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QUADRUPOLE ION TRAPS

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    The extraordinary story of the three-dimensional radio-frequency quadrupole ion trap, accompanied by a seemingly unintelligible theoretical treatment, is told in some detail because of the quite considerable degree of commercial success that quadrupole technology has achieved. The quadrupole ion trap, often used in conjunction with a quadrupole mass filter, remained a laboratory curiosity until 1979 when, at the American Society for Mass Spectrometry Conference in Seattle, George Stafford, Jr., of Finnigan Corp., learned of the Masters' study of Allison Armitage of a combined quadrupole ion trap/quadrupole mass filter instrument for the observation of electron impact and chemical ionization mass spectra of simple compounds eluting from a gas chromatograph. Stafford developed subsequently the mass-selective axial instability method for obtaining mass spectra from the quadrupole ion trap alone and, in 1983, Finnigan Corp. announced the first commercial quadrupole ion trap instrument as a detector for a gas chromatograph. In 1987, confinement of ions generated externally to the ion trap was demonstrated and, soon after, the new technique of electrospray ionization was shown to be compatible with the ion trap. © 2009 Wiley Periodicals, Inc., Mass Spec Rev 28:961–989, 2009

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I. INTRODUCTION

The three-dimensional radiofrequency quadrupole ion trap, also sometimes known as the QUISTOR, (see Section IV.B), is only one of a family of devices that utilize path or trajectory stability as a means of separating ions according to the mass/charge ratio (m/z). Other members of this family are the quadrupole mass filter, cylindrical ion trap, rectilinear ion trap, digital ion trap, and the recent arrival upon the path stability scene, the linear ion trap. As a prelude to the discussion of the physics, development, applications, and simulation of the quadrupole ion trap, we first examine the historical development of the ion trap leading up to its emergence as a commercial instrument, and then we consider briefly the theory of ion confinement in quadrupolar devices. The aim of this prelude is to provide the reader with a general account of the development of the ion trap together with a theoretical background for the understanding of the operation

and improvements in performance of the ion trap. The story of the development of the family of devices that utilize path stability as a means of separating ions is fascinating because it is a departure from the development of sector instruments that were pioneered by Thomson (1913) and others. Yet despite the entrenchment of sector instruments in mass spectrometry, the quadrupole ion trap has brought about a revolution in this field during the past quarter of a century.

This review of quadrupole ion traps is not without bias because of the chosen emphasis in this series of reviews on "Ion Chemistry and Mass Spectrometry in Canada." Nevertheless, we strive to present a balanced account of the efforts of all those who have contributed to the development of the ion trap with, perhaps, a soupçon of emphasis on those important contributions that have originated in Canada.

II. A HISTORICAL REVIEW OF THE QUADRUPOLE ION TRAP

The original public disclosure (filed in 1953) of the quadrupole ion trap, which it described as "still another electrode arrangement," is to be found in the same patent (Paul & Steinwedel, 1956) as that in which the authors working at the University of Bonn first described the operating principle of the quadrupole mass spectrometer, also known as the quadrupole mass filter. In 1948 N. C. Christofilos, an electrical engineer working in Athens, Greece, sent the first of a series of letters to the University of California Radiation Laboratory (UCRL) at Berkeley, in which he proposed an idea for improving accelerator performance through the use of electrostatic focusing and a proton synchrotron (Melissinos, 1995). He received a detailed response from the UCRL staff, pointing out the serious flaws in his design. Undeterred, Christofilos returned to the drawing board and the next year wrote to UCRL again, this time delineating what he called the strong focusing principle or, as it is also known, alternate gradient focusing. This unsolicited contribution was filed away without a response. Parenthetically, strong focusing refers to a linear dependence of the restoring force on the distance from the origin, as compared to a weaker dependence.

Later the UCRL staff would point to Christofilos' makeshift mathematics and claim that they had not understood what he was trying to say in that second letter. Despite UCRL's silence, on March 10 1950 Christofilos filed a patent application on his invention, which was granted eventually (Christofilos, 1956). In 1952, the theory of strong focusing of charged particle beams using alternating gradient quadrupole magnetic fields was proposed independently (Courant, Livingston, & Snyder, 1952). The following year basically the same idea was put forward for a "mass spectrograph using strong focusing principles"

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(Post & Heinrich, 1953) and for ''a particle containment device'' (Good, 1953). Evidently Courant et al. stimulated these proposals through the earlier publication. Wolfgang Paul and his co-workers at the University of Bonn (Paul & Steinwedel, 1953) recognized the principle of using strong focusing fields for mass analysis, and the first detailed account of the operation of a quadrupole ion trap appeared in the 1956 thesis of Berkling aus Leipzig (1956).

III. THEORY OF QUADRUPOLE DEVICES

This presentation of the theoretical treatment or derivation flows through three stages. First, the general expression for the electric potential within a quadrupolar device is modified by the Laplace condition. Second, it is recognized that the structure of each quadrupolar device is constrained by the requirement that the hyperbolic electrodes share common asymptotes. Third, the derivation is based on a demonstration of the equivalence of the force acting on an ion in a quadrupole field and the force derived from the Mathieu equation; this equivalence permits the application of the solutions of Mathieu's equation to the confinement of gaseous ions.

A. Introduction to Theory

Quadrupole instruments are described as ''dynamic'' in that ion trajectories therein are influenced by a set of time-dependent or dynamic forces. Ions in such quadrupolar fields experience strong focusing in which the restoring force, which drives the ions back toward the center of the device, increases linearly with displacement from the origin. The term ''quadrupolar'' refers to the dependence of the potential at a point within such a device upon the square of the distance from the origin of reference.

The motion of ions in quadrupole fields is described mathematically by the solutions to a second-order linear differential equation (Mathieu, 1868). The equations governing the motion of ions in quadrupole fields have been treated in an introductory fashion (Dawson & Whetten, 1968a,b; Campana, 1980) and in detail (Dawson, 1976b; March, Hughes, & Todd, 1989; Lawson, Todd, & Bonner, 1975; March & Todd, 1995, 2005; March, 1997). The relevant mathematics has been examined (McLachlan, 1947; Campbell, 1955). From Mathieu's investigation of the mathematics of vibrating stretched skins, he was able to describe solutions in terms of regions of stability and instability. These solutions can be applied here, including the concepts of stability and instability to describe the trajectories of ions confined in quadrupole devices and to define the limits to ion trajectory stability. For stable solutions the displacement of the ion periodically passes through the central radial plane of the device, whereas for unstable solutions the displacement increases without limit to infinity.

The path that we shall follow is to equate an expression for a force (mass × acceleration) in Mathieu's equation with an expression that gives the force on an ion in a quadrupole field. This comparison, that is laid out below in simple mathematical terms, allows us to express the magnitudes and frequencies of the potentials applied to the electrodes of quadrupolar devices, the sizes of these quadrupolar devices, and the mass/charge ratio of

ions confined therein in terms of Mathieu's trapping parameters, a_u and q_u where u represents either the Cartesian co-ordinate axes x, y, and z, or the cylindrical coordinate axes r and z. On this basis the concept of stability regions in a_u, q_u space is adopted to discuss the confinement, and limits thereto, of gaseous ions in quadrupole devices.

Let us consider an expression for the electric potential within a quadrupolar device that is *between* the electrodes. When this expression is subjected to the Laplace condition, the quadrupole field in each direction can be derived, in turn for both the two-dimensional quadrupole mass filter and the three-dimensional quadrupole ion trap. An expression for the force within a two-dimensional quadrupole field is derived and is compared with the corresponding expression from the Mathieu equation. Similarly, an expression for the force within a three-dimensional quadrupole field is derived and is compared with the corresponding expression from the Mathieu equation. In this manner, the values of the stability parameters for each of the quadrupole mass filter and the quadrupole ion trap are derived. Once the values of the stability parameters of the Mathieu equation have been derived in terms of the RF potential amplitude and frequency, the mass/charge ratio of an ion, and the dimensions of the quadrupole instrument, stable solutions to the Mathieu equation are examined for each quadrupole instrument. By examination of stability criteria we proceed to a discussion of regions of stability and instability in which we develop stability diagrams. Particular attention is devoted to the quadrupole ion trap stability diagram closest to the origin in stability parameter space (see Section III.B.3). Finally, a cursory treatment of the general expression for the potential is presented so as to introduce the concept of contributions of fields of higher order than quadrupole (hexapole and octapole).

In a logical mathematical approach to the theory of quadrupolar devices one should begin with an examination of the field in one dimension and proceed to examine two- and three-dimensional devices.

B. Quadrupolar Devices

The theory presented here is based on the behavior of a single ion in an infinite, ideal quadrupole field in the total absence of any background gas. In a quadrupolar device described with reference to rectangular coordinates, the potential $\phi_{x,y,z}$ at any given point within the device can be expressed in its most general form as

$$\phi_{x,y,z} = A(\lambda x^2 + \sigma y^2 + \gamma z^2) + C \qquad (1)$$

where A is a term independent of x, y, and z that includes the electric potential applied *between* the electrodes of opposing polarity [either a radiofrequency (RF) potential alone or in combination with a direct current (DC) potential], C is a ''fixed'' potential applied effectively to all the electrodes so as to ''float'' the device, and λ, σ, and γ are weighting constants for the x, y, and z co-ordinates, respectively. It can be seen from Eq. (1) that in each coordinate direction the potential increases quadratically with x, y, and z, respectively, and that there are no ''cross terms'' of the type xy, etc. This property of Eq. (1) has important implications for the treatment of the motion of ions within the

field, in that we can consider the components of motion in the x-, y-, and z-directions to be independent of each other.

