Ion/molecule reactions, mass spectrometry and optical spectroscopy in a linear ion trap

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Abstract

A linear-geometry, radio-frequency, quadrupole ion trap has been developed to generate, purify, accumulate and study atomic and molecular ions in the gas phase. By employing a trap-based system, both reactant and product ions can be stored for significant time periods, which can both enhance the efficiency of gas-phase reaction processes and create an environment to observe collision products after vibrational and rotational excitations have had time to relax. Relaxation occurs via viscous cooling with a dilute buffer gas or via laser cooling. Furthermore, the setup is particularly useful for performing optical spectroscopy on the trapped ions.

Atomic and molecular ovens are used to generate thermal beams of neutral species, which are then ionized by electron bombardment. The ions can be trapped, or they can be collided with neutral molecules (e.g. C₆₀) under well defined experimental conditions. The collision energies are variable over a range from nearly 0 to 200 eV. This feature makes possible studies of complex formation, charge transfer and collision-induced fragmentation as a function of kinetic energy. A wide range of masses of up to 4000 u can be stored and manipulated with this apparatus.

Two mass spectrometric techniques for the analysis of trapped ionic species are presented. In one method, parametric excitation of the secular motion is used to generate mass spectra with resolutions as high as 1 part in 800 with a simple experimental setup. The second method is capable of quickly generating mass spectra over the entire range of trapped masses, but has only moderate resolution. These spectra are generated by linearly sweeping the rf-trapping voltage to zero and detecting ions as their trap depth falls below a threshold value. In the trapping volume, which is 10 cm in length and 200 µm in diameter, 10⁶ ions can be loaded and stored, corresponding to an ion density above 10⁸ cm⁻³. Such densities facilitate spectroscopy of the stored ions. Both laser-induced fluorescence and photodissociation measurements have been carried out with a cw laser system providing near-infrared, visible, and ultraviolet beams. Absolute, total cross-sections and branching ratios of the photodissociation of MgC₆₀⁺ have been measured. © 1998 Elsevier Science B.V.

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1. Introduction

Gas phase, energy-resolved investigations of reaction products remain an experimental challenge in both physics and chemistry. Considerable efforts, therefore, are ongoing in this field due to the strong interest in many different reactions stemming from their dominant role in research areas such as the atmospheres of planets and stars, interstellar media, and plasma and fusion research. The pursuit of a fundamental
theoretical understanding of ion–molecule processes in these areas has resulted in a need for data to be used in the development of models. These models are not only for simple two-, three- and four-particle systems, but also for clusters and large molecular complexes such as are found in the various fullerene structures. The ideal apparatus for generating the required data should allow for a state-specific study of the reaction dynamics of the collisions over a wide range of collision energies. Although there have been significant improvements in the last four decades, most of the presently available experimental instruments were designed for the solution of specific problems, with few being ideally suited for answering many or all of the questions of interest. Furthermore, in nature the interaction of atoms and molecules with photons often plays a key role in understanding specific properties and reaction processes. In this situation optical spectroscopy provides a powerful general tool to advance the present knowledge due to its high sensitivity, state specificity, and ability to initiate photon-induced processes.

This paper describes a compact ion trap system suitable for the generation, purification, storage and analysis of ionic collision products, all carried out in the gas phase. The analysis techniques include both mass spectrometry and optical spectroscopy. The apparatus is depicted in Fig. 1. In general, ion/molecule apparatuses fall into one of two general categories, guided ion beams [1–3] or ion traps [4] of the Penning [5,6] or Paul [7–10] varieties. The present apparatus is designed to exploit the best features of each by combining the guided ion beam arrangement with ion trapping techniques in order to design and construct an apparatus which both accumulates and stores selected ionic collision products at densities which can exceed $10^8 \text{ cm}^{-3}$ for arbitrarily long time periods. The main component is a linear, radiofrequency (rf), quadrupole ion trap where particle collisions, accumulation, and product detection are carried out. In addition, the apparatus includes ion and atom beam generation.

Fig. 1. Photograph of the linear-geometry ion trap apparatus mounted on its vacuum flanges showing the trap electrodes, atomic and molecular ovens, and electron guns. The external ion source is located at the right end of the trap and can be identified by its curved focusing electrode. The scale of the photo is indicated by the 15 cm total length of the trap electrodes.
sections. The collision energy can be controlled over a variable range. The lower limit is below 3 eV and depends mainly on the ion generation technique. The maximum ion kinetic energy depends on the region of interest, and is presently 200 eV. In general, all ionic collision products within a selected mass range will be collected in the trap due to its large well depth, which can reach several hundred eV for light ions. In addition, by either employing a mass-selective parametric excitation of the ion’s harmonic motion with a suitable quadrupole field, or varying the stability regime of the trap, both of which are dependent on charge to mass ratios, it is possible to filter out unwanted ionic species. In this way, pure samples for analysis, as well as mass-resolved spectra of the trap population, can be generated. The former technique yields high resolution spectra over a narrow mass range, while the latter approach produces lower resolution spectra that cover the entire range of trapped masses in a single short sweep. Parametric secular excitation mass spectrometry is introduced as a complementary alternative to the more traditional techniques of quadrupole mass spectrometry [11], Fourier transform ion-cyclotron resonance mass spectrometry in Penning traps [6,12–14], or time-of-flight mass spectrometry [15,16]. The accumulated atomic and/or molecular ions can be stored for periods as long as several hours. This permits systematic optical spectroscopic measurements, such as laser-induced fluorescence (LIF) or photodissociation of vibrationally and rotationally relaxed species, to be carried out. LIF can be observed with a sensitive photon detection system which is capable of single ion detection. In general, both absolute and partial photodissociation cross-sections have been studied by employing both mass spectrometry and optical spectroscopy. Both were demonstrated in fragmentation studies of MgC$_{60}^+$, and were shown to permit the measurement of very slow dissociation rates. In these experiments, the spectral resolution was improved by cooling the translational ion motion with viscous drag forces in a dilute buffer gas. Modern laser cooling techniques such as Doppler cooling were also demonstrated with atomic ions, and should, in addition, be effective for cooling molecular ions via sympathetic processes [17]. Finally, by accumulating projectile ions inside the trap, it was possible to study multibody collision processes. Experiments involving collisions between C$_{60}$ fullerenes, electrons, Mg$^+$ ions and noble gas atoms have been used to demonstrate the operation of this system. Detailed analysis and more complete data of this work are presented elsewhere [18–21].

