection impedance vs frequency plot displays a high impedance resonance at $\omega/2\pi = 100$ kHz and low impedance at the rf drive $\omega/2\pi = 1$ MHz and excitation frequency $\Omega/2\pi = 1.1$ MHz.

vacuum feedthrough electrodes and mounted within the UHV chamber close to the trap. The critical resonance inductor (21 mH) has been wound on a ferrite core (Phillips 3B7) chosen for low loss and gapped to avoid variation of the resonant frequency with ambient temperature.

Detected signals are brought out of the UHV chamber through shielded cable to narrow-band amplifiers providing a gain of $G \approx 400$ and then input to a lock-in amplifier (Stanford Research SR530). The ring to endcap capacitance of $\sim 7$ pF couples the trap drive $V_{\text{rf}}(\Omega)$ into the detection electronics. Although the resonant circuit has been designed for low impedance near $\Omega$, the leakage of $V_{\text{rf}}(\Omega)$ and $V_{\text{det}}(\Omega + \omega_0)$ and subsequent mixing in the amplifiers is sufficient to produce a constant amplitude background at $\omega_0$ which saturates the lock in for $V_{\text{rf}}(\Omega) > 100$ V$_{0-p}$. To avoid this limitation, a nulling signal at frequency $\Omega$ has been applied at the LC resonance as shown in Fig. 7. The null is sufficient to reduce the lock-in background level to $\sim 1$ mV$_{\text{rms}}$ for $V_{\text{rf}}(\Omega) \approx 400$ V$_{0-p}$.

Computer (Macintosh IIcx) control of all voltages and timing in an experimental sequence of operations is accomplished by a program written with Labview software (National Instruments). This program provides the capability for instrument control, data acquisition, and performs initial data analysis and graphics in real time. Organization of the computer control and data acquisition is shown schematically in Fig. 6. The control lines in Fig. 6 are shown as dashed lines and solid lines indicate electronic equipment interconnections. Computer control gating for the e-beam pulse, cluster source shutter, and ion ejection electronics are not included in Fig. 6. An example computer controlled sequence is shown in Fig. 8(a) which illustrates the variation in $Q_z$, $V_{\text{rf}}$ amplitude, and the axial well depth $eD_z$ corresponding to a mass of $M_0 = 720$ amu. The time scale is characterized by the trap activity rather than specific time durations since these times can depend on the details of a particular experiment. In this sequence, $M_0$ is trapped at $q_z = 0.5$, $\alpha_z = 0$ near the stable point. Ions with an approximate mass interval $0.55M_0 \leq M_i \leq 5M_0$ about $M_0$ which correspond to operating points over the range $0.1 \leq q_z \leq 0.9$ could also be trapped. The number of ions of mass $M_0$ is then detected at the point $q_z = 0.3$, $\alpha_z = 0$. As indicated in Fig. 8(b), the detection sequence is composed of a series of weak rf excitation pulses of amplitude $V_{\text{det}}$ synchronized with a sequence of alternating polarity $V_{\text{dc}}$ bias pulses. Varying the dc bias over the range $0 \leq |V_{\text{dc}}| \leq 8.0$ V sweeps the $M_0$ resonance across the detector response. The detected signal derives from the current induced in the endcap electrode by this forced oscillation of the ion cloud. In Fig. 8(a), the mass $M_0$ is selected by resonance excitation in which (a) masses $M < M_0$ are ejected by sweeping ion resonances over an intense excitation $V_{\text{exc}} \geq 10$ V$_{0-p}$ at $q_z = 0.1$, and (b) masses $M > M_0$ are ejected by sweeping over excitation at $q_z = 0.55$. This sweep of the ion resonances is accomplished.
by varying $V_{rf}$ over the amplitudes shown in Fig. 8(a). The operation point is then returned to the load point for the experimental activity after which a final detection of the $M_0$ ion number is performed.

### E. C$_{60}$ source

Experiments described in Secs. III and IV were performed using a shuttered molybdenum oven driven by a Spectra-Mat E-292 heater as an effusive beam source of neutral C$_{60}$ molecules (MER Corp., C$_{60}$ purity >99.99%). The oven was loaded with 10–20 mg of C$_{60}$ and heated to ~260 °C for 24 h during chamber bakeout to further purify and crystallize the C$_{60}$ material. This oven was enclosed in a LN2 cooled copper shroud and when operating in the range of 400–500 °C, the vacuum system pressure maintained a pressure of ~5 × 10$^{-10}$ Torr. The oven temperature was controlled during experiments to increase data reproducibility. At these temperatures, the C$_{60}$ evaporation rate does not appear to degrade and the oven is reloaded when the material is exhausted after an interval of ~3–4 weeks. At 450 °C, the rate that neutral C$_{60}$ molecules entered the ring through a 1-mm-diam aperture is estimated from the vapor pressure at ~2 × 10$^9$ molecules/s. The entry port for the C$_{60}$ flux is indicated in Fig. 5. The C$_{60}$ flux was ionized by a crossed e-beam pulse entering through the endcap maintained at dc ground potential. The electron gun was constructed using a Spectra-Mat Y-728 cathode within a molybdenum heat shield and operated at ~1200 °C. The e-beam was pulsed by gating a negative bias voltage of ~150 V applied to a molybdenum screen grid. A single e-beam pulse of ~600 ms was sufficient to trap ~10$^4$ C$_{60}$ ions at the above oven temperature. This number of trapped ions is consistent with an estimated e-beam current density of ~2 mA/cm$^2$ and an excitation volume resulting from crossed beam diameters determined by the trap apertures.

### III. ION-NUMBER DETECTION

#### A. Excitation of coherent motion

A signal proportional to the number $N$ of trapped ions can be obtained by exciting a coherent response of the ion cloud with an external rf voltage $V_{det}(\omega_0)$ applied to the endcap electrode as shown in Fig. 7. Sideband excitation at $\omega = \Omega + \omega_0$ was used to avoid saturating the narrow-band detector at its peak response $\omega_0$. During detection the total field is a sum of the trapping quadrupole field at $\Omega$ and the external dipole field $E_{det}$ at $(\Omega + \omega_0)$ which is assumed to be spatially uniform. In the limit $\omega_0 = \Omega$, it is shown in Ref. 12 that the average force exerted on an ion is proportional to the square of the total field amplitude averaged over a rf period (2π/Ω). This nonlinearity results in excitation of the ion axial motion at $\omega_0$ by the force

$$f_z(t) = -\frac{q_z}{4}eE_{det} \cos \omega_0 t = -\frac{\omega_0}{2\Omega} \left(\frac{eV_{det}}{2z_0}\right) \cos \omega_0 t$$

(12)

in which the field $E_{det} = (eV_{det}/2z_0)$ and detection is assumed to occur at an operating point for which $a_z = 0$. This force coherently perturbs the secular motion $\tilde{z}(t)$ of each ion and the resulting amplitude is approximated by $z(t) = \tilde{z}(t) + \delta z$. In the secular approximation, the ion cloud center of mass will then execute an oscillation with amplitude $\delta z$ about the trap center exhibiting a resonance when the ion secular frequency $\omega_s = \omega_0$. Note that for sideband excitation, the force $f_z(t)$ and the response $\delta z(t)$ are reduced by a factor $\sim (\omega_0/\Omega)$ compared with direct excitation at $\omega_0$.