In any electric field, it is essential that the Laplace condition

$$\nabla^2 \phi_{x,y,z} = 0 \qquad (2)$$

be satisfied; that is, the second differential of the potential at a point be equal to zero, where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad (3)$$

Once the quadrupole potential given in Eq. (1) is substituted into the Laplace Eq. (2) we obtain

$$\nabla^2 \phi = \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0 \qquad (4)$$

The partial derivatives of the field are found as

$$\frac{\partial \phi}{\partial x} = \frac{\partial}{\partial x}(A\lambda x^2) = 2A\lambda x \qquad (5)$$

and

$$\frac{\partial^2 \phi}{\partial x^2} = 2\lambda A \qquad (6)$$

Likewise

$$\frac{\partial^2 \phi}{\partial y^2} = 2\sigma A \quad \text{and} \quad \frac{\partial^2 \phi}{\partial z^2} = 2\gamma A \qquad (7)$$

Substitution of Eqs. (6) and (7) into Eq. (4) yields

$$\nabla^2 \phi = A(2\lambda + 2\sigma + 2\gamma) = 0 \qquad (8)$$

Clearly, A is nonzero, therefore we obtain

$$\lambda + \sigma + \gamma = 0 \qquad (9)$$

While an infinite number of combinations of λ, σ, and γ exist which satisfy Eq. (9), the simplest that have been chosen in practice are, for the two-dimensional quadrupole mass filter (QMF) and the linear ion trap (LIT)

$$\lambda = -\sigma = 1; \quad \gamma = 0 \qquad (10)$$

and for the cylindrically symmetric three-dimensional quadrupole ion trap (QIT)

$$\lambda = \sigma = 1; \quad \gamma = -2 \qquad (11)$$

1. The Quadrupole Mass Filter (QMF)

Substituting the values in Eq. (10) into Eq. (1) gives

$$\phi_{x,y} = A(x^2 - y^2) + C \qquad (12)$$

To determine the constants A and C, we consider the configuration of a quadrupole mass filter comprising two pairs of electrodes having hyperbolic cross-sections formed according to equations of the general type:

$$\frac{x^2}{x_0^2} - \frac{y^2}{a^2} = 1 \qquad (13)$$

for the x-pair of rod electrodes, and

$$\frac{x^2}{b^2} - \frac{y^2}{y_0^2} = -1 \qquad (14)$$

for the y-pair of rod electrodes corresponding, respectively, to the conditions $x = \pm x_0$ when $y = 0$ and $y = \pm y_0$ when $x = 0$. Eqs. (13) and (14) describe two complementary rectangular hyperbolae and, to establish a quadrupolar potential, it is a condition that the hyperbolae share common asymptotes. Because Eqs. (13) and (14) are rectangular hyperbolae the asymptotes will, therefore, have slopes of $\pm 45°$, so that $a = \pm x$ and $b = \pm y$.

In practice, all the commercial mass filters using hyperbolic electrodes described to date have been constructed symmetrically according to the condition:

$$x_0 = y_0 = r_0 \qquad (15)$$

where r_0 is the radius of the inscribed circle tangential to the inner surface of the electrodes. From Eq. (15) the equations for the electrode surfaces become

$$x^2 - y^2 = r_0^2 \qquad (16)$$

for the x-pair of electrodes, and

$$x^2 - y^2 = -r_0^2 \qquad (17)$$

for the y-pair of electrodes.

a. QMF with round rods. It should be noted that most modern instruments use arrays of round rather than hyperbolic rods to reduce costs and to simplify construction. When circular rods of radius r are used, a good approximation to a quadrupole field can be obtained when the radius of each rod is made equal to $1.148 \times$ the desired r_0 value (Denison, 1971). Recently, this assertion has been questioned (Gibson & Taylor, 2001) and it has been claimed that it is not possible to give a single figure for r/r_0 because the results are influenced to a small extent by the form of the ion beam entering the quadrupole mass filter. They found that a value in the range $r = 1.12 \times r_0$ to $r = 1.13 \times r_0$ produces the best performance.

b. The structure of the QMF. A quadrupole mass filter comprised of circular rods is shown in Figure 1. Each pair of opposite rods is connected electrically, such that a two-dimensional quadrupole field is established in the $x-y$ plane. The ions enter and travel in the z-direction. While traveling in the z-direction the ions oscillate in the $x-y$ plane due to the potentials applied to the rods. This oscillation, which is described as the secular frequency, is a property of the mass/charge ratio of a given ion species. Therefore, all ions of a specific mass/charge ratio will execute trajectories having a common secular frequency in response to the electric potentials imposed by the quadrupole assembly. Under appropriate electrical and initial conditions, ions of a single mass/charge ratio will have a stable trajectory for the entire length of the quadrupole. A quadrupole mass filter can be operated so as to transmit either all ions or a specific range of mass-to-charge ratios and to focus them at the exit aperture. The ions transmitted impinge subsequently onto the detector or they are introduced into a subsequent device.
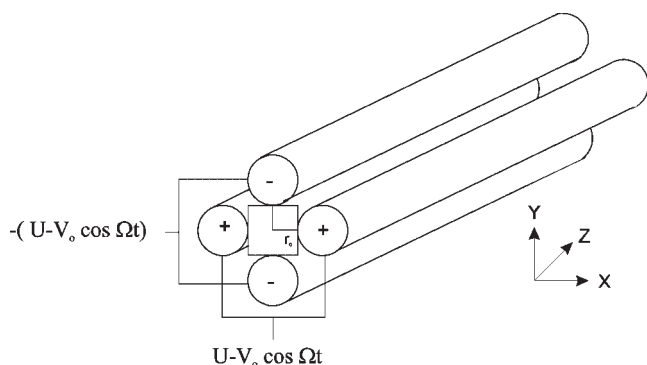
FIGURE 1. Quadrupole mass filter. The ions enter and travel in the *z*-direction, while oscillating in the *x*–*y* plane. The oscillation is controlled by the DC (*U*) and RF (*V*) potentials applied to each pair of rods. Only those ions with stable trajectories at the selected *U* and *V* values will travel the length of the quadrupole mass filter and be detected. Reproduced from March and Todd (2005, Fig. 2.1 of Quadrupole Storage Mass Spectrometry, QITMS), copyright at 2005, with permission of John Wiley & Sons, Ltd.

An electric potential ϕ_{y-y} is applied to the vertical rod pair in Figure 1 and ϕ_{x-x} is applied to the horizontal rod pair ring electrode, such that the potentials on the pairs of rods are out-of-phase with each other. Two points should be noted here: first, each rod (or electrode) in a rod array is either in-phase or out-of-phase with the remaining three rods and, second, the potential along the *z*-axis of the rod array is zero.

c. Quadrupolar potential. As noted earlier the actual quadrupolar potential to which an ion is subjected, ϕ_0, is given by the *difference* between the potentials applied to the *x*-pair and the *y*-pair of electrodes. Thus:

$$\phi_0 = \phi_{x-x} - \phi_{y-y} \tag{18}$$

Considering now, say, the *x*-pair of electrodes, since the potential must be the same across the whole of the electrode surface, we can write that when $y = 0$, $x_0^2 = r_0^2$, so that substituting in Eq. (12) we have:

$$\phi_{x-x} = A(r_0^2) + C \tag{19}$$

Likewise we have

$$\phi_{y-y} = A(-r_0^2) + C \tag{20}$$

so that from Eqs. (18), (19), and (20) we find

$$\phi_0 = 2Ar_0^2 \tag{21}$$

$$A = \frac{\phi_0}{2r_0^2} \tag{22}$$

Hence Eq. (12) becomes

$$\phi_{x,y} = \frac{\phi_0}{2r_0^2}(x^2 - y^2) + C \tag{23}$$

whence we note that at the origin ($x = 0$, $y = 0$) we have

$$\phi_{0,0} = C \tag{24}$$

If the electrode structure is floated at zero (ground) potential then $C = 0$, so that Eq. (23) becomes

$$\phi_{x,y} = \frac{\phi_0}{2r_0^2}(x^2 - y^2) \tag{25}$$

which is the expression for the potential often found in standard texts.

We proceed now to examine the motion of an ion when subjected to the potential given by Eq. (25). If we consider first the component of motion in the *x*-direction, then putting $y = 0$ in Eq. (25) gives

$$\phi_{x,0} = \frac{\phi_0 x^2}{2r_0^2} \tag{26}$$

so that the electric field at the point (x, $y = 0$) is

$$\left(\frac{d\phi}{dx}\right)_y = \frac{\phi_0 x}{r_0^2} \tag{27}$$

As a result, the force acting on an ion, F_x, at a point (x,0) is given by:

$$F_x = -e\left(\frac{d\phi}{dx}\right)_y = -e\frac{\phi_0 x}{r_0^2} \tag{28}$$

where the negative sign indicates that the force acts in the opposite direction to increasing *x*. Because force = mass × acceleration, from Eq. (28) we can write:

$$m\left(\frac{d^2x}{dt^2}\right) = -e\frac{\phi_0 x}{r_0^2} \tag{29}$$

Let us now consider a real system in which

$$\phi_0 = 2(U + V\cos\Omega t) \tag{30}$$

where *V* is the zero-to-peak amplitude of a radiofrequency potential oscillating with angular frequency Ω (expressed in radian sec^{-1}) and $+U$ is a DC voltage applied to the *x*-pair of electrodes whilst a DC voltage of $-U$ volts is applied to the *y*-pair of electrodes.

Thus from Eqs. (29) and (30):

$$m\left(\frac{d^2x}{dt^2}\right) = -2e\frac{(U + V\cos\Omega t)x}{r_0^2} \tag{31}$$

which may be expanded to

$$\left(\frac{d^2x}{dt^2}\right) = -\left[\frac{2eU}{mr_0^2} + \frac{2eV\cos\Omega t}{mr_0^2}\right]x \tag{32}$$

d. The Mathieu equation. The canonical or commonly accepted form of the Mathieu equation is:

$$\frac{d^2u}{d\xi^2} + (a_u - 2q_u\cos2\xi)u = 0 \tag{33}$$

where *u* is a displacement, ξ is a dimensionless parameter equal to $\Omega t/2$ such that Ω must be a frequency since *t* is time, and a_u and q_u are additional dimensionless stability parameters which, in the present context of quadrupole devices, are in fact "trapping"

parameters. It can be shown by substituting $\xi = \Omega t/2$ and using operator notation that

$$\frac{d}{dt} = \frac{d\xi}{dt}\frac{d}{d\xi} = \frac{\Omega}{2}\frac{d}{d\xi} \tag{34}$$

so that

$$\frac{d^2}{dt^2} = \frac{d\xi}{dt}\frac{d}{d\xi}\left\{\frac{d}{dt}\right\} = \frac{\Omega^2}{4}\frac{d^2}{d\xi^2} \tag{35}$$

and we can write:

$$\frac{d^2u}{dt^2} = \frac{\Omega^2}{4}\frac{d^2u}{d\xi^2} \tag{36}$$

Substitution of Eq. (36) into Eq. (33), substituting Ωt for 2ξ and rearranging yields:

$$\frac{d^2u}{dt^2} = -\left[\frac{\Omega^2}{4}a_u - 2 \times \frac{\Omega^2}{4}q_u\cos\Omega t\right]u \tag{37}$$

We can now compare directly the terms on the right hand sides of Eqs. (32) and (37), recalling that u represents the displacement x, to obtain:

$$-\left[\frac{2\,eU}{mr_0^2} + \frac{2\,eV\cos\Omega t}{mr_0^2}\right]x = -\left[\frac{\Omega^2}{4}a_x - 2 \times \frac{\Omega^2}{4}q_x\cos\Omega t\right]x \tag{38}$$

whence one deduces the relationships:

$$a_x = \frac{8eu}{mr_0^2\Omega^2} \tag{39}$$

and

$$q_x = \frac{-4\,eV}{mr_0^2\Omega^2} \tag{40}$$

When this derivation is repeated to obtain the force on an ion in the y-direction in a quadrupole mass filter, one finds that $a_x = -a_y$ and $q_x = -q_y$; this relationship is obtained because $\lambda = -\sigma = 1$. The a_u, q_u trapping parameters are particularly interesting because they are functions of the RF frequency (in radian sec^{-1}), the mass/charge ratio of a given ion species, and the size (r_0) of the device; in addition, a_u and q_u are functions of the DC and RF voltages, respectively, applied to a quadrupolar device. Thus, the trapping parameters are functions of the instrumental parameters that govern the various operations of a quadrupole device. Other parameters of interest, β_u and ω_u, can be derived from the a_u, q_u trapping parameters. Both β_u and ω_u describe the nature of the ion trajectories: β_u is a complex function of a_u and q_u, and ω_u is the so-called secular frequency of the ion motion in the u-direction.