2. Theory of ion manipulation with electric fields

2.1. Ion storage in rf quadrupole fields

The theory of trapping charged particles with oscillating electric quadrupole fields is well documented [22,23], and therefore this discussion will be restricted to the case of an ion trap with a linear geometry. The conceptually easiest approach is a treatment of the particle’s equation of motion in the adiabatic approximation [24]. This allows for the separation of the motion into two parts: a fast driven oscillation at the frequency $\Omega$ of the applied rf field, the so-called micromotion, and a slower, secular motion within the effective pseudopotential of the trapping field. The amplitude of the micromotion increases with increasing radial displacement $r = (x^2 + y^2)^{1/2}$ from the central, longitudinal Z-axis, where the X- and Y-axes are the transverse axes of the quadrupole field. The secular amplitude depends on the kinetic energy of the stored ions and is in this way temperature dependent.

For a particle with charge $ze$ and mass $m$, moving in a two-dimensional oscillating quadrupole field $\psi$ of the form

$$\psi(x, y, z, t) = \psi(t) \frac{x^2 - y^2}{2r^2_0}$$  

(1)
\[
\psi(t) = U_{rf} \cos \Omega t,
\]

the time-averaged pseudopotential \( \Psi \) is harmonic and is given by
\[
\Psi(\rho) = \frac{z^2 e^2 U_{rf}^2 \rho^2}{4m \Omega^2 r_0^2} = \frac{\rho^2}{r_0^2}
\]

The depth of the trap is denoted by \( \Psi_0 \), and \( 2r_0 \) is equal to the distance between two non-adjacent quadrupole trap electrodes. The motion of the ion in the Z-direction is that of a free particle.

The oscillatory secular motion of the ion in the pseudopotential is mass dependent, with the frequency of the motion given by
\[
\omega_{sec} = \frac{1}{\sqrt{8}} q \Omega
\]

where the dimensionless parameter \( q \), containing dependences on particle mass and rf field parameters, is given by
\[
q = \frac{2 \frac{z}{m} \frac{e U_{rf}}{\Omega^2} \rho}{r_0^2}
\]

The complete theory of this problem [22,23] is expressed in terms of the well known Mathieu differential equation and also includes a second parameter, \( a \), related to an additional DC term in Eq. (2). However, the experiments reported here did not employ a quadrupole DC voltage, and thus the parameter \( a \) has been set to 0 and does not appear in eqns (3)–(5) for ease of understanding.

The fundamental requirement for stable trapping is that the amplitude of motion of the particle must be finite and limited. The general solution of the Mathieu equation reveals the existence of both stable and unstable solutions, determined exclusively by the parameters \( q \) and \( a \) (see for example Figs. 2 and 3 in ref. [23]). In other words, the parameter space of \( q \) and \( a \) is subdivided into regions of stable trapping and unstable particle motion. The region of stability used in this work is the one closest to the origin, and requires \( |q| \leq 0.908 \) for \( a = 0 \).

A lower limit on the potential depth of the trap arises from the experimental goal of accumulating the products of ion–molecule collisions. Potential depths below the kinetic energy of the collision products allow the products to escape. In the case of a collision between a heavy, evaporated molecule (e.g., \( \text{C}_6\text{O} \)) with low kinetic energy, and an atomic ion \( \text{A}^+ \), an estimate of the kinetic energy of the product complex \( \text{AC}_6\text{O}^+ \) is given by
\[
E_{\text{kin}}(\text{AC}_6\text{O}^+) = \frac{1}{2} m_{\text{AC}_6\text{O}} v_{\text{AC}_6\text{O}}^2 = \frac{1}{2} \frac{m_{\text{A}}}{m_{\text{AC}_6\text{O}}} v_{\text{A}}^2
\]

As an example, collisions between thermal \( \text{C}_6\text{O} \) and \( ^{24}\text{Mg}^+ \) result in only 3.2% of the collision energy being transferred into kinetic energy in a generated \( \text{MgC}_6\text{O}^+ \) complex. The rest of the collision energy produces internal excitation of the complex. Therefore, for the accumulation of these complexes, it is sufficient to generate a pseudopotential with a depth for \( \text{MgC}_6\text{O}^+ \) in excess of \( m_{\text{Mg}}/m_{\text{MgC}_6\text{O}} \) times the collision energy. At the same time it is essential to quickly remove the excess internal excitation energy, for example by viscous collisions with a buffer gas, in order to prevent the complex from disintegrating.