The image current induced in the endcap electrode by a cloud of $N$ ions whose center of mass is oscillating at frequency $\omega_0$ with amplitude $\delta z$ is given by

$$i_{induced} = \frac{NCe\omega_0 \delta z}{2z_0} = Ni_1.$$

(13)

where $C = 0.8$ is a factor introduced by the hyperboloid geometry and $i_1$ is the current induced by a single ion. The in-phase and out-of-phase components of the ion resonance line shape are detected by varying the bias voltage $V_{dc}$ which tunes the ion resonance given by Eq. (4) across the detector resonance. In practice, this frequency scan is accomplished by applying a sequence of $V_{dc}$ bias pulses as shown in Fig. 8(b). During each $V_{dc}$ pulse length, the ion is excited by a rf pulse of amplitude $V_{det}$, frequency $(\Omega + \omega_0)$, and duration set by the desired noise bandwidth. This pulsed detection technique avoids sweeping the ion frequency during excitation by $V_{det}$. The detected signal at $\omega_0$ is amplified by a gain $G \sim 400$ and the lock-in amplifier output, $U_{sig} \sim \text{mV}$, is related to the peak value of $i_{induced}$ by $N_i = \sqrt{2}/GR_0$ where $R_0$ is the detector resonant impedance.

It is important to exercise caution applying line-shape measurements to determine ion number. In an experimental trap, the range of $V_{det}$ amplitude over which the detected peak ion response is nearly harmonic and proportional to $N$ is quite limited. Imperfections in trap fabrication and assembly will reduce trap cylindrical symmetry resulting in an anharmonic response at $\delta z$ increases for larger $V_{det}$ amplitudes. In the anharmonic regime, the peak response saturates with increasing $V_{det}$ and the linewidth broadens and becomes distorted near resonance as shown below in Sec. III C. In addition, as ion density increases for larger $N$ or lower cloud temperature, ion–ion interactions become important. In the presence of a nonuniform excitation field $V_{det}$, these interactions can cause the line shape to become dependent on $N$ which effects both the resonance width as well as the resonance center frequency. At lower cloud temperatures (300 K), the linewidth is observed to narrow and frequency shifts are readily measurable as will be shown in Sec. IV R.

Performing ion number measurements at a detuned frequency away from the resonance provides an ion response which is independent of linewidth and shift to first order. This is particularly important for the measurement of small ion number ($N < 1000$) which requires strong drive $V_{det}$ conditions. The in-phase component of a harmonic response $\delta z/\omega_0$ for $(\omega_z, \omega_0) \gg \text{lincwidth}$ is approximated by

$$\frac{\delta z}{\omega_0} = \frac{eV_{det}}{4Gz_0(\omega_z - \omega_0)},$$

(14)

where $\omega_z \equiv c \Omega$ is a factor introduced by the hyperboloid geometry and $i_1$ is the current induced by a single ion. The in-phase and out-of-phase components of the ion resonance line shape are detected by varying the bias voltage $V_{dc}$ which tunes the ion resonance given by Eq. (4) across the detector resonance. In practice, this frequency scan is accomplished by applying a sequence of $V_{dc}$ bias pulses as shown in Fig. 8(b). During each $V_{dc}$ pulse length, the ion is excited by a rf pulse of amplitude $V_{det}$, frequency $(\Omega + \omega_0)$, and duration set by the desired noise bandwidth. This pulsed detection technique avoids sweeping the ion frequency during excitation by $V_{det}$. The detected signal at $\omega_0$ is amplified by a gain $G \sim 400$ and the lock-in amplifier output, $U_{sig} \sim \text{mV}$, is related to the peak value of $i_{induced}$ by $N_i = \sqrt{2}/GR_0$ where $R_0$ is the detector resonant impedance.

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(14)

Estimates of ion number are then calculated from off resonance signals by Eqs. (13) and (14).
The change in ion frequency for an incremental change in dc bias voltage is given by

$$\delta \nu = - \frac{e}{4 \pi M \omega_0^2} \delta V_{dc} = - d \nu \delta V_{dc}. \quad (15)$$

This frequency-voltage dispersion at the detection point for masses near $M_0 = 720$ amu and $z_0 = 0.3$ cm is $d \nu = 1.86$ kHz/V. At each voltage increment, $V_{det}$ is pulsed on for 50–200 ms to detect the ion response at that position on the line shape. The trap operating point $q_2 = 0.29$, $a_{20} = 0$ shown in Fig. 2 was chosen to satisfy $\Omega \gg \omega_0$, and also to detect ions at low $V_{rf}$ voltage which improves the detection $S/N$ ratio. The $V_{rf}$ voltage is set so that at the detection operating point, the ion peak frequency equals the detector resonance frequency $\nu_0$ for $V_{dc} = 0$ and a drive frequency of $\Omega/2 \pi = 1.0$ MHz.

The preceding discussion of the electronic detection of ion oscillations has assumed that the only ion resonance excited by the external rf fields is the primary axial resonance $\nu_0$, arising from harmonic motion in a pure quadrupole field. It is important to consider the possibility of nearby resonance frequencies which might complicate the interpretation of detected signals. The experimental trap described in Sec. II B will include higher order fields resulting from the presence of apertures, deviation of the electrodes from hyperbolic geometry, and deviation from cylindrical symmetry. These higher order fields introduce nonlinear contributions to the ion motion resulting in the presence of additional resonant frequencies. Experimental assignment of ion resonance spectra indicate the frequency and strength of these higher order resonances. These previous studies suggest that the presence of higher order fields will not significantly affect electronic detection spectra provided the frequency region scanned by sweeping $V_{dc}$ is $\ll \nu_0/2$ to avoid resonances $\nu_2 \pm \nu_2$ arising from coupling of the radial and axial motions. In ion resonance spectra presented below, the frequency scans were adequately narrow and showed no evidence of additional nonlinear resonances even when the ion response was anharmonic.

### B. Detection sensitivity

The noise power spectrum determines the limiting detection sensitivity for ion number measurements. Noise measurements were performed for the narrow-band detector used in these experiments which has a LC resonance occurring at $\omega_0/2 \pi = 101.94 \pm 0.03$ kHz. The noise power spectrum shown in Fig. 9 is a plot of the variance of the noise voltage over the bandwidth measured by a lock-in amplifier.