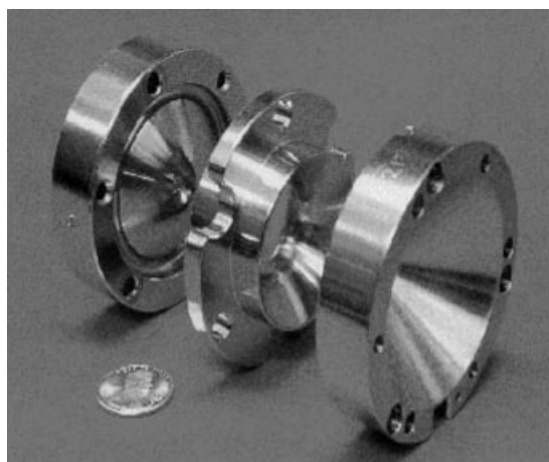## 2. The Quadrupole Ion Trap (QIT)

The quadrupole ion trap is an extraordinary device that functions both as an ion store in which gaseous ions can be confined for a period of time, and as a mass spectrometer of large mass range variable mass resolution, and high sensitivity. As a storage device the quadrupole ion trap confines gaseous ions, either positively or negatively charged and, when required, ions of each polarity. The confining capacity of the quadrupole ion trap arises from

the formation of a trapping potential well when appropriate potentials are applied to the electrodes of the ion trap.

That the basic theory underlying operation of quadrupole devices was enunciated almost 100 years before the quadrupole ion trap and the related quadrupole mass filter were invented by Paul and Steinwedel is a shining example of the inherent value of basic research. The pioneering work of the inventors was recognized by the award of the 1989 Nobel Prize in Physics to Paul (1990), together with Norman Ramsay and Hans Dehmelt.

a. The structure of the QIT. The quadrupole ion trap mass spectrometer consists essentially of three shaped electrodes that are shown in exploded array in Figure 2. Two of the three electrodes are virtually identical and, while having hyperboloidal geometry, resemble small inverted saucers; these saucers are the so-called end-cap electrodes and each has one or more holes in the center for transmission of electrons and ions. One end-cap electrode contains the ''entrance'' aperture through which electrons and/or ions can be gated periodically whilst the other is the ''exit'' electrode through which ions pass to a detector. The ring electrode has an internal hyperboloidal surface: in some early designs of ion trap systems a beam of electrons was gated through a hole in this electrode rather than an end-cap electrode. The ring electrode is positioned symmetrically between the two end-cap electrodes as shown in Figure 3; Figure 3a shows a photograph of an ion trap cut in half along the axis of cylindrical symmetry while Figure 3b is a cross-section of an ideal ion trap showing the asymptotes and the dimensions r_0 and z_0, where r_0 is the radius of the ring electrode in the central horizontal plane and $2z_0$ is the separation of the two end-cap electrodes measured along the axis of the ion trap.

The electrodes in Figure 3 are truncated for practical purposes but in theory they extend to infinity and meet the asymptotes. The asymptotes arise from the hyperboloidal geometries of the three electrodes. The geometries of the electrodes are defined so as to produce an ideal quadrupole potential distribution that, in turn, will produce the necessary trapping field for the confinement of ions.

FIGURE 2. The three electrodes of the quadrupole ion trap shown in open array. Reproduced from March and Todd (2005, Fig. 2.11 of QITMS), copyright at 2005, with permission of John Wiley & Sons, Ltd.
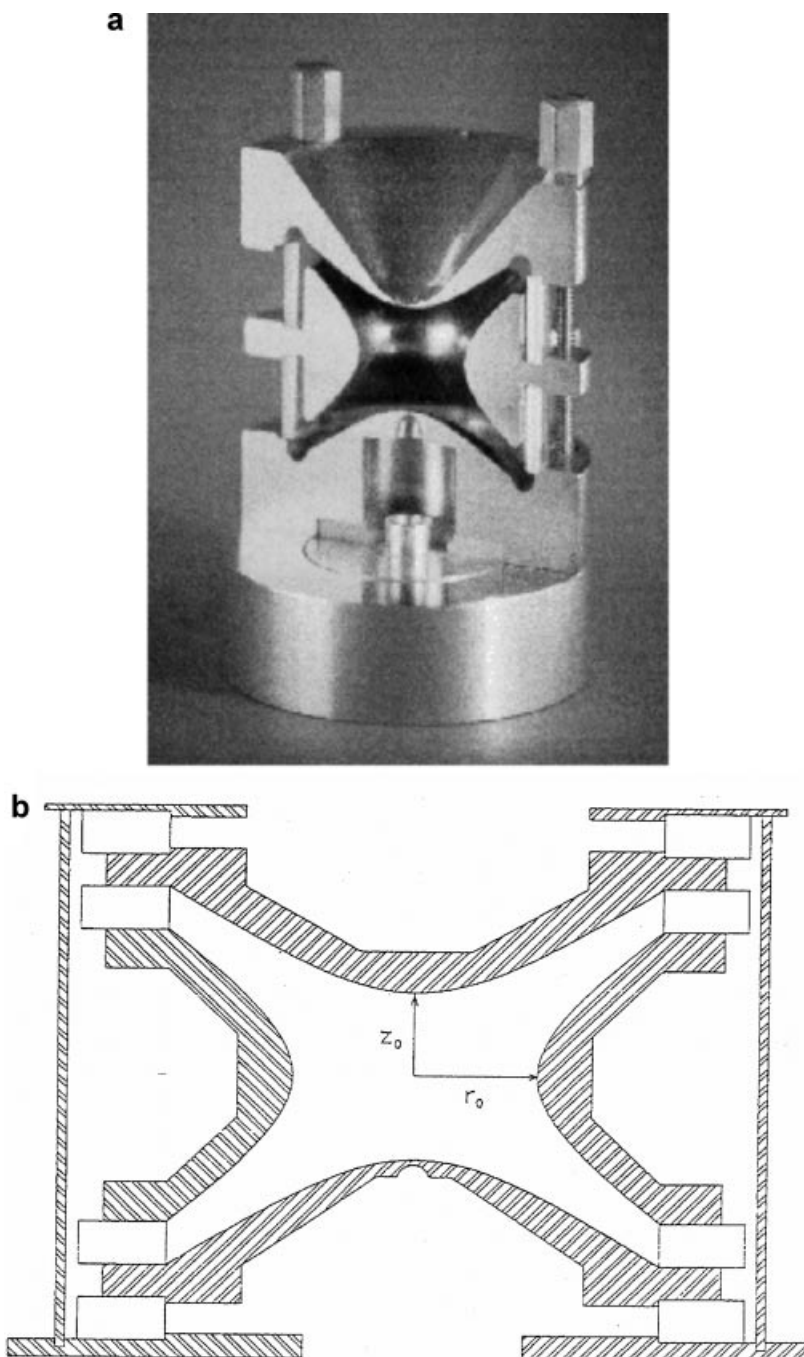
FIGURE 3. Quadrupole ion trap; (**a**) photograph of an ion trap cut in half along the axis of cylindrical symmetry, (**b**) a schematic diagram of the three-dimensional ideal ion trap showing the asymptotes and the dimensions r_o and z_o. Reproduced from March and Todd (2005, Fig. 2.12 of QITMS), copyright at 2005, with permission of John Wiley & Sons, Ltd.

b. Electrode surfaces. We have seen that, for the cylindrically symmetric QIT, the values of λ, σ, and γ given in Eq. (11) satisfy the Laplace condition (Eq. 2) when it is applied to Eq. (1). Thus we have:

$$\phi_{x,y,z} = A(x^2 + y^2 - 2z^2) + C \qquad (41)$$

To proceed we convert Eq. (41) into cylindrical polar co-ordinates employing the standard transformations $x = r\cos\theta$, $y = r\sin\theta$, $z = z$. Thus Eq. (41) becomes

$$\phi_{r,z} = A(r^2 - 2z^2) + C \qquad (42)$$

It should be noted that, in making this transformation, there is an implicit assumption that the ion possesses zero angular velocity around the z-axis. To determine the constants A and C, we

consider the configuration of a quadrupole ion trap ring electrode and two end-cap electrodes.

We can write the equations for the cross-sections of the electrodes as:

$$\frac{r^2}{r_0^2} - \frac{2z^2}{r_0^2} = 1 \quad \text{(ring electrode)} \tag{43}$$

and

$$\frac{r^2}{2z_0^2} - \frac{z^2}{z_0^2} = -1 \quad \text{(end-cap electrode)} \tag{44}$$

The gradients of the asymptotes, m, are given by

$$m = \pm\frac{1}{\sqrt{2}} \tag{45}$$

This relationship corresponds to the asymptotes having an angle of $35.264°$ with respect to the radial plane of the ion trap. The surfaces of the electrodes can be generated by rotation of the electrode cross-sections through $180°$.

c. Quadrupolar potential. As in the case of the quadrupole mass filter one proceeds to evaluate the constants A and C in the general expression for the potential within the ion trap, Eq. (42). By analogy with Eq. (18) we define a quadrupolar potential ϕ_o in terms of the difference between the potentials applied to the ring and the pair of end-cap electrodes:

$$\phi_o = \phi_{\text{ring}} - \phi_{\text{end-caps}} \tag{46}$$

Recalling that $r = \pm r_0$ when $z = 0$ and $z = \pm z_0$ when $r = 0$, substitution into Eq. (42) gives:

$$\phi_{\text{ring}} = A(r_0^2) + C \tag{47}$$

and

$$\phi_{\text{end-caps}} = A(-2z_0^2) + C \tag{48}$$

so that from Eq. (46):

$$\phi_o = A(r_0^2 + 2z_0^2) \tag{49}$$

whence

$$A = \frac{\phi_o}{(r_0^2 + 2z_0^2)}, \tag{50}$$

and therefore from Eq. (42):

$$\phi_{r,z} = \frac{\phi_o(r^2 - 2z^2)}{(r_0^2 + 2z_0^2)} + C \tag{51}$$

As with the quadrupole mass filter the constant C is evaluated by taking account of the potentials actually connected to the electrodes of opposing polarity. In the quadrupole ion trap the end-cap electrodes are normally held at ground (i.e., zero) potential whilst a unipolar RF potential plus any DC voltage are applied to the ring electrode only. Thus Eq. (51) becomes:

$$\phi_{0,z_0} = \phi_{\text{end-caps}} = \frac{\phi_o(0 - 2z_0^2)}{(r_0^2 + 2z_0^2)} + C = 0$$

$$C = \frac{2\phi_o z_0^2}{(r_0^2 + 2z_0^2)} \tag{52}$$

whence

$$\phi_{r,z} = \frac{\phi_o(r^2 - 2z^2)}{(r_0^2 + 2z_0^2)} + \frac{2\phi_0 z_0^2}{(r_0^2 + 2z_0^2)} \tag{53}$$

From Eq. (53) we see that the potential at the center of the ion trap (0,0) is no longer zero, but is equal to a fraction $(= 2z_0^2/(r_0^2 + 2z_0^2))$ of that applied to the ring electrode.