The above discussion describes the two-dimensional dynamic trapping in the X- and Y-directions by an oscillating rf quadrupole field. Additional confinement in the Z-direction could also be achieved by oscillating inhomogeneous fields, but is impractical in the present case, since it does not allow for the efficient injection of projectile ions into the trap or the creation of a well defined collision energy. The alternative approach, which was developed here, is to use static fields to confine the ion’s motion in the Z-direction. Two DC-confinement electrode arrangements are employed. In one, confinement is achieved by subdividing the four quadrupole trap electrodes into three adjacent, but electrically isolated, segments. Different DC potentials are then applied to the three segments such that a square well potential is created in the Z-direction.
(Fig. 2(b)). It should be pointed out that the generated confinement fields are not quadrupolar in nature, since the same DC potential is applied to all four electrodes in one segment. The other approach is to confine the ions in the Z-direction by applying DC potentials to small endcap electrodes suspended at either end of the trap. Both arrangements allow for selectivity between positively and negatively charged particles, a freedom which is not present with charge-insensitive rf trapping fields. In the present experimental set-up, a combination of these fields is used to provide efficient injection of ions into the trap, as is described in Section 3.

2.2. Mass spectrometry and mass-selective expulsion

Most of the trapping parameters are mass dependent. Thus the rf-quadrupole ion trap is a natural mass filter. This mass selectivity can be used either to purify stored samples by expelling unwanted masses or to record accurate mass spectra by detecting the masses as they are expelled. This section will outline three mass-selective expulsion techniques which have been utilized, in combination or individually, for a variety of different purposes.

The first technique is the approach common to many quadrupole mass spectrometers, in which the trap stability parameters are varied to move selected masses from the stable to the unstable regions of \((q, a)\)-parameter space (see Fig. 2 in ref [23]). As stated earlier, for \(a=0\) the stability region nearest the \((q, a)\) origin requires \(|q| \leq 0.908\). Therefore, for a given \(U_{rf}\) and \(\Omega\), all masses given by

\[
\frac{m}{z} < 2.203 \frac{eU_{rf}}{r_0^2 \Omega^2}
\]

are destabilized out of the trap. This lower mass limit could be used to take mass spectra by gradually increasing \(U_{rf}\) or reducing \(\Omega\), although other techniques were employed in this system. It was used in this work to set a lower limit on the masses collected by the trap. Due to the inverse mass dependence of \(q\) (see Eq. (5)), there is a low mass threshold below which masses escape from the trap, but no upper limit when \(a=0\). Employing an additional quadrupole DC voltage \((a \neq 0)\) can be useful because it results in an upper limit on the ionic mass for stable trapping. Only those masses between the low and high mass limits are trapped. By operating the trap near the tip of the stability region, trapping of a narrow range of masses is permitted. This is the technique used in an rf quadrupole mass filter. However, it is not the appropriate method to determine a mass spectrum from samples trapped for long time periods, because the case of a \((q, a)\) combination close to the border of the stability regime results in strong rf heating, which leads to very short storage times [25].

The second technique, referred to as q-scanning, has been developed to obtain low resolution mass spectra over the complete range of masses stored in the trap in a short time. The method uses a perturbative static electric field to provide a lower limit to the stability region of \((q, a)\)
parameter space, which corresponds to an upper limit on the stored masses. Although a complete theoretical description of this method would require more complexity than the Mathieu equation model, it is possible to provide a rough theoretical description in terms of the stability diagram for the Mathieu equation and the related pseudopotential. In the preceding discussion it was stated that for \( a = 0 \) there is no lower limit on the stability diagram and that masses remain stable as \( q \) approaches 0. However, the trap depth is also proportional to \( q \) and thus, at low \( q \)'s, any small perturbing forces can empty the trap. For example, if a homogeneous electric field \( e \) is applied perpendicular to the \( Z \)-axis, then an estimate for the threshold above which masses are pulled out of the trap is expressed by the condition that the force due to the external field exceeds the force from the trapping field. Combining this condition with Eq. (3) yields the following approximate lower bound for ion expulsion:

\[
\frac{m}{z} > \frac{1}{2} \frac{eU^2}{\varepsilon_0 \Omega^2}.
\]  

This approach can be used to set an upper limit on the collected masses, or it can be used to take a mass spectrum by detecting the ions pulled out of the trap as the parameters \( U_0 \) or \( \Omega \) are varied. The generated spectrum will always appear from high to low masses. Although the resolution with this approach is only moderate, the technique is valuable because of the wide mass ranges which can be quickly observed. Moreover, in the present work the electric field \( e \) is simply generated by negatively biasing the front cathode of the external ion detector, as is described further in Section 3.

The third technique has been implemented to yield the highest resolution mass spectra that we generate with this apparatus, and is referred to as secular scanning. Rather than exploiting the stability thresholds in \((q, a)\)-parameter space, this approach is based on direct, parametric excitation of the classical ion motion within the harmonic pseudopotential (Eq. (3)). An ion of mass \( m \) oscillates at its secular frequency \( \omega_{\text{sec}} \) as given by Eq. (4). In principle, this oscillation could be excited by a homogeneous and/or a mixed multipoles, oscillating, electric field with frequency \( \omega_{\text{exc}} = \omega_{\text{sec}} \) (e.g. \[9,26,27\]), but the particular geometry of the trap electrodes suggests an alternative approach in which the ion motion is driven as a parametric oscillator. This requires a quadrupole excitation field with frequency \( \omega_{\text{quad}} = 2\omega_{\text{sec}} \), which can be generated simply by applying an additional oscillating voltage at frequency \( \omega_{\text{quad}} \) to the trap electrodes. Parametric excitation with a pure quadrupole field offers both theoretical and experimental advantages over the previously demonstrated mixed multipolar field excitation techniques [9,26,27]. One theoretical advantage is the possibility of modeling this method on the basis of the well known theory of parametric excitation [28], while a more practical advantage is the reduction in the number of possible resonances for an ion with a given charge to mass ratio. The mass which is selected with a given \( \omega_{\text{quad}} \) is

\[
\frac{m}{z} = \sqrt{2} \frac{eU_0}{\omega_{\text{quad}}^2 \varepsilon_0 \Omega^2}.
\]  