The rms noise voltage $\langle \nu_0 \rangle$, in the absence of drive voltage $V_{rf}(\Omega) = 0$, was determined by averaging the peak values of several power spectra measurements similar to that shown in Fig. 9 yielding a value $\langle \nu_0 \rangle_{\text{peak}} = 0.20 \pm 0.02 \mu$V/Hz$^{1/2}$. In the presence of $V_{rf}(\Omega) = 400 \text{ V}_{0-p}$, the noise voltage peak increases slightly to $\langle \nu_0 \rangle_{\text{peak}} = 0.25 \pm 0.02 \mu$V/Hz$^{1/2}$. The sensitivity limit imposed by Nyquist thermal noise is given by the rms voltage $\langle \nu_0 \rangle_{\text{thermal}} = \sqrt{4kT R_0} (\text{V/Hz})^{1/2}$ where $R_0$ is the resonant impedance of the LC circuit and is obtained from the width of the noise power spectrum $\Delta \omega/\omega_0 = Q = R_0/\omega_0 L$. The measured width of the power spectrum yields the resonance $Q \approx 175$ and an impedance of $|K| = 2.4 \pm 0.2 \text{ Mfl}$ for $L = 21 \text{ mH}$. The corresponding thermal noise voltage $\langle \nu_0 \rangle_{\text{thermal}} = 0.21 \pm 0.01 \mu$V/Hz$^{1/2}$ was obtained at 300 K and indicates that the maximum rms noise measured in Fig. 9 represents a detector sensitivity at the thermal limit.

The sensitivity of measurements obtained with a single ion loading cycle, such as estimates of ion number and trapped ion lifetime are limited by thermal noise. The signal-to-noise ratio of data taken over many loading cycles are limited by the statistical fluctuations in ion number, $\Delta N = \sqrt{N}$. These noise measurements determine the minimum number of ions $N_{\text{min}}$ detectable with a unity signal to noise ratio. The rms thermal noise current associated with $N_{\text{min}}$ is given by

$$i_{\text{induced}} = \frac{\langle \nu_0 \rangle_{\text{thermal}} \Delta f_N}{R_0} = - N_{\text{min}} i_1,$$

where $i_1$ is defined by Eq. (13) and $\Delta f_N$ is the equivalent noise bandwidth associated with the data sampling interval. Calculating $i_1$ for off-resonance detection using Eq. (14) yields the expression for $N_{\text{min}}$

$$N_{\text{min}} = 29.2 \frac{M (v_e - v_0) \sqrt{\Delta f_N}}{V_{\text{det}}},$$

where the units are $M$ amu, $(v_e - v_0)$ kHz, $V_{\text{det}}$ mV$_{0-p}$, and $\Delta f_N$ Hz. The ion noise level at $(v_e - v_0) = 2$ kHz is 240 ions for $V_{\text{det}} = 200 \text{ mV}_{0-p}$ and $\Delta f_N = 1.25 \text{ Hz}$. As discussed more thoroughly below in Sec. IV C, the maximum excitation amplitude, $V_{\text{det}}$, will be determined by the acceptable level of ion translational heating and also by the degree of dissociation induced by collisions with the background He gas.

### C. Line-shape measurements

Figures 10(a) and 10(b) show a line-shape measurement obtained at low excitation amplitude $V_{\text{det}} = 10 \text{ mV}_{\text{rms}}$ for $C_{60}$
FIG. 10. C$_{60}$ ion line-shape measurements displaying out-of-phase (a), (c), (e) and in-phase (b), (d), (f) signal components. (a) and (b) line shapes exhibit near-harmonic behavior for $V_{det}=10$ mV$_{rms}$ and yield an estimated ion number $N=3.5 \times 10^4$ ions. Solid curves are Lorentzian fits of a harmonic oscillator model. (c) and (d) display anharmonic distortion of detected signals for $V_{det}=190$ mV$_{rms}$ and ion number $N=2 \times 10^3$ ions; (e) and (f) display detected line shapes for an ion number $N=160$ ions measured with $V_{det}=600$ mV$_{rms}$. Solid lines in (c)-(f) are guides.

ions in the absence of background He gas. The measurements shown in Figs. 10(a) and 10(b) are the detected signals at the lock-in input and were obtained in a single scan over the ion resonance taking 13 s. Each data point represents a sampling of the lock-in amplifier output at a rate corresponding to an equivalent noise bandwidth of $\sim 12$ Hz. These scan parameters apply to all single resonance line-shape measurements. Note that the effective rf amplitude exciting the ions during detection is actually $(\omega_0/\Omega) V_{det}/10$. At this low excitation voltage, the ions are executing nearly harmonic motion as evidenced by comparison with fits of the dispersive and resonance line shapes, respectively, to the in-phase and out-of-phase signal components of a harmonic oscillator. The ion current induced by a single C$_{60}$ ion oscillating at $\omega_0=8.7 \times 10^{-16}$ A for this $V_{det}$ amplitude. This corresponds to a displacement of $(\pi/\tau_0)\approx 0.01$ which is consistent with the small anharmonic distortion observed. The linewidth in Fig. 10(a) is $\sim 0.37$ kHz using the frequency-voltage dispersion given by Eq. (15). The C$_{60}$ signals shown in Figs. 10(a) and 10(b) correspond to $N=3.5 \times 10^4$ ions derived from the harmonic fit and an estimate of $N$ obtained from the off-resonance amplitudes at $\pm 0.8$ kHz is $2.8 \times 10^4$ ions consistent with the near harmonic line shape. In Figs. 10(a) and 10(b), the noise level of $\pm 0.2$ mV$_{rms}$ measured at the lock-in input is equal to the thermal noise limit.

At higher excitation amplitudes, the C$_{60}$ response becomes anharmonic near resonance exhibiting an asymmetric cusp as shown in Fig. 10(c) for $V_{det}=190$ mV$_{rms}$. In this case, the peak amplitude is no longer proportional to $N$; however, estimates of the ion number can be obtained from off-resonance measurements on the in-phase line shape shown in Fig. 10(d). An ion number of $N=2000$ ions is estimated by the signal amplitude at $\pm 3.6$ kHz. Note that at this $V_{det}$ amplitude the linewidth has broadened to $\sim 1$ kHz estimated from the in-phase line shape. The noise level in these line shapes is again at the thermal limit, and the measured signal to noise ratio of $\sim 2$ at 3.6 kHz is consistent with $N_{min}\approx 950$ ions calculated for the equivalent noise bandwidth of $\Delta f_N=12$ Hz. The line shapes shown in Figs. 10(c) and 10(d) were measured with a background He pressure of $7 \times 10^{-6}$ Torr. All reported helium pressures have been corrected for gauge sensitivity.