Having set the pair of end-cap electrodes at ground potential, we must now define the value of ϕ_0 in terms of the real-system potentials applied to the ring electrode. Thus

$$\phi_o = (U + V\cos\Omega t) \tag{54}$$

where the quantities are defined in the same manner as those in Eq. (30). Substituting from Eq. (54) into Eq. (53) yields:

$$\phi_{r,z} = \frac{(U + V\cos\Omega t)(r^2 - 2z^2)}{(r_0^2 + 2z_0^2)} + \frac{2(U + V\cos\Omega t)z_0^2}{(r_0^2 + 2z_0^2)} \tag{55}$$

As with the quadrupole mass filter, the components of the ion motion in the radial (r) and the axial (z) directions may be considered independently, so for the axial direction we can write, by analogy with Eqs. (28) and (29):

$$F_z = -e\left(\frac{d\phi}{dz}\right)_r = e\frac{4\phi_o z}{(r_0^2 + 2z_0^2)} = m\left(\frac{d^2z}{dt^2}\right) \tag{56}$$

Hence from Eq. (54) we have:

$$m\left(\frac{d^2z}{dt^2}\right) = \frac{4e(U + V\cos\Omega t)z}{(r_0^2 + 2z_0^2)} \tag{57}$$

which may be expanded to give:

$$\left(\frac{d^2z}{dt^2}\right) = \left[\frac{4\,eU}{m(r_0^2 + 2z_0^2)} + \frac{4\,eV\cos\Omega t}{m(r_0^2 + 2z_0^2)}\right]z \tag{58}$$

d. The Mathieu equation. As with the mass filter, we recognize the similarity of Eq. (58) with the Mathieu Eq. (33)

$$\frac{d^2u}{d\xi^2} + (a_u - 2q_u\cos 2\xi)u = 0 \tag{33'}$$

so that using the transformations given in Eqs. (34), (35), and (36) and replacing u by z we can write:

$$\left[\frac{4\,eU}{m(r_0^2 + 2z_0^2)} + \frac{4\,eV\cos\Omega t}{m(r_0^2 + 2z_0^2)}\right]z = -\left[\frac{\Omega^2}{4}a_z - 2\times\frac{\Omega^2}{4}q_z\cos\Omega t\right]z \tag{59}$$

whence one deduces the relationships:

$$a_z = -\frac{16\,eU}{m(r_0^2 + 2z_0^2)\Omega^2} \tag{60}$$

and

$$q_z = \frac{8\,eV}{m(r_0^2 + 2z_0^2)\Omega^2} \tag{61}$$

When this derivation is repeated for the radial component of motion at a fixed value of z one finds that:

$$a_z = -2a_r \quad \text{and} \quad q_z = -2q_r \tag{62}$$

again arising from the values of λ, σ, and γ inserted into the general Eq. (1) when it is applied to the quadrupole ion trap.

So far in this formulation of the motion occurring within the ion trap we have made no assumption concerning the relationship between the dimensions r_0 and z_0. Historically we see that ever since the early descriptions of the ion trap (Paul, Osberghaus, & Fischer, 1958; Paul, Reinhard, & Von Zahn, 1958; Wuerker, Shelton, & Langmuir, 1959) the relationship

$$r_0^2 = 2z_0^2 \tag{63}$$

has been selected as a requirement for forming the ideal quadrupolar potential distribution. Furthermore, we note that with the identity given in Eq. (63) the asymptotes with the gradients $\pm 1/\sqrt{2}$ (Eq. 45) will pass through the co-ordinates $(\pm r_0, \pm z_0)$. Knight has shown that in practical ion trap systems with truncated electrodes, under the conditions of Eq. (63) the asymptotes bisect the gaps between the ring electrode and the end-cap electrodes at high values of r and z, thereby minimizing the contributions to the potential of higher-order terms (Knight, personal communication); the personal communication is reproduced in March and Todd (2005). It should be noted that inserting the relationship given in Eq. (63) into Eq. (53) shows that, under the conditions where the end-cap electrodes are held at earth potential, the potential at the center of the ion trap is equal to half that applied to the ring electrode.

e. An alternative approach to quadrupole ion trap theory. The approach now described has the advantage of introducing explicitly components of the trapping potential of order higher than quadrupolar. A solution of Laplace's equation in spherical polar co-ordinates (ρ, θ, ϕ) for a system with axial symmetry (such as is the case for the quadrupole ion trap) is obtained from the theory of differential equations and has the general form:

$$\phi(\rho, \theta, \varphi) = \phi_o \sum_{n=0}^{\infty} A_n \frac{\rho^n}{r_o^2} P_n(\cos\theta) \tag{64}$$

where A_n are arbitrary coefficients and $P_n(\cos\theta)$ denotes a Legendre polynomial. When $\rho^n P_n(\cos\theta)$ is expressed in cylindrical polar co-ordinates, Eq. (65) is obtained as:

$$\phi_{r,z} = \phi_o \left[A_2 \frac{(r^2 - 2z^2)}{2r_o^2} + A_3 \frac{(3r^2 z - 2z^3)}{2r_0^3} \right.$$

$$+ A_4 \frac{(3r^4 - 24r^2 z^2 + 8z^4)}{8r_o^2} + A_5 \frac{(15r^4 z - 40r^2 z^3 + 8z^5)}{8r_o^5}$$

$$\left. + A_6 \frac{(5r^6 - 90r^4 z^2 + 120r^2 z^4 - 16z^6)}{16r_o^6} + \ldots \right] \tag{65}$$

The values of $n = 0$, 1, 2, 3, 4, 5, and 6 correspond to the monopole, dipole, quadrupole, hexapole, octapole, decapole, and docecapole components, respectively, of the potential field ϕ. Higher-order field components such as hexapole and octapole can play important roles in the operation of modern ion trap mass spectrometers (see Section IV.A.3.d.).

3. Regions of Ion Trajectory Stability

Quadrupole ion trap operation is concerned with the criteria that govern the stability (and instability) of the trajectory of an ion within the field, that is, the experimental conditions that determine whether an ion is stored within the device or is ejected from the device and either lost or detected externally.

The complete solution to the Mathieu Eq. (33) is composed of two linear independent solutions, $u_1(\xi)$ and $u_2(\xi)$, such that:

$$u = \Gamma u_1(\xi) + \Gamma' u_2(\xi) \tag{66}$$

where Γ and Γ' are constants of integration that depend upon the initial conditions of position u_o, velocity $\dot{u}_0$, and RF phase ξ_o.

A corollary of Floquet's theorem states that there will always exist a solution to Eq. (66) of the form:

$$u(\xi) = e^{\mu n} \varphi(\xi) \tag{67}$$

where μ is a constant and φ has period π. The functions u_1 and u_2 are chosen to be even and odd, respectively, such that:

$$u_1(\xi) = u_1(-\xi); \quad u_2(\xi) = -u_2(\xi) \tag{68}$$

Thus we can write:

$$u(\xi) = \Gamma e^{\mu\xi} \varphi(\xi) + \Gamma' e^{-\mu\xi} \varphi(-\xi) \tag{69}$$

From Fourier's theorem a periodic function may be expressed as an infinite sum of exponential terms so that we may write:

$$\varphi(\xi) = \sum_{n=-\infty}^{\infty} C_{2n} \exp(2ni\xi) \quad \text{and}$$

$$\varphi(-\xi) = \sum_{n=-\infty}^{\infty} C_{2n} \exp(-2ni\xi) \tag{70}$$

so that Eq. (69) becomes:

$$u(\xi) = \Gamma e^{\mu\xi} \sum_{n=-\infty}^{\infty} C_{2n,u} \exp(2ni\xi)$$
$$+ \Gamma' e^{-\mu\xi} \sum_{n=-\infty}^{\infty} C_{2n,u} \exp(-2ni\xi) \tag{71}$$

The $C_{2n,u}$ coefficients are factors that describe the amplitudes of ion motion and depend only on a_u and q_u.

The term μ is referred to as the characteristic exponent and may be real, imaginary or complex; its value determines the type of solution to the Mathieu equation, and it may be expressed as $\mu = \alpha + i\beta$.

The solutions are of two types:

(i) stable where μ remains finite as ξ increases and
(ii) unstable where μ increases without limit as ξ increases.

Only solutions where $\alpha = 0$ are possibly stable; if $\alpha \neq 0$, then one of the terms $e^{\mu\xi}$ or $e^{-\mu\xi}$ will tend to infinity as ξ increases, thus such solutions must be unstable.

These four possibilities and their consequences have been summarized by Dawson (1976b) as follows:

1. μ is real and not zero; here one of the terms $e^{\mu\xi}$ or $e^{-\mu\xi}$ will increase without limit and the solution is not stable.
2. μ is complex; with this condition the solutions are not stable.
3. $\mu = im$, where m is an integer; here the solutions are periodic but unstable. These solutions are called Mathieu functions of integral order and form the boundaries between stable and unstable regions on the stability diagram. The boundaries are referred to as characteristic curves or characteristic values.
4. $\mu = i\beta$, that is imaginary, and β is not a whole number. These solutions are periodic and stable.

From the constraint that α must be zero, the solution of the Mathieu equation becomes:

$$u(\xi) = \Gamma \sum_{n=-\infty}^{\infty} C_{2n}\exp(2n + \beta)i\xi$$
$$+ \Gamma' \sum_{n=-\infty}^{\infty} C_{2n} \exp -(2n + \beta)i\xi \tag{72}$$

and with substitution of the trigonometric identity

$$\exp i\theta = \cos\theta + i \sin\theta \tag{73}$$

the expression for stable solutions becomes:

$$u(\xi) = A \sum_{n=-\infty}^{\infty} C_{2n}\cos(2n + \beta)\xi + B \sum_{n=-\infty}^{\infty} C_{2n}\sin(2n + \beta)\xi \tag{74}$$

where

$$A = (\Gamma + \Gamma') \quad \text{and} \quad B = i(\Gamma - \Gamma') \tag{75}$$

The differential of Eq. (74) gives an expression for the ion velocity in the quadrupole field:

$$\frac{du}{dt} = A \sum_{n=-\infty}^{\infty} C_{2n}(2n + \beta)\sin(2n + \beta)\xi$$
$$- B \sum_{n=-\infty}^{\infty} C_{2n}(2n + \beta)\cos(2n + \beta)\xi \tag{76}$$

that is useful for simulation studies.