If the driving field is applied for a sufficient time period, the ion is driven out of the trap. High resolution mass spectra can be taken by slowly scanning \( \omega_{\text{quad}} \) and simultaneously counting the escaping ions. The resolution of this system depends both on the width of the parametric resonance [28] and on the frequency dependence of the energy deposition rate of the secular excitation process. The latter mechanism is highly dependent on the scanning rate during the collection of spectra. The secular excitation technique can also be used to drive any selected mass range out of the trap in order to purify a sample before experimentation by scanning \( \omega_{\text{quad}} \) over the required frequency range calculated by Eq. (9).
3. Experimental apparatus and general procedures

Fig. 1 shows a photograph of the linear ion trap which has an overall electrode length of 15 cm. The quadrupole electrodes are depicted in Fig. 2(a). They are constructed out of 6 mm diameter, non-magnetic, stainless steel, cylindrical rods. The ratio of the electrodes’ diameters to their diagonal spacing (5.22 mm) was chosen to be 1.146 in order to minimize higher order multipole contributions to the trapping field [29]. The trapping field used in this work had a maximum amplitude of about 3 kV at a constant frequency of 8.55 MHz. This feature permitted simultaneous transverse trapping of ions over the broad range of masses from 20 to over 4000 u, in a mass-dependent potential greater than 1 eV. For example, with a trap amplitude of 2 kV, the potential depths for $^{24}$Mg$^+$ and MgC$_{60}$ are 248 eV and 8 eV, respectively. In order to generate an rf trapping field with the required amplitude, the trap itself forms part of a resonance circuit. The circuit for operating the linear-geometry trap is shown schematically in Fig. 3. It includes the trap itself as the capacitor (~45 pF) which is combined with an inductor coil (~8 μH) mounted outside the vacuum chamber. The electrical connections to the trap are designed to allow for the generation of identical rf quadrupole fields on all three segments of the trap simultaneously while independent, non-quadrupole, DC fields can be applied to each segment. A quality factor $Q$ of about 80 has been achieved for the tank circuit by using a low-loss Teflon core for the inductor coil, as well as for the high voltage, low pass, filter coils. The rf amplitude is actively stabilized to a relative variation of less than 0.05%. This is required for high resolution mass spectrometry because the secular frequency is proportional to the rf amplitude.

In order to control the ion motion along the longitudinal axis of the trap, adjustable potential steps can be generated due to the subdivision of all four quadrupole electrodes into three adjacent but electrically isolated segments, each 50 mm in length. Applying different DC potentials to the resulting three trap segments (see Section 2.1) permits either the generation of a square well potential for ion storage or the acceleration (or deceleration) of ions moving from one segment

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Fig. 3. Schematic diagram of the trap and electric filtering circuits. The center of the diagram illustrates how the secular excitation field is applied only to the center segment of the trap.
to the adjacent one (Fig. 2). Potential steps as large as 200 eV are possible with the present experimental arrangement. The space between the electrodes of two adjacent trap segments is only 0.1 mm in order to minimize any perturbations in the quadrupole rf trapping field and to match the phase of the rf trapping fields in all three segments. The electrodes making up the left and right outer segments of the trap are held in position by macor spacers. However, the center segment electrodes are not mounted on their own spacers, but instead are connected directly to the ends of the outer electrodes with ceramic spheres which fit into holes drilled into the ends of the electrodes. These spheres hold the center electrodes in place while maintaining electrical isolation. This kind of suspension reduces the possibility of disturbances of the ion motion in the center segment resulting from surface charge buildup on the spacers. Simultaneously, the lack of large spacers in the central region of the trap allows for easier access to the trapped ions for measurement purposes. For instance, the opening angle of 25.4° for LIF detection is limited only by the electrode spacing and not by any mounting pieces.

The separation of the quadrupole electrodes into three adjacent segments only allows for trapping in the center segment. In order to introduce more flexibility to the apparatus by permitting trapping in the outer segments as well, additional longitudinal potential steps can be generated by biasing small tubular electrodes mounted on the central axis at either end of the trap. The use of tubular end electrodes also allows access to the central trap axis, which is useful for laser illumination of a trapped ion cloud collinear with the long axis. In these experiments, use of the tubular electrodes for efficient injection of neutral and ionic beams into the collision region of the trap prevents laser access directly along the trap axis. Injection of ions along the trap axis is ideal because the kinetic energy can be conserved only under conditions of zero rf field, which occurs along the trap axis inside and outside the trap when equal-amplitude rf fields are applied in the X- and Y-directions (see Eq. (1)). Experimentally, this condition was achieved by using one of the end-cap electrodes as a pick-up loop to measure the rf field on the central axis. The grounding point on the external inductor coil was adjusted while the antenna signal was minimized. Although, in the present setup, the atomic and molecular ovens block the trap axis, it is still possible to direct a laser beam off axis between the trap electrodes and irradiate ions stored in the center section of the trap. The selected angle of incidence of the laser beam with respect to the trap axis is 15°.