Figures 10(e) and 10(f) display ion signals obtained for an ion number of $N=160$ ions estimated by the signal at $\pm 2.0$ kHz. These scans were taken with an excitation amplitude of $V_{det}=600$ mV$_{rms}$ and exhibit linewidth distortion near resonance and a linewidth of $\sim 2$ kHz. The measured signal to noise ratio of approximately 2–3 compares favorably with the ratio of 3 predicted by Eq. (17) for an equivalent noise bandwidth of $\Delta f_N=1.5$ Hz. The linewidth measurements shown in Figs. 10(e) and 10(f) were obtained in a total scan duration of 50 s with a background He pressure of $1.2 \times 10^{-5}$ Torr.

These results are generally characteristic of line-shape data taken over a wide range of parameters for both Xe$^+$ and C$_{60}^+$ including $V_{det}$, He pressure, ion cloud temperature, and ion number. In particular, line-shape experiments using Xe$^+$ ions determined the range of $V_{det}$ over which off-resonance detection is proportional to ion number at several off-resonance frequencies. Since this data may be useful to estimate the linear range for heavier masses, they are presented...
in Fig. 11. The slopes shown in Fig. 11 scale \( \sim 1/(\omega_z - \omega_0) \) as expected for the in-phase off-resonant amplitude, and linearity extends to higher \( V_{\text{det}} \) for increased detuning. Each detuning curve corresponds to identical ion loading conditions for which the Xe ion number was estimated to be \( N \sim 2 \times 10^4 \) ions.

Ion-number measurements obtained by this detection method are particularly sensitive to the ion line shape. This line shape exhibits nonlinear effects from both anharmonic dynamics and ion–ion interactions, so that care is required to ensure the response is proportional to ion number. Nearharmonic line shapes can be achieved for very low \( V_{\text{det}} \) amplitudes. However, a more interesting result of these line-shape measurements is that the wings of the resonance line shape remain proportional to ion number at high values of \( V_{\text{det}} \) for which the resonance region is distorted and broadened. This suggests that the nonlinear effects are most severe near resonance and that off-resonance measurements can provide detected signals proportional to ion number. The estimates of ion number obtained by these off-resonance measurements are probably accurate to within \( \sim 25\% \) as a result of residual uncertainty caused by line shape distortions from ion–ion interactions. Ion-number measurements obtained from off-resonance signals on the in-phase component were found to be reproducible to within \( \sim 15\% \) for identical ion loading and detection conditions.

D. Mass spectra

A detected spectrum of many components will result after loading a range of cluster masses or from the dissociation of clusters in a mass selected ion cloud. An important issue for this detection technique is the extent of linewidth overlap for neighboring cluster masses. The mass dispersion of the resonant frequency at the operating point \( (q_z, a_z = 0) \) is obtained from Eq. (4) as

\[
\delta \nu_z = \frac{(\Omega q_z)^2 \delta M}{16 \pi \omega_0} M_0 \sim -\frac{\omega_0 \delta M}{2 \pi M_0}.
\]

The resonance of a second mass \( M_0 + \delta M \) will be resolved if the frequency shift \( \delta \nu_z \) is greater than the ion linewidth. For a detector resonance of \( \omega_0/2\pi \) \( \sim 100 \) kHz, the ion resonance for a mass difference of \( \delta M \sim 10 \) amu at \( M_0 \sim 1000 \) amu will be shifted by \( \sim 1 \) kHz from the parent ion resonance, which is comparable to the ion linewidth shown in Fig. 10. In the current trap design, ion detection will resolve clusters differing by an atomic mass for a cluster number up to \( \sim 100 \) atoms.

The mass spectra in Fig. 12 were obtained by extending the \( V_{\text{dc}} \) bias range to cover masses \( C_{60} \) to \( C_{34} \) and then detecting over this mass range with increasing \( V_{\text{det}} \) amplitudes. Spectra are shown in Fig. 12 for \( V_{\text{det}} = 300 \) and 900 mVrms and each spectrum was obtained in a single scan over the mass range taking 40 s. At each \( V_{\text{dc}} \) data point, the lock-in amplifier output was sampled at a rate corresponding to an equivalent noise bandwidth of \( \sim 3 \) Hz. The He background pressure of \( 2.4 \times 10^{-6} \) Torr was sufficient to induce dissociation by ion-neutral collisions during the spectral scan for increasing \( V_{\text{det}} \) which is clearly evident for \( V_{\text{det}} = 900 \) mVrms.

The dissociation products of \( C_{60} \), each spaced by 24 amu, are separated by \( \sim 3.6 \) kHz and as shown in Fig. 12 are clearly resolved. The calculated ion resonance frequencies for each mass are indicated by lines placed at the corresponding \( V_{\text{dc}} \) bias values in Fig. 12 and show good agreement with the measured spectrum.

Nondestructive ion detection offers the opportunity to study the slow time evolution of dissociation products; as an example, the collision-induced dissociation of trapped \( C_{60} \) is presented in Sec. IV C. The quantitative capability of this detection technique to measure the ion number for different masses in a multicomponent ion cloud will be degraded for masses separated by less than several linewidths. However
the ability to continuously monitor a mass spectrum, even qualitatively, during an experiment will be an important option for metal cluster studies whose interpretation is intimately connected with determining the presence or threshold of dissociation products.

IV. C$_{60}$ MEASUREMENTS

A. Trapped ion lifetime

The lifetime of trapped C$_{60}$ ions has been measured by detecting the induced ion current at 3 s intervals throughout the decay of trapped ion number. Each measurement is taken at only two $V_{dc}$ points denoted by $v_+$ and $v_-$ in Fig. 13 in order to reduce the detection time, and also to minimize excitation of the ion translational energy. The $v_+$ and $v_-$ detection points used in these lifetime measurements correspond to off-resonance frequencies $\delta v_\pm = \pm 5.4$ kHz. The measurement S/N ratio shown in Fig. 13 results from limiting $V_{det}$ to 100 mV$_{t_{max}}$ to detect the decay of an initial ion number $N = 1.6 \times 10^4$ ions. The $V_{det}$ amplitude is chosen as small as possible consistent with a reasonable S/N ratio to avoid reduction of the trapped ion lifetime by translational heating.

Figure 14 shows the variation of C$_{60}$ ion lifetime with He background pressure. The ion lifetime decreases at low pressures because the He collision rate cannot compete with rf heating of the ion kinetic energy and the hot C$_{60}$ ions subsequently evaporate from the trap. As shown in the lower inset plot of Fig. 14, a rapid single exponential decay dominates ion loss at the lower helium pressures. As He pressure increases, collisional cooling competes with rf heating to establish the cloud temperature and the data points in Fig. 14 represent the dominant exponential decay. At the highest He pressures, ion loss results from ion-neutral collisions which produce excessive interruptions of the ion motion and subsequent ion diffusion outward to less stable orbits. The decay at higher He pressure is indicated in the upper inset plot of Fig. 14.