Solutions of type (i) are called Mathieu functions of integral order and form the boundaries of unstable regions on the stability diagram. The boundaries, that are referred to as characteristic curves or characteristic values, correspond to those values of the new trapping parameter β_z that are integers, that is, 0,1,2,3,...; β_z is a complex function of a_z and q_z but can be approximated as given in Eq. (77) for the limited range $q_r < 0.2$ and $q_z < 0.4$. The boundaries represent, in practical terms, the point at which the trajectory of an ion becomes unbounded.

$$\beta_u \approx \sqrt{\left(a_u + \frac{q_u^2}{2}\right)} \tag{77}$$

It should be noted that the approximation for β_u given in Eq. (77) is known as the "Dehmelt approximation." A precise value of β_u is obtained from a continued fraction expression in terms of a_u and q_u.

Solutions of type (ii) determine the motion of ions in an ion trap. The stability regions corresponding to stable solutions of the Mathieu equation in the z-direction are shaded and labeled z-stable in Figure 4a. The stability regions corresponding to stable solutions of the Mathieu equation in the r-direction are shaded and labeled r-stable in Figure 4b; it can be seen that they are doubled in magnitude along the ordinate and inverted, that is, multiplied by -2. It is seen from Eq. (62) that $a_z = -2a_r$ and $q_z = -2q_r$, that is, the stability parameters for the r- and z-directions differ by a factor of -2.

Ions can be stored in the ion trap provided that their trajectories are stable in the r- and z-directions simultaneously; such trajectory stability is obtained in the region closest to the origin, that is region A in Figure 5. Regions A and B are referred to as stability regions; region A is of the greatest importance at this time (region B remains to be explored) and is shown in greater detail in Figure 6. The co-ordinates of the stability region in Figure 6 are the Mathieu parameters a_z and q_z. Here we plot a_z versus q_z rather than using the general parameters a_u versus q_u to avoid confusion. In Figure 6 the $\beta_z = 1$ stability boundary intersects with the q_z axis at $q_z = 0.908$; this working point is that of the ion of lowest mass/charge ratio, that is the low-mass cut-off which can be stored in the ion trap for given values of r_o, z_o, V, and Ω.

4. Secular Frequencies

A three-dimensional representation of an ion trajectory in the ion trap, as shown in Figure 7, has the general appearance of a
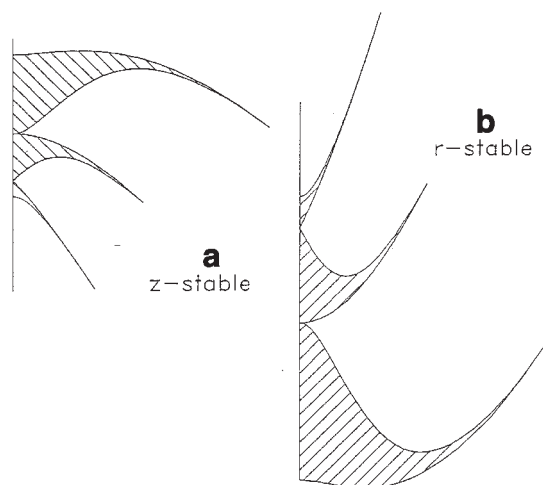
FIGURE 4. Graphical representation of three Mathieu stability regions: (**a**) z-stable, (**b**) r-stable. The r-stable region is obtained as $-2 \times$ the z-stable region. Reproduced from March and Todd (2005, Fig. 2.13 of QITMS), copyright at 2005, with permission of John Wiley & Sons, Ltd.
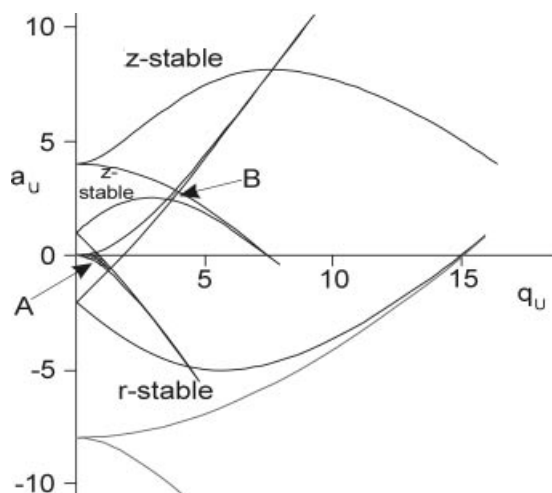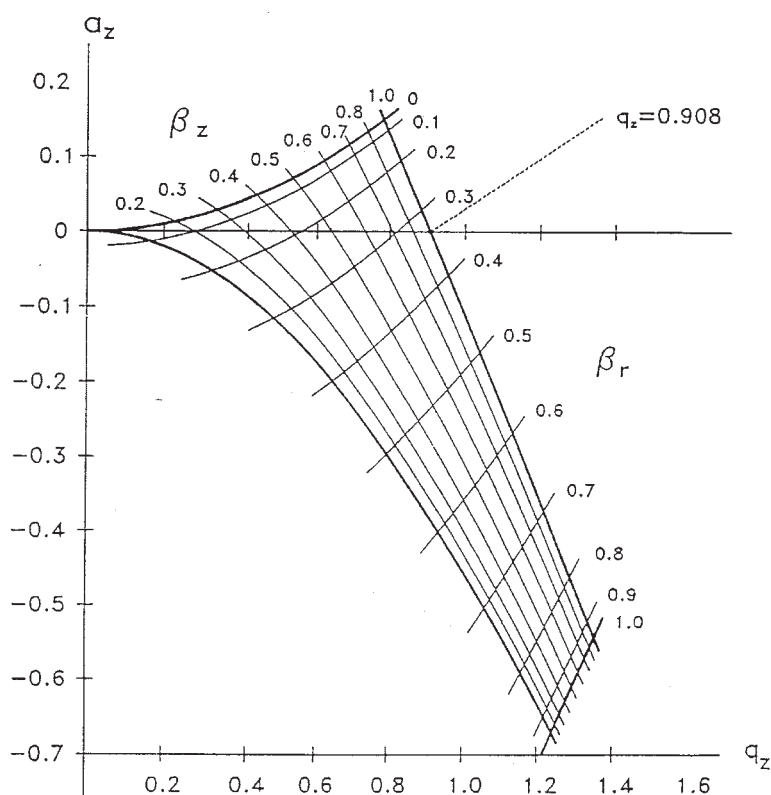
FIGURE 5. The Mathieu stability diagram in (a_z, q_z) space for the quadrupole ion trap in both the r- and z-directions. Regions of simultaneous overlap are labeled A and B. While the axes are labeled a_u and q_u, the diagrammatic representation shown here shows the ordinate and abscissa scales in units of a_z and q_z, respectively. Reproduced from March and Todd (2005, Fig. 2.14 of QITMS), copyright at 2005, with permission of John Wiley & Sons, Ltd.

Lissajous curve or figure-of-eight, composed of two fundamental frequency components $\omega_{r,o}$ and $\omega_{z,o}$ of the secular motion (Nappi et al., 1997). The description "fundamental" implies that there exist other higher-order (n) frequencies, and the entire family of frequencies is thus described by $\omega_{r,n}$ and $\omega_{z,n}$. These secular frequencies are given by:

$$\omega_{u,n} = \left(n + \frac{1}{2}\beta_u\right)\Omega, \quad 0 \leq n \leq \infty \qquad (78)$$

While the fundamental axial secular frequency $\omega_{z,o}$ is usually given in units of hertz in the literature and referred to simply as ω_z, it should be expressed in radians/second because Ω in Eq. (78) is expressed in radians/second. In the literature the frequency of the RF drive potential, f in hertz, is expressed as $\Omega/2\pi$. At this time, the higher-order frequencies are of little practical significance.

The resemblance of the simulated ion trajectory shown in Figure 7 to a roller coaster ride is due to the motion of an ion on the potential surface shown in Figure 8. The oscillatory motion of the ion results from the undulations of the potential surface that can be envisaged as rotation of the potential surface. The simulation of the ion trajectory was carried out using the ITSIM simulation program (Reiser, Julian, & Cooks, 1992), while the

FIGURE 6. Stability diagram in (a_z, q_z) space for the region of simultaneous stability A in both the r- and z-directions near the origin for the three-dimensional quadrupole ion trap; the iso-β_r and iso-β_z lines are shown in the diagram. The q_z-axis intersects the $\beta_z = 1$ boundary at $q_z = 0.908$, that corresponds to q_{max} in the mass-selective instability mode. Conventionally, the stability diagram in a_z, q_z space is presented. Reproduced from March and Todd (2005, Fig. 2.15 of QITMS), copyright at 2005, with permission of John Wiley & Sons, Ltd.
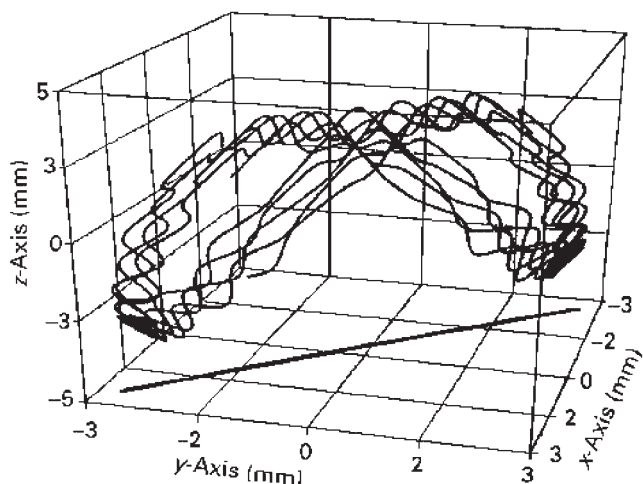
FIGURE 7. Trajectory of a trapped ion of m/z 105. The initial position was selected randomly from a population with an initial Gaussian distribution (FWHM of 1 mm); $q_z = 0.3$; zero initial velocity. The projection onto the $x-y$ plane illustrates planar motion in three-dimensional space. The trajectory develops a shape that resembles a flattened boomerang. Reproduced from Nappi et al. (1997), copyright at 1997, with permission of Elsevier.

potential surface was generated (Splendore, personal communication) from Eq. (65) by calculating $\phi_{r,\phi,z}$ for $A_2^o = 1$ and all of the other coefficients equal to zero for increment steps of 1 mm in both radial and axial directions.