The method of choice for ion generation depends on the desired ion species and other experimental needs such as kinetic energy resolution or ion beam intensity. In general, any type of ion source could be employed in combination with this compact linear ion trap. There are two approaches which are generally used in our experiments. In the first one, ions are generated inside one of the outer trap segments by crossing a collimated atomic beam with an ionizing electron beam. The two beams are at right angles to each other and pass separately through the spacings between the trap electrodes. This is a simple technique to implement, but the ion collection and generation efficiencies are relatively low and there is little control over the initial kinetic energy of the trapped ions. The second method provides higher injection and generation efficiencies and better kinetic energy control, but requires additional focusing electrodes not required for the preceding technique. Ions are produced by electron bombardment of an atom beam outside one end of the ion trap. Focusing electrodes (Fig. 4, inset) biased with applied DC fields are used to inject the ions along the trap axis. In addition, the injection electrodes can be used to cut off the low kinetic energy fraction of the generated ions by generating a step potential at the input end of the trap. This simple ion source generated a broad kinetic energy spectrum peaked at approximately 4 eV, with a width of
about 6 eV (Fig. 4). The energy spread could be reduced to 4 eV with only the indicated loss in ion intensity by applying a 2.5 V cut-off potential.

The results presented in this paper required the generation of Mg$^+$, rare gas ions, and C$_{60}^+$. In the cases of Mg and C$_{60}$, pure samples were evaporated from miniature ovens, which can be heated to their operating temperature in only a few seconds. They consist of a small tantalum or nickel tubes (diameters of 1 or 1.8 mm, respectively) that are closed at one end, filled with the required material in solid or powder form, and then heated by passing a current of approximately 1.5 A through a 0.3 mm diameter tantalum wire which has been spot welded to the tube. The external Mg$^+$ ion source yields an ion current of up to 200 pA, but more typically was operated at 30 pA. Its performance was limited by a weak electron gun. Without mass filtration the purity of the generated Mg$^+$ ion beam was better than $10^{-3}$ due to the high purity of the source materials and the low background pressure inside the UHV chamber. Multiply charged atomic ions, such as Mg$^{2+}$, which may be produced in small numbers, are not stored in the trap, since their $q$-value is outside the chosen stability range of the rf trapping field. However, for other background ions the procedures outlined in Section 2.2 could be used to mass-selectively purify the sample. In addition, rare gas ions can be loaded into the trap. Rather than generating a collimated beam of rare gas atoms, the chamber is filled with a low partial pressure of the desired noble gas atom, and then ions are generated using the electron gun in the Mg$^+$ ion source with the Mg oven turned off.

With this trap it is possible to store more than $10^6$ ions, corresponding to an ion density exceeding $10^8$ cm$^{-3}$. The ions can be held in the trap for
periods as long as several hours. Once a sample has been loaded into the trap, probing and analysis can be carried out with mass spectrometry and/or laser irradiation spectroscopy. Quartz windows in the vacuum chamber allow ultraviolet (UV), visible (vis) and infrared (IR) radiation to probe the trapping volume. Resonance fluorescence was observed by high sensitivity photon detection using a collimating objective and a photomultiplier tube (PMT) positioned perpendicular to the trap axis (Fig. 5). Accurate imaging through suitably located spatial and bandpass filters was used to reduce the detection of radiation scattered directly from the trap electrodes and the walls of the vacuum chamber. These measures improved the signal to noise ratio to the point where single ions could be easily detected. Furthermore, the LIF signal was used to optimize the overlap of the employed laser beams with the trapped ion cloud. Specifically, Mg\(^+\) was used in these experiments because of its strong resonance line at 280 nm (\(^3\)S\(_{1/2} \rightarrow \(^3\)P\(_{3/2}\)). The first step was to load the trap with Mg\(^+\) so that the 280 nm laser beam path could be overlapped with the ions by maximizing the LIF signal. All other laser beams would then be overlapped with this path by precise matching of the pointing and focal position. The laser beams were all gaussian in cross-section, and were focused down to beam waists of 90–100 \(\mu\)m at the centre of the trapping volume. Light resonant with the \(^3\)S\(_{1/2} \rightarrow \(^3\)P\(_{3/2}\) transition of Mg\(^+\) was generated by doubling the output from a cw ring dye laser with a KDP crystal positioned inside an external intensity enhancement cavity. The system provided a maximum of 30 mW of UV power, but LIF from Mg\(^+\) was already observable with incident powers well below 1 mW.

The mass spectrometric techniques discussed in Section 2 require the detection of ions ejected from the trap. We employed a simple, compact set-up consisting of an electron multiplier tube (EMT) mounted adjacent to the trap electrodes and perpendicular to the trap axis. For high collection efficiencies it was displaced from the trap by merely 15 mm (Fig. 5). Positively charged ions were detected by biasing the front cathode of the EMT at \(-3.5\) kV. In the q-scanning mode, ions for which the potential depth is less than

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**Fig. 5.** Diagram of the ion trap inside its vacuum chamber indicating the laser beam path, the optical system for fluorescence collection and detection with a photomultiplier tube (PMT), and the position of the electron multiplier tube (EMT) for ion detection.
\( \sim 1 \text{ eV} \) are pulled out of the trap through the space between the trap electrodes. This threshold was measured empirically with a mixture of noble gases as a test sample. In the secular scanning mode the potential depth for the masses of interest was adjusted to be about 6 eV. The secular excitation field was then applied only to the center section of the trap (see Fig. 3) in order to eject ions mainly when they were close to the detector.

The entire beam generation, collision and storage apparatus is located in a single 30 cm diameter ultra-high vacuum (UHV) chamber. A 150 l s\(^{-1}\) turbo pump evacuates the system to a background pressure of \( 10^{-10} \text{ mbar} \). This vacuum is advantageous for both long storage times and for the generation of pure ionic particle beams. A gas filling system permits operation with a buffer gas background, typically helium, at a pressure of \( P \approx 5 \times 10^{-6} \text{ mbar} \). In this way it is possible to quickly cool the trapped ions to nearly room temperature. The cooling has a noticeable effect on improving the mass resolution of the trap spectrometry [30,31], due to the small initial energy spread of the cooled ions. For \( \text{Mg}^+ \) ions, laser cooling has also been successfully employed to reach the mK temperatures regime, demonstrating this as an alternative cooling technique for trapped atomic ions with spectrally narrow, optically accessible resonances. For molecular ions, sympathetic laser cooling is also a possible method for achieving similarly low sample temperatures [17].