The decay shown in Fig. 13 was obtained for $p_{He} = 8.7 \times 10^{-7}$ Torr. At these pressures, the cloud kinetic energy is approaching equilibrium with the He bath, as will be discussed in the next section, and the evaporative ion loss is not significant. The initial decay results from small frequency shifts of the resonance line shape as the ion cloud reaches a slightly higher kinetic temperature in the presence of the weak detection excitation. We have observed similar behavior for Xe ion decays and thus the early exponential is probably not associated with C$_{60}$ dissociation products. After this initial equilibration of the ion cloud, the decay proceeds at a slower exponential rate yielding an ion lifetime of $\tau_{ion} = 36$ min.

The highest He pressures will be required to rapidly relax the translational and internal energy of heavy cluster ions trapped from supersonic beams. For example, Ag$_{20}^+$ ions would require $\sim 2$ s at $10^{-4}$ Torr to reduce the cloud kinetic energy from 10 eV to a He gas temperature of 300 K. The corresponding ion lifetime at this pressure will be adequate for most experiments and it is probably reasonable to consider He background pressures as high as $10^{-3}$ Torr.

B. Translational relaxation

Collisional relaxation of the ion kinetic energy is not only essential to achieve long ion lifetimes, but He collisions are also required to establish a well-defined cluster internal temperature by energy exchange with the vibrational levels. Measurement of ion translational energy relaxation is important because the kinetic temperature serves as the baseline for relaxation to thermal equilibrium for all other dynamic processes.
Collisional relaxation of the kinetic energy of trapped C$_{60}$ ions has been determined by measuring the shift of the ion cloud resonance frequency with He pressure. Before describing these measurements, let me consider the physical basis for such shifts and their detection. As the collisional cooling rate increases with pressure, the equilibrium cloud temperature $T_e$ decreases and the peak ion density $n_{i0}$ increases leading to stronger ion–ion interactions. Although a shift in ion cloud frequency has been related to ion–ion interactions in previous measurements, in principle these interactions will not introduce a frequency shift of the ion cloud center-of-mass motion excited by a uniform field. It has been suggested that the observed shift may arise from the nonuniformity of the excitation field which is applied to detect ions. However, a frequency measurement associated with a single ion or ensemble of ions having a resonance different from the surrounding cloud will experience a shift as the cloud density increases. This can occur for the case of two different atomic ions, such as the detection of H$_2^+$ within a cloud composed of He$^+$ as discussed in Ref. 36. In the experiment described here, detection occurs by tuning through the ion cloud linewidth which can be inhomogeneously broadened by ion–ion interactions. Each individual ion trajectory traverses a different volume of the nonuniform ion cloud density. Ion–ion interactions will introduce an average force on each ion tending to expand the cloud. This force can be estimated by considering the $z$ component of the equations of motion for an ion interacting with a spherical Gaussian charge density $\rho(r')$ in a mean field approximation

$$ \frac{d^2z}{d\tau^2} + (a_z - 2q_z \cos 2\tau)z = \frac{2}{\Omega} \frac{1}{M} F_z $$

$$ = -\frac{2}{\Omega} e \frac{\partial}{\partial z} \int \frac{\rho(r')}{r} d^3r', $$

(19)

where $|r| = \sqrt{x^2 + y^2 + z^2}$ is the ion position measured from the center of the trap. For the purposes of this discussion, the charge density can be approximated by an ion distribution in the trap potential $\phi_T$ given by Eq. (3) at an equilibrium temperature $T_e$, $\rho(r') = e n_{i0} \exp(-e\phi_T/kT_e)$ where $n_{i0}$ is the peak ion density. The average force $F_z$ is then obtained by transforming the three-dimensional integral to a convolution integral and applying several variable transformations which reduce $F_z$ to the following one-dimensional integral:

$$ F_z = e^2 n_{i0}^4 \pi^2 \int_0^1 u^2 e^{-(u^2 r^2 / 2a_z^2)} du, $$

(20)

where $a_z^2$ is the variance of the ion distribution. For an ion having a trajectory near the center of the cloud, $r \ll a_z$, $\rho(r')$ is approximately constant and the force is approximately $F_z = (4\pi/3)e^2 n_{i0} a_z = K_z$. This trajectory will experience the maximum effect of the ion–ion interactions. In this case, the ion resonance given by Eq. (4) becomes

$$ \omega_z^2 = \frac{\Omega^2}{2} \left[ a_z - \frac{2}{\Omega} \frac{K_z}{M} + \frac{q_z^2}{2} \right], $$

(21)

and approximating $(\omega_z^2 - \omega_{z0}^2) \approx 2\omega_z(\omega_z - \omega_{z0})$ yields the frequency shift

$$ \Delta \omega_z = \frac{(4\pi/3)e^2 n_{i0}}{\omega_z M}. $$

(22)

The single ion resonance associated with this trajectory is shifted to lower frequency and this shift increases linearly with the peak ion density $n_{i0}$. Trajectories having $r \gg a_z$ sample the tail of the Gaussian ion cloud distribution and result in smaller resonance shifts but are still proportional to $n_{i0}$. Finally, the distribution of single ion trajectories within the cloud leads to a distribution of resonance frequencies. Although this explanation for the frequency shift may be somewhat over simplified, the current experiment presents strong evidence that the observed shift depends linearly on the peak ion density.

Figure 15 displays frequency shift data for a C$_{60}$ cloud as a function of He pressure. Each data point is obtained from an independent ion loading but under identical conditions so that the ion number was $\sim 10^4$ ions at each pressure. Ions are loaded at $q_z \sim 0.35$ in a well depth of $eD_z \sim 21$ eV and remain there for 20 s during which the cloud relaxes to some steady state temperature $T_e$ depending on the He collision rate and the rate of rf heating. The cloud is then detected with a minimal $V_{dc} \approx 20$ mV rms and the value of the $V_{dc}$ bias for which the in-phase signal zero crossing occurs is measured to an accuracy of $\pm 0.2$ V. At each pressure, the space-charge-induced shift of the C$_{60}$ resonance is compensated by this value of the $V_{dc}$ bias voltage which calibrates the frequency shift as $1.8$ kHz/V using Eq. (4). The inset in Fig. 15 indicates the $V_{dc}$ shift to lower voltages corresponding to a resonance shift to lower frequency for increasing pressure. The resonance shift saturates with increasing pressure near $10^{-5}$ Torr.

As indicated in Eq. (22), the temperature dependence of the peak ion density is required to relate the frequency shift data to ion cloud temperatures. The ion cloud density...
\[ n_i(r, T_i) \] has been calculated as described in the Appendix for a spherical cloud of \( N \) ions at temperature \( T_i \) interacting via Coulomb forces. The solid curve in Fig. 16 represents the dependence of the peak density \( n_{i0} \) at \( r = 0 \) on \( T_i \) for \( N = 10^4 \) ions. As discussed in the Appendix, the maximum density limit \( (T \to 0) \) for \( 10^4 \) ions and \( q_s = 0.35 \) is \( (n_i)_{\text{max}} = 2.75 \times 10^8 \text{ cm}^{-3} \) as indicated in Fig. 16. For large ion–ion separations resulting in the limit of high temperature, the Coulomb forces can be neglected and then the ion cloud density approaches the Maxwell–Boltzmann limit as shown in Fig. 16. It is interesting to note that even at 300 K there is a significant difference between the calculated distribution and the Maxwell–Boltzmann limit.