Some of the secular frequencies defined by Eq. (78) are illustrated in Figure 9. In this figure are shown the results of a power spectral Fourier analysis of the trajectory of an ion of m/z 100 calculated using ITSIM (Reiser, Julian, & Cooks, 1992). The essential trapping parameters were $r_0 = 10$ mm, $z_0 = 7.071$ mm, $\Omega/2\pi = 1.1$ MHz, $q_z = 0.40$, and the background pressure was zero. The ion's fundamental axial secular frequency $\omega_{z,0}$ is of
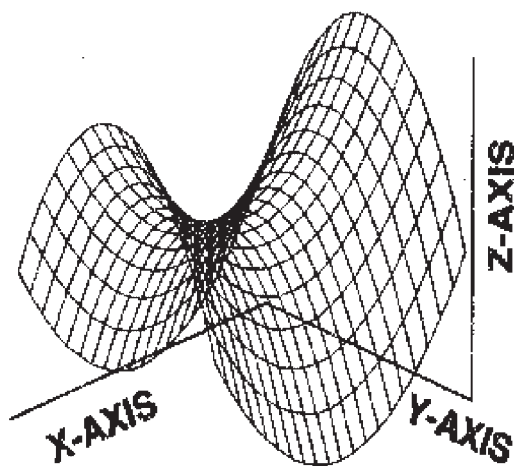
FIGURE 8. Pure quadrupole field, or potential surface, for a quadrupole ion trap. Note the four poles of the surface and the similarity of the field shape to the trajectory in Figure 7. Reproduced from March and Todd (2005, Fig. 2.17 of QITMS), copyright at 2005, with permission of John Wiley & Sons, Ltd.
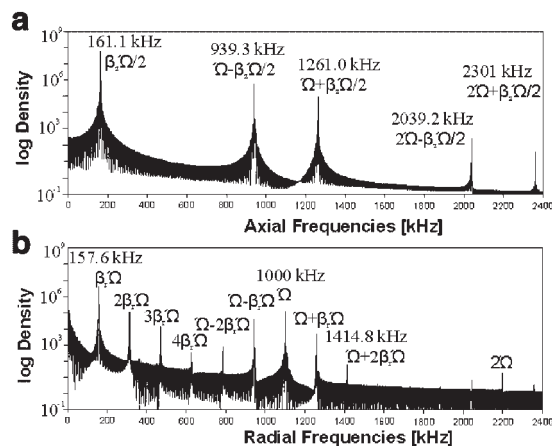
FIGURE 9. Power spectral Fourier analysis of the trajectory of an ion of m/z 100 calculated using ITSIM. The essential trapping parameters were $r_o = 10$ mm, $z_o = 7.071$ mm, $\Omega/2\pi = 1.1$ MHz, $q_z = 0.40$, and the background pressure was zero. The data were collected at intervals of 100 nsec for 1 msec: (**a**) axial frequencies; (**b**) radial frequencies. The magnitude of the frequency band is plotted on a logarithmic scale and shows the intensity of each harmonic lower by several orders of magnitude from the fundamental secular frequency. Note that the radial position data were obtained from $r = \sqrt{(x^2 + y^2)}$, and not from either x or y; thus the radial fundamental secular frequency is observed at $\beta_r\Omega$ rather than $\beta_r\Omega/2$. Reproduced from Forbes et al. (1999, Fig. 13), copyright at 1999, with permission of John Wiley & Sons, Ltd.

interest because it is the axial motion of an ion that is excited during axial modulation (see Eq. 78); this frequency, $\beta_z\Omega/2$, was observed at 160.91142 kHz and is shown at the left hand side of Figure 9a. Also shown here are two sets of complementary frequencies corresponding to $\Omega \pm \beta_z\Omega/2$ and $2\Omega \pm \beta_z\Omega/2$. In Figure 9b, where the radial frequencies are shown, the central feature is the RF drive frequency Ω; also shown are two sets of complementary frequencies corresponding to $\Omega \pm \beta_r\Omega$ and $2\Omega \pm 2\beta_r\Omega$, the harmonic frequencies $\beta_r\Omega$, $2\beta_r\Omega$, and $3\beta_r\Omega$, and the set of frequencies corresponding to 2Ω and $2\Omega \pm \beta_r\Omega$.

IV. UTILIZATION OF THE QUADRUPOLE ION TRAP

Thus far, we have considered the geometry or structure of the quadrupole ion trap and the underlying principles of the means by which ions may be stored within it. As for the size of the quadrupole ion trap, r_0 is usually 1 cm; ion traps with $r_0 < 1$ cm have special appeal as miniature ion storage devices and rarely is $r_0 > 1$ cm. Thus the size of the ion trap is about that of a fist. Until 1987 ions were formed exclusively by electron impact ionization of atoms or molecules flowing through the quadrupole ion trap; a fraction of the ions formed thus followed stable trajectories within the ion trap and were confined therein. We now proceed to trace the various early applications of the device, concentrating mainly on its use as a mass spectrometer or as an ion storage source employed in conjunction with an external mass analyzer. However, there are other avenues of development, in particular its use for studying the spectroscopy of trapped ions as an atomic

clock; in this application, the narrow line emission from a cooled single electronically excited ion can be used to improve the accuracy of the unit of time (the second). For its use as a mass spectrometer one clearly has to provide means both for the creation of ions and for their detection, and it is the development of the latter which has facilitated the history of the ion trap over the past 50 years. Indeed, the milestones in the development of the ion trap for mass spectrometric applications may be divided into three distinct periods, as suggested in Table 1. Each of the periods will be discussed in turn and, while every effort is made to acknowledge the contributions of numerous researchers, we shall shockingly but unabashedly highlight the contributions of Canadian researchers.

A. Early Mass-Selective Modes of Operation

The first methods employed for the detection of trapped ions were based on the principle of *mass-selective detection*, in which the presence of ions in the trap was recorded through sensing the motion of the ion by means of a harmonic oscillator oscillating in two dimensions connected between the end-cap electrodes. These methods were followed by *mass-selective storage*, in which confined positive ions were ejected through holes in one of the end-cap electrodes into an electron multiplier; this method was extended further by interposing a mass analyzer between the trap and the detector to give a tandem arrangement that permitted the external mass analysis of stored ions. It is perhaps significant that up to this stage ion trap mass spectrometers were not available as commercial instruments, probably reflecting the complexity of the systems and the fact that they did not appear to offer any appreciable advantage over other types of analytical mass analyzers. More recently, we have seen the use of *mass-selective axial ejection* as the means of generating mass spectra, and it is this core technique that has caused a revolution in mass spectrometry due to the performance of ion trap instruments.

1. Mass-Selective Detection

Mass-selective ion detection was presented briefly by Paul and Steinwedel (1956) in the original ion trap patent, wherein they

TABLE 1. Milestones in the mass spectrometric development of the quadrupole ion trap

Year	Description	Mode
1953	First disclosure (Paul and Steinwedel)	Mass-selective detection
1959	Storage of microparticles (Wuerker, Shelton, and Langmuir)	
1959	Use as a mass spectrometer (Fischer)	
1962	Storage of ions for RF spectroscopy (Dehmelt and Major)	
1968	Ejection of ions into an external detector (Dawson and Whetten); use as a mass spectrometer (Dawson and Whetten)	Mass-selective storage
1972	Combination of QUISTOR with quadrupole mass filter for analysis of ejected ions (Todd, Lawson, and Bonner); characterization of the trap, CI, ion/molecule kinetics, etc. (Todd *et al.*)	
1976	Collisional focusing of ions (Bonner, March, and Durup)	
1978	The selective ion reactor (Fulford and March)	
1979	Resonant ejection of ions (Armitage, Fulford, Hoa, Hughes, March, Bonner, and Wong)	
1980	Use as a GC detector (Armitage and March)	
1982	Multi-photon (IR) dissociation of ions (Hughes, March, and Young)	
1984	Disclosure of ion trap detector, (ITD)™ (Stafford, Kelley, Syka, Reynolds, and Todd)	Mass-selective ejection
1985	Ion trap mass spectrometer ITMS™ (Kelley, Stafford, Syka, Reynolds, Louris, and Todd)	
1987	MS/MS (Louris, Cooks *et al.*). CI, photo-dissociation, injection of ions, mass-range extension, etc. Fourier transform quadrupole ion trap (Syka and Fies)	
1984; 1988	Deliberate addition of contributions from non-linear field using stretched geometry and non-hyperbolic electrode surfaces (Kelley, Stafford, Syka, Taylor; Franzen)	
1989	Extension of mass/charge range *via* resonant ejection (Kaiser, Louris, Amy, Cooks)	
1990	High resolution mode of operation (Schwartz, Syka, Louris)	
1994; 1998	Linear ion traps (Schwartz, Senko, Syka; Hager)	
1997	Use of ion/molecule reactions in isotope ratio measurements (Barber, Wright, Morse, Pillinger. Kent, Todd)	
2002	Digital ion trap (Ding)	

indicated that while ions which possess unstable trajectories and thus impinge upon the electrodes represent an ohmic charge in the high-frequency circuit, ions with stable orbits are inductive charges because they do not contribute to the flow of current. The stable ions add to the inductive load of the system, and their presence may thus be detected by means of power-measuring devices.

The precise means of achieving this non-destructive ion detection was described in the pioneering publications (Paul, Osberghaus, & Fischer, 1958) and (Fischer, 1959). The main source of RF power was a 500 kHz generator coupled to the ring electrode, upon which was superimposed a DC voltage which could be swept with a sawtooth waveform. Ions were created continuously by an electron beam injected through one of the end-cap electrodes, and the secular motion of the ions along the axis of the trap was then detected by the resonant absorption of power from an auxiliary generator oscillating at 150 kHz, the output of which was applied across a 5 MΩ resistor and across half the pure resistance of a resonator. For resonance to occur the a_u, q_u coordinates of the ions were slowly swept through the $\beta_z = 0.6$ line on the stability diagram. At resonance the voltage developed was proportional to the resistance of the resonator and inversely proportional to the attenuation, such that the presence of ions led to the appearance of a y-deflection on an oscilloscope display. Fischer succeeded in recording a mass spectrum of krypton, however, the mass range and resolution of the instrument were severely limited (Fischer, 1959). The lowest detectable partial pressure was reported to be ca 3×10^{-6} Pa, equivalent to $ca.$ 2×10^4 ions cm^{-3} in the trap.

Some 8 years after Fischer's work, Rettinghaus (1967) described an alternative means for operating the ion trap utilizing mass-selective detection. The trap was fabricated with spherical electrode surfaces ($r_o = 12$ mm, $z_o = 8.5$ mm), and ions were created at low pressure (3×10^{-7} Pa) by injecting a long-duration (5 sec) pulse of electrons through an aperture in the ring electrode. The main drive frequency was 1.6 MHz, and the "detection" and "comparison" circuits were first balanced in the absence of ions in the trap. The spectrum was then generated by scanning the RF amplitude V along the $a_z = 0$ line (i.e., zero applied DC potential, $U = 0$ or the q_z axis) such that when the operating point for each m/z value crossed the $\beta_z = 0.5$ line the secular motion of the ions oscillating at 0.41 MHz came into resonance with the detection circuit. It was noted that, with a longer ionization time, the relative intensities of the higher masses decreased, and Rettinghaus ascribed this behavior to the effects of space charge causing discrimination against these species. Space charge is in fact a very important consideration in ion trap operation, since it limits the extent to which ion density may be increased. As first noted by Fischer, the presence of this space charge acts so as to defocus the ions in all directions and is manifested as a shift in the boundaries of the stability diagram (Fischer, 1959).