Two networked personal computers are employed with this experimental system. The master computer is used to control the overall operation of the apparatus in order to repeatably load ionic samples into the trap, and to record the relevant experimental parameters, whereas the slave computer is solely tasked with collecting data from the PMT or the EMT. A careful sequence of oven preheat, ion loading, collisional cooling, analyse and pause times (see Fig. 6) is required to achieve well defined ion samples and repeatable collision conditions within the trap.

4. Experimental results and discussion

4.1. Mass spectrometry and mass-selective purification

Q-scan mass spectrometry was utilized to generate low resolution mass spectra covering large mass regions. Fig. 7 displays examples of such measurements with either a mixture of various noble gases or assorted ionic states of \( \text{C}_{60} \) loaded into the trap. An entire spectrum could be generated in one second and covered a mass/charge range in excess of two orders of magnitude. Experimentally, this is accomplished by scanning the trapping field amplitude down to zero. The sacrifice accepted in generating these large mass range spectra in a short time is that of poor resolution. The maximum observed resolution (\( m/\Delta m \) or \( z/\Delta z \)) was between 5 and 6 and was relatively mass independent over large mass ranges within the experimental domain of 20-1000 u. An advantage of this technique is that the positioning of the strongly biased EMT just outside the electrodes results in a very high collection efficiency. In this geometry the masses are actually pulled out of the trap by the EMT biasing field, with relatively few ions striking the electrodes as they leave the trapping volume.

The data in Fig. 7 demonstrate both the strengths and weaknesses of the simple theoretical model proposed for this system. Calibration of the abscissa (mass axis) of Fig. 7(a) employed the predicted quadratic dependence of the mass on the rf-field amplitude \( U_{rf} \). This figure shows that this model holds well for a single charge state, and further measurements have shown that a single mass calibration can hold over a range of masses as large as 20–800 u. However, it appears that the same does not hold true for samples with differing charge states. Although Eq. (8) suggests that the charge state of a q-scan ejected ion should have an inverse quadratic dependence on \( U_{rf} \), experimental measurements with multiply charged fullerenes indicated that different charges were ejected with a \( U_{rf}^{-1.38} \).
dependence. At present, we do not completely understand this empirically determined exponent, probably because the present model is too simplified to describe the process perfectly.

Figs 8 and 9 demonstrate mass spectra generated by secular excitation of mass-selected ions out of the trap. These scans took approximately 5–10 s to cover a mass range of 150 u by scanning the frequency of the quadrupole field driving the secular excitation. With this technique, only a limited range of masses can be analysed in one scan, since the detection efficiency depends on the mass. However, the mass range is easy to change by simply readjusting the experimental parameters between scans. This inconvenience is more than compensated for by the high resolution that is possible with this technique. Fig. 8 shows an m/Δm resolution of approximately 800 near 130 u. The resolution is mass dependent and drops off to about 250 at 720 u (Fig. 9). This resolution was demonstrated for a simple experimental geometry, and obvious improvements should make even higher values achievable (see ref. [32] for a high resolution ωexc = ωsec technique). The collection efficiency with this technique is over an order of magnitude lower than the q-scan technique. This lower efficiency results from the expulsion of many of the ions directly into the trap electrodes rather than towards the EMT. Both the mass and charge dependences of the excitation field given in Eq. (9) were confirmed experimentally.

Mass resolution and collection efficiency are rather sensitively dependent on the selection of the parameters of the driving field, i.e. amplitude and scan rate. The physical reason for this is the dynamic response of a trapped ion to the driving field. The ion can gain energy only at a certain rate, and it must build up the energy in order to escape from the trap. Therefore, there is an
Fig. 7. Mass spectra generated in the linear ion trap using the q-scan technique. Plot (a) shows a single scan of a mixed sample of neon, argon, krypton and xenon ions while plot (b) shows the spectra generated by averaging 10 scans of samples containing several charge species of fullerene molecules. Only the first four charge states of C\textsubscript{60} are observable due to the resolution limits of the system. The abscissa calibrations were based on \( m \sim U_0' \) and \( z \sim U_0^{1/3} \) for plots (a) and (b), respectively. At low mass, unresolved peaks of background ions are present.

optimum for the secular scan field amplitude and frequency scan rate and for the trapping potential depth. For example, if the driving field amplitude is too low the collection efficiency drops off sharply, while too high an amplitude can adversely effect the resolution. Typical parameters used in our work were secular scan amplitudes of 1 V\textsubscript{pp}, scan rates of 200 kHz s\textsuperscript{-1}, and trapping potential depths of about 6 eV. Under these conditions the driving field is only a small perturbation compared to the rf trapping field. For maximum resolution, a small number of ions should be cooled to near room temperature by viscous collisions in helium before scanning.