The data have been plotted in Fig. 16 by positioning the saturation plateau at the 300 K point on the calculated density curve to within an uncertainty of ±10% introduced by the shift measurement. The peak \( ^{197}\text{Cn}^+ \) ion density corresponding to \( T_i \sim 300 \text{ K} \) is \( n_{i0} \sim 1.6 \times 10^8 \text{ cm}^{-3} \). This assignment of the saturation plateau assumes only that the shift is linearly dependent on \( n_{i0} \), and that the saturation of the shift data represents the cooling limit of the 300 K He background gas established by collisions with the trap electrodes. Saturation of the frequency shift could also result at the maximum density \( 2.75 \times 10^8 \text{ cm}^{-3} \), but this is only approached for a cloud temperature \( T_i < 50 \text{ K} \) as shown in Fig. 16. With assignment of the plateau at 300 K, the data closely follow the calculated density curve except at higher temperatures for which the ion number was measured to be slightly less than \( 10^4 \) ions. An ion temperature can be derived for each He pressure shown in Fig. 16 by first relating the peak frequency shift to density using \( n_{i0} \approx 1.6 \times 10^8 \text{ cm}^{-3} \) at 300 K as a calibration, and then scaling the measured shifts with the calculated \( n_{i0}(T_i) \) to obtain \( T_i \) at each pressure. This procedure provides the plot of frequency shift versus He temperature shown in Fig. 17(a) and the plot of temperature versus He pressure shown in Fig. 17(b).

The experimental frequency shifts were compared with theoretical estimates calculated\(^{49}\) from a set of equations similar to Eq. (19) but describing a spheroidal ion density with trap parameters appropriate for the current measurements. These calculations yield the average shift of the ion resonance for \( N = 10^4 \) \( ^{197}\text{Cn}^+ \) ions at kinetic temperatures of 300, 1000, and 5000 K. The calculated shift values are plotted in Fig. 17(a) and are in agreement with the experimental measurements. This calculation is expected to overestimate shifts for \( T_i > 300 \text{ K} \) since the space charge is not treated self-consistently. The \( ^{197}\text{Cn}^+ \) ion density \( n_{i0} \) near 300 K shown in Fig. 16 is a factor of 2–3 higher than previous measurements\(^{50}\) of translationally cooled \( \text{Hg}^+ \) ions which is consistent with a higher value of \( (n_{i0})_{\text{max}} \) expected for \( M = 720 \text{ amu} \).

The variation of \( T_i \) with helium pressure derived from the density analysis can be shown to result from the competition between rf heating and collisional cooling. A steady state temperature can be defined by

\[
\frac{d\langle E_{\text{KE}} \rangle}{dr} = -a_i \langle E_{\text{KE}} \rangle \frac{m_{\text{He}}}{M} \frac{T_i}{T_{\text{He}}} = 0, \tag{23}
\]

where \( \langle E_{\text{KE}} \rangle = 3k T_i \) is the average ion kinetic energy and other terms are defined as follows. The ion–ion collision rate\(^{51}\) given by
estimates the rate that rf energy is distributed among ions in the cloud. The rate at which the ion cloud absorbs energy from the rf fields is assumed proportional to the average ion kinetic energy \(13\) with the proportionality constant \(a_i\) where \(a_i \ll 1\). Ion–neutral collisions extract a fraction \((M_{\text{He}}/M)\) of the kinetic energy from the cloud at the rate \(\dot{\eta}_{\text{He}} = n_{\text{He}} \sigma_{\text{rel}}\) where \(n_{\text{He}}\) is the neutral number density, \(\sigma\) the collision cross section, and \(v_{\text{rel}} \approx v_{\text{He}}\) the relative velocity. Equation (23) yields an expression for the steady-state ion temperature

\[
T_i = 5.1 \times 10^{-9} \left(\frac{a_i}{\sigma}\right)^{2/3} \left(\frac{n_{\text{He}}}{P}\right)^{2/3}
\]

(25)

where \(P\) is in units of \(10^{-8}\) Torr. A linear fit of Eq. (25) to the data shown in Fig. 17(b) yields a value for the parameter ratio \((a_i/\sigma) = 5.3 \times 10^{10} \text{ cm}^{-2}\). For a hard sphere collision cross section using the C\(_6\) radius, \(\sigma = \pi (3.5 \text{ Å})^2\), the rf heating fraction is \(a_i = 2 \times 10^{-4}\). This fit indicates that the \(T_i\) vs \(p_{\text{He}}\) data derived from the assumption that the saturation plateau occurs at 300 K are consistent with a sequence of steady-state temperatures.

At the highest temperatures in Fig. 17(b), the steady state is not determined by the rates included in Eq. (23). As originally derived by Dehmelt, \(13\) a steady-state temperature in the limit \(p_{\text{He}} \to 0\) can be established by the rates of rf heating and evaporative cooling. In this steady state the parameter \(a_i\) is related to the ratio of ion kinetic energy and trap well depth given by \(0.85 \left(\epsilon D/k T_i\right) = \ln(a_i) + 2.75\). For \(a_i = 2 \times 10^{-4}\) and \(\epsilon D = 10.5 \text{ eV}\) at \(q_z = 0.35\), this predicts a temperature \(T_i \approx 9000\) K which is consistent with the temperature asymptote at low pressure shown in Fig. 17(b) and also with previous \(^{53,55}\) ion-cloud-temperature measurements for \(p_{\text{He}} = 0\). The measurements performed here suggest that cloud temperatures of \(\lesssim 100\) K can be achieved using a LN2 bath at He pressures of \(\sim 10^{-4}\) Torr for which long-trapped ion lifetimes can still be expected.

C. \(\text{C}_{60}^+\) collision-induced dissociation

The dissociation of \(\text{C}_{60}^+\) has been studied extensively \(^{30-39}\) within the last several years and Ref. \(59\) includes a thorough review of the current status. Values for the activation energy of the primary reaction step, \(\text{C}_{60}^+ \rightarrow \text{C}_{58}^+ + \text{C}_2\), obtained from photodissociation and electric impact dissociation of effusive beams extend over the range 4.5–10 eV. Collision-induced dissociation of \(\text{C}_{60}^+\) was also studied in a rf Paul trap \(^{22}\) and similar results were obtained for the distribution of dissociation products. The data presented in the current experiments are not sufficient to extract quantitative information about the dissociation reaction energetics which would require more accurate estimates of the ion kinetic energy and the fraction transferred to vibrational energy per collision. However, these measurements demonstrate the sensitivity of the detection technique to monitor the time evolution of dissociation products produced at dissociation rates orders of magnitude smaller than previously observed.