Another feature observed by Rettinghaus (1967) in the mass spectra of background gases was the appearance of a peak at m/z 29. This peak was ascribed to the species COH^+ formed through ion/molecule reactions occurring between $CO^{+\cdot}$ and hydrocarbon molecules present in the background. Evidence for this mechanism was presented in the form of a plot of the signal intensity due to m/z 29 divided by the ratio of the sum of the signal intensities due to m/z 29 plus m/z 28; this ratio showed an approximately sixfold increase with storage time over a range of 0–7 min. This is the first recorded observation of ion/molecule reactions within an ion trap; such processes have been the subject of much subsequent study. Other secondary effects occurring within quadrupole ion traps were noted by Burnham and Kleppner (1968) at about this time, but no detailed account of their work seems to have appeared.

The main aim of Rettinghaus' investigation was to examine the potential of the ion trap for use as a partial pressure gauge in ultrahigh vacuum systems, and he reported that it was possible to detect partial pressures as low as 10^{-11} Pa, corresponding to approximately four ions in the trap. The longest trapping time (half-life of the ion concentration) observed was about 20 min. However, there seemed to be little commercial advantage to be gained over the quadrupole residual gas analyzers that were being manufactured at that time.

Until relatively recently this appeared to be the end of the history of quadrupole ion trap operation using *in situ* mass-selective detection, but lately there has been renewed interest in this approach. Syka and Fies (1987) demonstrated the feasibility of implementing Fourier transform techniques to transient ion image currents by producing mass spectra obtained in this manner from an ion trap. Essentially, the scheme is to excite the resonances of ions having a broad range of m/z values at a specific value of β_z and then to perform a Fourier transformation on the output from the receiving circuit coupled between the end-cap electrodes. Studies to date indicate that this mode of detection does not offer any advantages over other mass spectrometric modes of operating the ion trap; the relatively prolonged image current decay transients require low pressure, thereby negating a strength of the ion trap which is to yield mass spectra of high quality at elevated pressures. Goeringer, Crutcher, and McLuckey (1995) employed image current detection to demonstrate multiple re-measurement of the same population of ions held in an ion trap at a pressure of ca 10^{-4} Torr; the efficiency of ion re-measurement was >99%. Cooks and co-workers (Frankevich et al., 1997; Nappi et al., 1998) have explored the potential of broadband Fourier transform ion trap mass spectrometry.

2. Mass-Selective Storage

The middle to late 1960s saw a major renewal of interest in the ion trap and, at this stage, the history of its development really begins to follow two parallel branches. On the one hand, spectroscopists, led by H. G. Dehmelt at the University of Washington, Seattle, saw the radiofrequency quadrupole ion trap as a means of enabling a wide variety of gas-phase spectroscopic experiments to be performed with isolated simple atomic and molecular ions. Dehmelt has summarized this early work in two important reviews (Dehmelt, 1967, 1969), and these have acted as significant stimuli for further work on the physical characterization of the ion trap as an ion source and as a mass spectrometer (Wineland & Dehmelt, 1975; Schuessler, 1977; Schuessler, 1979; Wineland et al., 1983a; Wineland, Itano, & Van Dyck, 1983b; Wineland et al., 1985a,b,c). The other branch of development, as a mass analyzer, originates from the realization by Dawson and Whetten (1968a,b, 1970) that ions could be

ejected efficiently from the trap through holes in one of the end-cap electrodes onto the first dynode of an electron multiplier or into a ''channeltron'' and thus be detected externally, thereby avoiding many of the difficulties associated with mass-selective detection. Dawson, who carried out a series of such studies with Whetten at the General Electric Laboratories in Schenectady, NY, was the first Canadian to contribute to this field. In addition, Dawson edited and contributed to the first book (Dawson, 1976b) on quadrupole mass spectrometry.

To use the ion trap as a mass spectrometer, the method of mass-selective storage was developed. The idea follows closely the operating principle of the quadrupole mass filter and involves selecting a working region of the stability diagram where only ions with a single value of *m/z* possess stable trajectories and hence are stored (Dawson & Whetten, 1969). Ions were created by admitting a beam of electrons from a filament *via* a gating electrode through holes in one of the end-cap electrodes. This ionization pulse lasted *ca* 5 msec, after which the ions were stored for a delay time of 25 μsec before being extracted into the multiplier by means of a pulse applied to the other end-cap electrode. Mass selection occurred during the delay time and, to generate a mass spectrum, the amplitudes of the DC and RF fields were scanned slowly at constant *U/V*. With a total duty period of *ca.* 5 msec the maximum repetition frequency was approximately 200 Hz, with the signal duration being in 3 μsec bursts. Thus, to avoid the loss of intensity that would otherwise result from the averaging of the output and to eliminate the detection of the excess of ions present during the storage and detection periods, a ''boxcar detector'' system was incorporated into the signal-processing circuit. Compared to the earlier mass spectra produced employing mass-selective detection, the quality of the data obtained with this new method of operation was excellent.

The idea of detecting ions by ejecting them from the ion trap really represents a watershed in the development of the device for mass spectrometric applications, and within a short space of time various other groups of workers including Harden and Wagner (1971a,b), Dawson and Lambert (1975), Mastoris (1971), and Sheretov and co-workers (Sheretov, Zenkin, & Boligatov, 1971; Sheretov & Zenkin, 1972; Sheretov et al., 1973a; Sheretov, Zenkin, & Samodurov, 1973b; Sheretov et al., 1974, 1978; Sheretov, Zenkin, & Mogil'chenko, 1976), reported further developments and refinements of this method. Mastoris and Lambert were graduate students at the University of Toronto Institute of Aerospace Studies (UTIAS) and at the Centre de Recherches sur les Atomes et Molécules (CRAM) de l'Université Laval in Québec City, respectively. The doctoral theses of Mastoris and Lambert were the first such theses in Canada on the quadrupole ion trap; Mastoris' thesis is in English and Lambert's thesis (Lambert, 1974) is in French.

3. Adventitious Ion Loss Processes

The sensitivity of any mass spectrometer is determined directly by the fraction of the ions formed from a given quantity of sample and which, after analysis, reaches the detector. For mass analyzers based upon principles involving beam transport, for example magnetic sector, time-of-flight, or quadrupole mass filter, the sensitivity is related to the ionization efficiency and to

the transmission characteristics of the analyzer. With the ion trap the corresponding parameter is the rate of ion loss during the period between creation and detection, and it is hardly surprising, therefore, that considerable attention has been paid to the study of this phenomenon. Ion loss may occur through a number of different processes.

a. Unstable trajectories. There are essentially two types of unstable trajectories:

(i) Intrinsically (mathematically) unstable trajectories, where the a_u, q_u coordinates for a given ionic species correspond to a working point that lies outside the stability boundary. The trajectory is unbounded, so that the ion is rapidly removed from the trap; this mechanism is, of course, the means by which mass-selective storage is achieved wherein unwanted ions are ejected from the ion trap.

(ii) Quasi-unstable trajectories, where the mathematical conditions for stability exist but nevertheless the ion is lost because the limit of excursion of the ion exceeds the internal dimensions of the device. Such an ion might, for example, have been formed very near one of the electrode surfaces and/or have a significant initial velocity.

b. Interactions. The occurrence of ion/neutral molecule collisions and ion/ion interaction processes may lead to the charged species developing unstable orbits. A number of different kinds of effects are important here: for example, depending upon the nature of the species, ion/neutral collisions may variously lead to damping, elastic scattering, inelastic scattering, charge-transfer, and ion/molecule reactions.

In scattering collisions one can visualize an ion with a stable trajectory being suddenly deflected such that its new situation is effectively one of having an unfavorable initial starting position and/or initial velocity; in addition there may be a transfer of kinetic energy (i.e., velocity) from one co-ordinate direction to another so that the original simple assumption relating to the independence of the three components of motion no longer applies. Such collisions have been the subject of a number of studies (Londry, Alfred, & March, 1993; Julian et al., 1995; Bui & Cooks, 1998; Forbes et al., 1999), in which it has been shown that the relative masses of the ion and the neutral species are critical in determining whether or not the ion trajectory is destabilized (when the neutral mass is heavier than that of the ion) and whether or not the ion trajectory is stabilized (neutral mass less than that of the ion). Indeed, the latter effect plays a crucial rôle in improving the performance of the modern ion trap mass spectrometers (Stafford et al., 1984) through the influence of momentum-moderating collisions with helium buffer gas which, by reducing the kinetic energies of the ions and causing the trajectories to ''collapse'' toward the center of the trap, improves dramatically both the sensitivity and resolution of the device. Collisional cooling has also been important in the uses of radiofrequency quadrupole ion traps for the study of the spectroscopy of trapped ions.

In the case of charge transfer, an ion in a stable trajectory is removed and a new one, probably with effectively zero initial

velocity, is created. Whether or not this new species will remain stable again depends upon the precise operating conditions at the time of the event, as well as upon the m/z value of the product ion. Provided the conditions are chosen correctly, charge transfer does not necessarily lead to ion loss; for example, low pressure kinetic studies on argon-methane mixtures have shown that within experimental error the rate of loss of Ar^+ is balanced exactly by the rate of formation of CH_3^+ and CH_2^+ (Bonner et al., 1974; Lawson et al., 1975). March and co-workers (Bonner, March, & Durup, 1976; Bonner & March, 1977) reported on detailed experiments and the theoretical modeling of systems such as $Ar^+ + Ar$, where it has been shown that such interactions can again lead to the migration of ions toward the center of the trap, thus improving the storage efficiency of the device.

c. Space-charge perturbation. The problems associated with ion/ion scattering may be visualized as giving rise to two different kinds of effects. On the one hand, at the microscopic level of individual collisions, a pair of like-charged ions will repel one another, possibly leading to either or both of them developing unstable trajectories. This effect will clearly become more important as the concentration of ions within the trap is increased, for example, by lengthening the ion-formation period. Attempts have been made to quantify the process of ion/ion scattering in terms of the kinetic approach described below. On the other hand, the theory of ion containment within the trap is based on the assumption that there is only a single ion in the trap. As the ion concentration increases, the trapping potentials are modified by a defocusing effect due to the space charge, which has the effect of modifying the locations of the boundaries of the stability diagram. The importance of space-charge perturbation was first recognized by Fischer (1959), and has been examined in more detail by other workers (Mathurin et al., 1997).

Reference was made to the idea that ion scattering could be considered in terms of a kinetic approach. The first such approach was employed by Fischer, who determined a "mean ion lifetime" $\overline{\tau_i}$ by observing how the signal height h varied as the ionization time was increased (Fischer, 1959). Thus over a period of $5-20\,\mu\text{sec}$ (depending upon the electron beam current) the signal was found to first increase linearly and then reach saturation, corresponding to level h_∞. The equation

$$\overline{\tau_i} = \frac{h_\infty}{\dot{h}_o} \qquad (79)$$

then gave a value for $\overline{\tau_i}$, where $\dot{h}_o$ is the rate of increase of the signal with time over the initial linear period.