As mentioned in Section 2.2, the mass selective techniques have also been used to purify trapped samples. By increasing the trapping rf amplitude, the trap can be used as a high-pass filter by removing low masses as their \( q \)-values exceed 0.908 (Eq. (7)). This technique was used to efficiently remove Mg\textsuperscript{+} from samples of collisionally generated MgC\textsubscript{60}\textsuperscript{+}. Reducing the trap amplitude could be used to operate the trap as a low-pass filter as the large mass ions can be pulled out of the trap when their trapping depth becomes too low (q-scanning). Given a reasonably large mass separation, either one of these techniques can be used to give basically 100% purification with almost no loss of the ions of interest. If the desired result is to selectively remove ions of a mass which is close to the mass to be studied (e.g. remove C\textsubscript{60} while keeping MgC\textsubscript{60}\textsuperscript{+}), then secular excitation is the best approach due to its high resolution. However, for such close masses it has only been possible to achieve about a 10 to 1 improvement when small losses at the desired masses were required. It appears that collisional heating of the wanted masses or collective heating of the entire ion cloud may be limiting the efficiency of this technique. The best approach we have utilized so far is to scan the excitation frequency back and forth over a small mass range around the unwanted mass with parameters similar to those used for secular scans.

4.2. Collision reaction measurements

The experimental arrangement for typical ion-molecule collision experiments is shown in Fig. 2(c). A small molecular oven is positioned collinear with the trap axis at one end of the trap. The diffusive beam of molecules generated by this oven is densest at that end of the trap within the trapping volume. The ion source described in Section 3 is positioned at the opposite end of the
Fig. 8. Secular scan mass spectrum of a sample of Xe\(^+\) ions with a resolution of \(m/\Delta m \approx 800\), showing the presence of the major naturally occurring isotopes. A spectral fit based on the known natural abundances of xenon (inset) demonstrates a mass-insensitive detection efficiency over this limited range of masses. The main fitting parameter was the fraction of XeH\(^+\) present in the trapped sample (11%).

The molecular end of the trap has its potential lowered relative to the ion end, to accelerate the ions to kinetic energies of up to about 200 eV before they interact with the molecules. During the collision process several types of reactions have been observed including complex formation, charge transfer, and molecular fragmentation. In general, a helium buffer gas

Fig. 9. A mass spectrum of the products resulting from controlled energy collisions between Mg\(^+\) and C\(_{60}\). The collision energy was 60 eV and the products from fragmentation, charge exchange and complex-formation reactions are indicated.
at a pressure of roughly $5 \times 10^{-6}$ mbar is used to remove much of the energy which was transferred in the collisions into the internal degrees of freedom of the products, before analysis is carried out. For a small cloud of ions, this reduces the temperature of the vibrational and rotational population distributions to close to room temperature. The trap is set to collect almost all of the reaction products, so that mass spectrometry can be used to quantify the results (see Fig. 9).

In order to maximize control over the collision energy involved in the reactions, it is necessary to avoid trapping the reactant ions for times long enough to lose significant energy through scattering off of trapped ions, neutral molecules, buffer gas atoms, or background particles. Therefore, the trapping field amplitude is modulated in order to periodically destabilize the mass of the injected ions above and below the storage threshold given by Eq. (7) (Fig. 10). A typical frequency for this modulation was 5 kHz, with the amplitude of the modulation selected so that the ions were stable for about $2/3$ of the time. In this manner, the average lifetime is of the order of the time necessary for an ion to pass the length of the trap, which means that ions which do not react with the molecular cloud fall out of the trap. In our experiments, the higher mass reaction products were unaffected by this modulation. In this way it is possible to collect energy resolved collision reaction data of the type shown in Fig. 11. The drawback of this approach is that only a small fraction of the incident ions produce collision reactions, and the yields of the product ions are low. Naturally, this modulation technique is only applicable for the investigation of reaction products of sufficiently high mass relative to the injected ions.

In an alternative approach, the reactant ions are not removed periodically from the trap and their density increases with time, resulting in a strongly increasing rate of collisions. The advantage of this approach is an improvement of up to four orders of magnitude in the generation of product ions. However, the energy resolution of the measurement is lost and the ability to work at high collision energies is limited by the possibility of collisional destruction through fragmentation of the product ions held in the trap by the large number of high energy reactant ions also held in the trap. One other aspect of this technique is that the reactant ion densities can be increased such that multibody collision processes can be observed.

Several different types of collision studies have already been carried out with this apparatus and the details will be published elsewhere [19,21]. The following gives a brief compilation, with the goal of demonstrating the capabilities of the system rather than discussing the details of the physical processes themselves. Fig. 9 shows a demonstration of the types of reaction which are observable in the trap. Neutral C$_{60}$ molecules are impacted by accelerated Mg$^+$ ions. The mass

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Fig. 10. Plots of the time dependence of the q-factors for Mg$^+$ and MgC$_{60}$ ions during the amplitude modulation of the trapping field which is used to reduce the lifetime of the Mg$^+$ reactant ions in the trap during energy-resolved collision reactions. The line at $q = 0.908$ indicates the stability threshold of the trap.
spectrum demonstrates the presence of MgC\textsubscript{60}\textsuperscript{+} from complex formation reactions, C\textsubscript{60}\textsuperscript{+} from charge transfer reactions, and C\textsubscript{58}\textsuperscript{+}, C\textsubscript{56}\textsuperscript{+}, C\textsubscript{54}\textsuperscript{+} etc. molecules formed by fragmentation. All of these reactions have been observed as a function of collision energy (e.g. Fig. 11).

Another type of collision study exploits the storage feature of an ion trap. It is possible to perform collision experiments at very low reactant-ion kinetic energies such as $E < 100$ meV. Such an experiment consists of first loading the trap with reactant ions, cooling the ions to near room temperature (buffer gas cooling) or below (laser cooling), and then interacting the cold ions with neutral reactants. Data near 0 eV for collisions between Mg\textsuperscript{+} and C\textsubscript{60} have been obtained with this technique [19,21], and an example is shown in Fig. 11(b).

Finally, electron beams passing through the center of the trap have been used for electron impact studies such as single and multiple ionization and fragmentation of fullerene molecules. Results from this type of experiment are compiled in Fig. 12.