Collision-induced dissociation of \(\text{C}_{60}^+\) in the He background gas was observed to occur during detection scans over the ion line shape for detection amplitudes \(V_{\text{det}} \geq 450 \text{ mV}_{\text{rms}}\) as shown in Fig. 12. To examine this process in more detail, excitation and detection rf amplitudes were set independently so that dissociation was observed only when excitation was present. The ion cloud kinetic energy was increased by applying near-resonant rf excitation pulses of amplitude \(V_{\text{exc}}\) to the trap endcap during a lifetime measurement. This excitation of the \(z\) axial motion is repeated at 2 s intervals until a time \(t_m\) at which a line-shape measurement is taken to determine the mass distribution of the trapped ions.

### 1. Translational heating

The ion cloud is heated as the energy absorbed from the near-resonant rf field is randomized through ion–ion collisions. The following rate equation for the average ion kinetic energy includes the processes relevant to ion excitation

\[
\frac{d\langle E_{\text{KE}}\rangle}{dt} = \langle P\rangle - \frac{m_{\text{He}}}{\tau_{\text{evap}}} \frac{\langle E_{\text{KE}}\rangle}{\eta_{\text{He}}}
\]

(26)

The change in ion kinetic energy \(\Delta E_{\text{KE}}\) through resonant absorption is proportional to \(V_{\text{exc}}^2 n_{\text{He}}^2\). The power absorbed by the ion cloud is then proportional to \(\langle P\rangle \sim \Delta E_{\text{KE}}/\eta_{\text{He}} \approx V_{\text{exc}}^2 / n_{\text{He}}^2\). This absorption is accompanied by vaporization of fast ions from the tail of the Boltzmann distribution whose kinetic energy increases beyond the trap well depth \(E_0\). The evaporation rate \(1/\tau_{\text{evap}}\) is derived in Ref. \(13\) and is proportional to the ion–ion collision rate given by Eq. (24). The cloud is also cooled by ion collisions with the cold helium gas in which a fraction of the center of mass energy is converted into ion internal energy. The rf heating rate at frequency \(\Omega\) included in Eq. (23) is assumed to be negligible compared to the rates in Eq. (26). The relaxation processes in Eq. (26) drive the cloud toward thermal equilibrium at a temperature determined by the dominance of either ion–ion collisions or ion–neutral collisions. Although these rate processes can be roughly estimated, a quantitative comparison with data is hindered by the accuracy with which \(\langle P\rangle\) can be calculated as a result of uncertainties introduced by the presence of anharmonicity and ion–ion interactions. These relaxation rates will impose limits on the degree of dissociation and need to be considered in a more detailed quantitative analysis.

As \(\langle P\rangle\) heats the cloud kinetic energy, the loss of ions that accompanies evaporative cooling will be observed as a decrease in the ion lifetime. The ion decay is detected by applying \(V_{\text{det}} = 250 \text{ mV}_{\text{rms}}\) at bias \(V_{\text{dc}}\) values \(V_+\) and \(V_-\) corresponding to \(\pm 7 \text{ kHz}\) off resonance as depicted in Fig. 18. The excitation amplitude \(V_{\text{exc}}\) is also applied off resonance, by \(\sim 700 \text{ Hz}\) as shown in Fig. 18. The decay of trapped ions in the presence of translational heating is shown in Fig. 19 for a He pressure of \(2.4 \times 10^{-5}\) Torr. As the \(V_{\text{exc}}\) amplitude increases from 0 to 900 \text{ mV}_{\text{rms}}, the lifetime is observed to decrease from 22 to 0.5 min. Ion excitation pulses extend throughout the decay measurement and at this He pressure the ion–neutral collision rate of \(\sim 30 \text{ s}^{-1}\) does not relax the ion translational energy between excitation pulses. The de-
FIG. 18. The rf excitation and detection pulses in dissociation experiments are applied at the frequency positions shown on the C60 line shape. The width and repetition period of the excitation pulses are shown on the right.

cays shown in Fig. 19 are nearly exponential and exhibit a complete loss of C60 ions at the higher $V_{\text{exc}}$ amplitudes. Under these conditions, the dominant C60 loss results from the evaporation of energetic ions and the average translational energy is established by ion–ion collisions.

2. Dissociation mass spectra

Experimentally, we detect the evolution of Cn+ as energy is deposited by collisions in the ground state vibrational levels. Figure 20 displays mass spectra obtained from the in-phase detection component by a single scan over the bias range of $V_{\text{dc}} = \pm 8$ V which covers C60 to C50. An initial ion number of $N_{0} \approx 7 \times 10^{3}$ was stored in a He background pressure of 2.4 x 10^-6 Torr. Each spectrum was taken after $t_m = 420$ s with $V_{\text{det}} = 250$ mVrms and was obtained by a single scan over the mass range taking 40 s with an equivalent noise bandwidth of $\sim 3$ Hz. The signal detected for $V_{\text{dc}} = -3$ V at frequencies below the C60 resonance displays the noise level (S/N = 1). By comparison, the stronger ion signals for $V_{\text{dc}} > 0$ V show $2\leq \text{S/N} = 5$. For display purposes, the spectra shown in Figs. 20 and 21 have been minimally smoothed (three-point) These spectra were taken for increasing values of $V_{\text{exc}}$ as indicated in Fig. 20. The effective rf amplitude exciting the ions is actually $(\omega_{\text{rf}}/\Omega) V_{\text{exc}} V_{\text{rms}} / 10$ for the sideband excitation used here. In the presence of this excitation, the C60 lifetime $\tau_{\text{ion}} < t_m$ for all spectra except $V_{\text{exc}} = 200$ mVrms. Although the parent C60 ion has decayed away, the C4+ daughters have not been excited and exhibit long lifetimes, comparable to cold C60. This is consistent with previous results56 which measured formation of C5+ peaked at small center of mass kinetic energy $\sim 0.2$ eV.

Figure 21 displays another set of mass spectra obtained at a lower He pressure of 8.8 x 10^-7 Torr with excitation applied on the low frequency side on the C60 line shape to avoid the dissociation products. The lower collision rate at this He pressure leads to an increased excitation rate as well as slower relaxation of the C60 kinetic energy. As a result, the C60 lifetime was considerably decreased and as a consequence the mass spectra were recorded after $t_m = 180$ s. These mass spectra exhibit clear differences from those taken at higher He pressure. Figure 21 indicates that the C60 daughter dominates the C60 product at all excitation amplitudes. In previous trap measurements22 of C60 collisional dissociation, the C60 daughter is similarly produced as a larger fraction compared to C58. The basis for the different product distributions shown in Figs. 20 and 21 has not been determined. In both Figs. 20 and 21, the position of the various dissociation products agree well with the dashed vertical lines which indicate the predicted positions of the daughter ions. A closer examination of the resonance positions in Fig. 20 does indicate slight shifts of the frequency resulting from heating of the ion cloud.

The total dissociated fraction of C60, $N_{\text{p}}/N_{0}$, is estimated from the spectra in Fig. 20 by off-resonance measurements on the line shape of each dissociation product. The
The mass spectra of C& parent ions are shown for increasing rf excitation amplitudes V$_{\text{exc}}$ (mV$_{\text{rms}}$) given on the left. Spectra were obtained at a helium pressure of 8.8X 10$^{-7}$ Torr. Note that the vertical axis scales for the spectra obtained at 600–800 mV$_{\text{rms}}$ are identical and differ from the scales for the 400 and 500 mV$_{\text{rms}}$ spectra. The dashed vertical lines indicate the predicted positions of dissociation products.

The number of ions associated with each individual product range from 200 to 500 ions. The dissociated fraction is plotted in Fig. 22 versus $(V_{\text{exc}})^2$ which is proportional to the gain in kinetic energy during ion excitation. The error bars in Fig. 22 correspond to a ±25% measurement uncertainty in N$_r$, resulting from the small C$_{60}^+$ ion numbers and overlap in the wings of adjacent line shapes. The data shown in Fig. 22 exhibit a peak for V$_{\text{exc}}$=600 mV$_{\text{rms}}$ which can also be observed in the sequence of mass spectra. This peak results for the excitation amplitude at which the C$_{60}^+$ loss rate due to kinetic energy heating reduces the C$_{60}^+$ source before vibrational heating can reach a level that the dissociation rate is sufficient to increase N$_r$ during the time $t_m$. Then, the increase of N$_r/N_{60}$ with excitation amplitude up to 600 mV$_{\text{rms}}$, results from higher ion vibrational energy through collisions with increasingly energetic ions. But for higher excitation amplitudes, Fig. 22 shows a decrease in N$_r$ consistent with the reduced C$_{60}^+$ lifetimes in the trap observed at higher V$_{\text{exc}}$ in Fig. 19. This suggests that the dissociation process is occurring throughout a significant fraction of the lifetime of the parent species.

This conclusion is further supported by measurements taken at He pressure of 1.9X 10$^{-6}$ Torr for constant excitation amplitude V$_{\text{exc}}$=600 mV$_{\text{rms}}$ but at different time intervals between excitation pulses varying from 2 to 12 s. The ion lifetime increases as the interval increases since the collisional relaxation rate of the kinetic energy competes more favorably as the excitation rate is reduced. The lifetime measured for a 12 s interval is equal to the lifetime observed in the absence of excitation. This is comparable to the relaxation time constant of the kinetic energy estimated to be ~8 s at this pressure. In addition, C$_{60}^+$ dissociation becomes less significant for longer intervals and is completely absent at 12 s. These data further suggest that the collision induced dissociation appears to be occurring continuously throughout the C$_{60}^+$ lifetime rather than for short periods after each excitation pulse.

The dissociation data indicate that slow rate processes on the order of ~100 s$^{-1}$ can be measured with these detection techniques. On these time scales, radiative processes have been shown to be an important vibrational relaxation mechanism. In order to extract instantaneous dissociation rates, information about the radiative rates of C$_{60}^+$ infrared transitions is required to model the vibrational energy kinetics. as well as more accurate estimates of the ion kinetic energy and the fraction transferred to vibrational energy per collision.

V. SUMMARY AND EXPERIMENTAL POSSIBILITIES

This paper has introduced rf trap techniques which have been designed to confine heavy ions in a controlled environment in which the kinetic and vibrational temperature can be prepared for spectroscopic and collisional experiments. Trapped ion lifetimes have been achieved over interesting experimental time scales in the presence of background gas collisions. In situ detection of ~200 ions with S/N ~3 has been demonstrated to provide a unique capability to measure slow rate processes. The kinetic energy of cluster ions in the 1000 amu range can be relaxed to the temperature of a background helium gas at 300 K in times ~10 s. Collision-induced dissociation of C$_{60}^+$ has been measured evolving over a time scale of ~100 s. These measurements provide confi-
dence that quantitative measurements of trapped cluster ions as a function of vibrational temperature can be extended to atom–cluster collisions and excited state spectroscopy.

Low energy collisions of metal cluster ions with atoms or molecules are of particular interest. The possibility of measuring the growth of metal clusters by the sequential addition of a single atom provides an opportunity to study the occurrence of “magic number” clusters. In this case, the cross section for atom-cluster association or the lifetime measuring the growth of metal clusters by the sequential assembly of the computer interface for controlling electron- ics and acquiring data. One of the authors (J.H.P.) would like to thank Abraham Szöke for thoughtful discussions and careful review of the manuscript. Finally, let me thank the referee for a critical and helpful review of the manuscript, and for suggesting additional references of recent trap research and technology. This research was fully supported by The Rowland Institute for Science.

APPENDIX: ION CLOUD DENSITY

The ion cloud density has been calculated for a spherical cloud of N ions at temperature $T_i$ interacting via Coulomb forces. The total potential acting on a trapped ion can be written in terms of the secular coordinates as $\Phi = \phi_s + \phi_r$: a sum of the potential that is due to ion space charge $\phi_s$, and the effective trap potential $\phi_r$ defined by Eq. (5). The space charge potential satisfies Poisson’s equation $\nabla^2 \phi_s = -4\pi e \rho$, for the ion density. In thermal equilibrium, the ion spatial charge becomes negligible ($\phi_s \rightarrow 0$) and, as shown by Eq. (5), the density will become Gaussian with a mean square space charge radius $\left\langle r^2 \right\rangle = \frac{2}{9}\left\langle r_i \right\rangle^2$. The parameter $\lambda$ in Eq. (A1) is related to $\left\langle r^2 \right\rangle$ by

$$\lambda = \left\langle r^2 \right\rangle / \left\langle r_i \right\rangle^2 = \frac{3}{4\pi e D r_i} \left\langle r_i \right\rangle.$$  

The critical radius is defined by the spherical volume for which $\lambda = \lambda_c$ and this yields a maximum density given by $n_{i,\text{max}} = 3D / 2\lambda_i^2$. In the high temperature limit, space charge becomes negligible ($\Phi \rightarrow \phi_r$) and, as shown by Eq. (5), the density will become Gaussian with a mean square trap potential.

29 (a) M. A. Armitage, J. E. Fulford, N.-H. Duong, R. J. Hughes, and R. E. March, Can. J. Chem. 57, 2108 (1979); (b) J. E. Fulford, D.-N. Hao, R. J.
Although an ion cloud in a trap having $r_0 = 2r_0$ will form an oblate spheroid with minor axis in the $z$ direction, we simplify the calculation by assuming a spherical ion distribution. This will introduce a constant factor which will not change the scaling of ion density with helium pressure in the data analysis.