4.3. Optical spectroscopy

Two optical spectroscopic techniques have been demonstrated with this apparatus: resonance fluorescence and molecular photofragmentation. The techniques are not exclusive and in fact can be employed simultaneously, with the results often yielding complementary information.

The observation of laser-induced fluorescence (LIF) is a sensitive technique for the detection and analysis of trapped ions with a strong electric dipole transition. In fact, samples as small as a single ion have been observed [34,35]. In principle, the most effective approach for detecting LIF in a linear trap is to probe collinearly with the trap axis to permit the largest overlap between the trapped ion cloud and the laser beam. With the present set-up the positioning of the ion source and molecular oven prevent axial illumination. Instead, the probe beam travels at a 15\textdegree angle to the trap axis and probes only the central region of the trapping volume. Nevertheless, LIF from atomic ions is still observable and has been carried out using stored Mg\textsuperscript{+} ions (Fig. 14, inset). In principle, LIF spectroscopy of trapped molecular ions is possible, although to date the only molecules which have been loaded into the trap are fullerenes, whose gas-phase visible spectrum is expected to be very weak, with only solid and solution phase spectra known at present (e.g. [36]).

Laser photodissociation (LPD) studies have recently been carried out with MgC\textsubscript{60}\textsuperscript{+} complexes [18,20]. In these experiments, the trap is loaded...
with collisionally generated fullerene complexes and then exposed to dissociating laser radiation (see Fig. 5). We have two techniques for studying the photodissociation processes which have proven to be complementary in practice.

The first technique is widely applicable to a large variety of molecules. It is a direct mass spectrometric measurement of LPD made by examining the mass distribution of the samples after various laser exposures. These measurements yield the photodissociation rate of the compound of interest. A computer is employed to repeatedly load the trap with equivalent molecular samples. After each loading the trap is exposed to laser radiation for a chosen period of time. In general, four different periods are selected, with the trap content being measured after each. The number of undissociated ions is plotted semi-logarithmically as a function of time. In the case of the fullerene complexes, the MgC$_{60}^+$ count is plotted versus time and an exponential fit yields the rate constant for photodissociation (Fig. 13). Since the necessary parameters of the trapped sample and of the laser beam are known, it is possible to convert the rate constant directly to the absolute, total, photodissociation cross-section [18,20]. Measurement of the photodissociation cross-section as a function of photon energy can provide useful information on the molecular potential energy surfaces. One of the interesting features of this approach is that the long trapped lifetime of the ions permits the measurement of extremely slow reaction rates. Using exposure times of 0.5, 2, 4 and 6 s we have measured rates below 0.2 s$^{-1}$. Much longer exposure times are in principle possible and would permit the determination of even slower rates.

A related point is that the ability to measure exceedingly slow rates permits the use of very low cw-laser intensities such as, typically, below 100 W cm$^{-2}$. This in turn results in measurements of pure first-order reaction processes with no interference from multiphoton effects.

In addition to measuring total cross-sections, the present technique can also be utilized for the
measurement of photodissociation branching ratios. In the case of MgC$_{60}$, we have determined that the complex dissociates into either Mg$^+$ + C$_{60}$ or Mg + C$_{60}$. By simultaneously measuring the destruction of MgC$_{60}$ and the production of C$_{60}$, it was possible to determine the branching ratio for this reaction [20]. For accurate measurements care must be taken to avoid loading too many ions into the trap, which can result in the loss of the fragment ions after photodissociation.

The complementary technique for the determination of absolute photodissociation cross-sections is LIF measurements of LPD. This approach is less generally applicable as it requires reactions where a product ion has a strong LIF transition. However, it is a complementary and fast approach to the same measurement. Rather than monitoring the destruction of the reactant molecule, this technique monitors the generation of a product such as Mg$^+$ in MgC$_{60}$ $\rightarrow$ Mg$^+$ + C$_{60}$. This pump-probe approach requires two lasers, one to photodissociate the sample, and the second to probe for the appearance of the dissociation products. By monitoring the LIF as a function of time, a $(1 - e^{-\text{RT}})$ curve is observed (Fig. 14) which yields the reaction rate and thus the cross-section. This is done with a single loading of the trap rather than the multiple loading of the mass spectrometric approach. In order to measure slow reaction rates, good stability of the wavelength
and intensity of the probe laser is required. In addition, one must minimize any photodissociation by the probe laser by using low laser intensities, and by chopping the probe laser beam.

Finally, it should be noted that similar techniques should be equally applicable for laser photoionization measurements.

5. Conclusions

A compact experimental system for the generation, storage, purification and analysis of gaseous ionic complexes has been developed. The system can handle atomic and molecular ions as well as ionic complexes. Precise, mass-dependent, purification of the samples is possible, and the apparatus has been used to study both unimolecular (photodissociation, photoionization) and bimolecular (collisional) reactions. Control over most of the reaction conditions is possible. In our apparatus it includes the application of collision energies of up to 200 eV, and the use of buffer gas cooling and/or laser cooling to reach low reaction temperatures. In addition, the reactant ion and neutral densities and buffer gas pressures during the reaction process can be controlled. Analysis of the reactants and products is carried out with both mass spectrometric and laser spectroscopic techniques. Both low resolution, wide mass range, and high resolution mass spectrometric analysis is possible. The former relies on the manipulation of the q-parameters of the trapped ions, and the latter results from exciting the secular ion motion by parametric excitation. In addition, laser-induced fluorescence and absolute and partial photodissociation cross-section measurements have been carried out. The particular feature of studying ion–molecule complexes in their vibrationally and rotationally relaxed state has been carried out for the first time and is expected to find ongoing applications.
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