The problem was considered subsequently by Dawson and Whetten in terms of a rate law analogous to those employed in chemical kinetics, and this approach was also adopted by other workers (Harden & Wagner, 1971b; Schermann & Major, 1971, 1978; Lawson, Bonner, & Todd, 1973). Consider the situation where the trap contains N ions cm^{-3}; then during the ion formation period the rate of change of N with time must represent the difference between the rate of formation of ions and the rate of their loss:

$$\frac{\text{d}N}{\text{d}t} = k_1 p - (k_2 N^2 + k_3 N p) \qquad (80)$$

where p is the pressure of neutral molecules, k_1 is a rate constant for ion formation, k_2 the rate constant for loss by ion/ion scattering, and k_3 the rate constant for loss by ion/neutral scattering. In practice, a plot of N versus t is obtained by increasing progressively the length of the ionization period, allowing a short period for the quasi-unstable ions to be rejected; the ions are ejected then into the detector by pulsing an end-cap electrode.

To evaluate the rate constants we can simplify Eq. (80) by imposing certain sets of conditions. Thus over the initial linear period we can put $N \cong 0$ so as to obtain:

$$\frac{\text{d}N}{\text{d}t} = k_1 p \qquad (81)$$

from which k_1 may readily be found for a given value of p. Similarly, if we work under saturation conditions ($N = N_\infty$), then we have that $\text{d}N/\text{d}t = 0$, so Eq. (80) becomes

$$k_1 p = k_2 N_\infty^2 + k_3 N_\infty p \qquad (82)$$

Operating at relatively high pressure allows us to assume that $k_3 p \gg k_2 N$, so that k_3 may be found from

$$k_3 = \frac{k_1}{N_\infty} \qquad (83)$$

The value of k_2 may now be obtained using a curve-fitting routine on the first derivative of the buildup plot of N versus t. An alternative approach, which is more precise, is to monitor the decay in the value of N after the electron beam has been switched off. Thus:

$$\frac{\text{d}N}{\text{d}t} = -(k_2 N^2 + k_3 p) \qquad (84)$$

Further details of these two methods and comparisons of different sets of results have been published elsewhere (Lawson, Bonner, & Todd, 1973; Lawson et al., 1975). A typical set of data for Ar^+ ions (Todd, Lawson, & Bonner, 1976) is given in Table 2, from which one can deduce the following rates of ion loss:

TABLE 2. Typical ion-loss parameters for Ar^+ from an ion trap

r_0	1.0 cm
Pressure	32 mPa
Drive frequency	0.762 MHz
V	140 V (zero to peak)
q_z	0.59
N_∞	$1.04 \times 10^7\ \text{cm}^3$
k_1 (ion formation)	$1.05 \times 10^{13}\ \text{cm}^3\,\text{Pa}^{-1}\,\text{s}^{-1}$
k_2 (ion/ion scattering)	$2.7 \times 10^{-4}\ \text{cm}^3\,\text{s}^{-1}$
k_3 (ion/neutral scattering)	$1.3 \times 10^5\ \text{Pa}^{-1}\,\text{s}^{-1}$

Ion/ion scattering: $k_2 N^2 = 2.9 \times 10^{10}\,\text{cm}^{-3}\,\text{sec}^{-1}$
Ion/neutral scattering: $k_3 Np = 4.2 \times 10^{9}\,\text{cm}^{-3}\,\text{sec}^{-1}$

Thus under these conditions it would appear that ion/ion scattering is slightly the more dominant effect, although ion-neutral scattering will become progressively more important as the value of N falls. Dawson, Hedman, and Whetten (1969) deduced that in their trap ion/neutral scattering was the major ion loss mechanism above $10^{-6}\,\text{Pa}$ in the mass-selective storage mode, whereas Harden and Wagner concluded that the corresponding pressure was ca. $10^{-4}\,\text{Pa}$ (Harden & Wagner, 1971b).

d. Nonlinear resonances. So-called non-linear resonances constitute another mechanism for ion loss. Because of deliberate or unintentional imperfections in the quadrupole field due, for example, to non-ideal electrode spacing, non-perfect surfaces, truncation of electrodes, and perforations in electrodes for entry and egress of ions, there may exist higher-order terms for the expression for the potential in addition to the ideal second-order form of the potential. These effects were first considered by von Busch and Paul in relation to the behavior of the mass filter (Busch & Paul, 1961), and detailed applications to the ion trap have been presented (Whetten & Dawson, 1969; Franzen et al., 1995). Nonlinear resonances constitute a classic case of weeds turning to flowers; the early work on nonlinear resonances highlighted the adverse effects, such as peak splitting, whereas recent work has increased our understanding of nonlinear resonances to the point where they are employed in the rapid ejection of ions from the ion trap with good mass resolution. All commercial quadrupole ion traps today use nonlinear resonances to enhance their performance.

e. Self-emptying. A final means of ion loss from the low-pressure trap, which is less well characterized than that of nonlinear resonances, is "self-emptying." Thus both Fischer (1959) and Whetten and Dawson (1969) observed that at high ion concentrations (continuous ionization) the ion signal was oscillatory. Fischer attributed this to the effects of space charge causing a shift in the position of the resonance lines within the stability diagram so that ions were removed, leading to a reduction in the space charge and relaxation of the resonance line back to its former position. Because of the continuous creation of ions, this cycle was then repeated, with a frequency of 50–1,000 Hz depending upon the operating conditions. In the experiments described by Whetten and Dawson it was found that when the (a_z, q_z) working points were close to the $\beta_z = \frac{1}{2}$ or $\frac{2}{3}$ lines, the output of the detector exhibited an oscillatory character, the period of which (ca. 6×10^{-4} sec) was inversely proportional to the ionization rate (which was changed by varying either the gas pressure or the electron current) and was proportional to the square of the frequency of the applied RF power. The phenomenon was explained on the basis of the idea that the ions are able to gain additional energy from plasma oscillations of the charge cloud.

B. The Low Pressure QUISTOR-Quadrupole Combination

The ability of the ion trap to store ions with a wide range of m/z values in the RF-only mode prompted Todd and co-workers to utilize the low pressure trap as the ion source for a quadrupole mass filter in a series of experiments designed originally to study the fragmentation behavior of metastable ions. Thus in this early form of tandem instrument ions could be created by electron ionization, trapped for a defined period of time (along with any product ions from metastable decay reactions), and then pulse-ejected into the quadrupole mass filter for mass analysis. This development led to the creation of the name QUISTOR (QUadrupole Ion STORe) (Lawson & Todd, 1971), and this tandem instrument has proved to be an excellent vehicle for characterizing the physical aspects of ion trap operation as well as for studying the kinetics of ion/molecule reactions. Ionization was effected by pulsing in a beam of electrons through a hole in the ring electrode such that, after a defined storage time, the application of appropriate pulses to either or both of the end-cap electrodes caused the ion packet to be ejected from the ion trap into the quadrupole mass filter. The "detection pulse" corresponded to the opening of the amplifier gate of a boxcar detector circuit whose function was to eliminate spurious background signals arising from unstable ions ejected during the creation and storage periods and to retrieve the signal pulses which would otherwise be averaged out over the complete duty cycle. A typical repetition frequency was 100 Hz. Depending upon the particular experiment being conducted, the quadrupole mass filter could be set to transmit a specific m/z value or scanned slowly to generate a mass spectrum of the ejected ions.

1. Chemical Ionization

Early results showed that, despite the presence of RF voltages applied to the QUISTOR, the trap behaved like a conventional ion source when used for the determination of the ionization energy of helium (Lawson, Bonner, & Todd, 1973). Ion/molecule reactions could be investigated readily by recording the mass spectra of the ejected ions as a function of the storage time and it was found that, with a pressure of ca. $10^{-2}\,\text{Pa}$ of methane and storage times in the range of 0–3 msec, the distribution of primary and secondary ions closely resembled those obtained with conventional ion sources operating at around 130 Pa pressure. This observation led to the demonstration that analysis by chemical ionization could easily be performed with the QUISTOR (Todd, Bonner, & Lawson, 1972), and detailed investigations of the reactions of CH_5^+ ions with water and with ammonia were carried out (Lawson et al., 1976). The rate constant values obtained in this latter work made use of data (Smith & Futrell, 1973) for the reaction.

$$CO_2^{+\cdot} + H_2 \rightarrow CO_2H^+ + H \qquad (85)$$
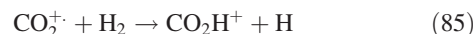
for calibration purposes, and suggested average ion kinetic energies in the 1–3 eV range, which were consistent with calculations based on the pseudopotential well model proposed by Dehmelt (1967). The reaction represented by Eq. (85) is also employed in the measurement of isotope ratios using the ion trap as part of the Rosetta mission to characterize a comet; see Chapter 9 in March and Todd (2005).

2. Collisional Focusing

The investigation of charge-transfer effects has led to important increases in our understanding of the processes occurring within the

ion trap. The first system studied was the reaction $Ar^{+\cdot} + CH_4$, which was a quasi-standard process in ion/molecule reaction kinetics; excellent data for Ar/CH_4 ratios in the range 1.0:0.1 to 1.0:3.4 were obtained (Bonner et al., 1974). Subsequently, in a study of the variation in the ratios of detected currents for $Ar^{+\cdot}$ and Ar^{2+} ions formed in the QUISTOR from argon under a variety of conditions, March and co-workers invoked charge transfer as a process which leads to the selective migration of ions toward the center of the trap from which ions are extracted more efficiently (Bonner, March, & Durup, 1976). An alternative explanation (Todd et al., 1978) was based on the premise that space-charge-induced shifts in the $\beta_z = 0$ boundary of the stability diagram would affect the stability of the two ionic species differently. However, in a subsequent experimental and theoretical study of mixtures of neon and carbon dioxide, the March group demonstrated unequivocally the importance of ion migration (Doran et al., 1980), both for ions formed from these species and from the compound d_6-dimethyl sulfoxide (Fulford, Dupuis, & March, 1978).

3. Space Charge

Mention has already been made of the non-ideal behavior of the ion trap that can be caused by space-charge-induced defocusing of the ion cloud. Todd and co-workers examined these effects in some detail using a technique in which the application of accurately measured DC and RF potentials to the ring electrode of a low pressure trap allowed them to determine the precise working points at which the trapping of specific types of ions became possible (Mather, Waldren, & Todd, 1978). The results of these experiments indicated that distortion from the theoretical (single-ion) diagram becomes more pronounced as the value of m/z is reduced. When the data were re-plotted in terms of $U - V$ coordinates, it was found that the lower apex (i.e., the operating region employed in the mass-selective storage mode) for each of the ions did indeed lie on a scan line, but one that had a positive intercept (of $ca.$ 8.0 V) along the a_z-axis. This is equivalent to a net defocusing potential acting along the axis of the trap. Todd, Waldren, and Mather (1980b) have discussed their observations of space-charge-induced effects in terms of the pseudo-potential well model (Dehmelt, 1967) and in relation to theoretical treatments given by Fischer (1959) and by Schwebel, Moller, and Manh (1975).

4. Selective Ion Reactor

Progress in the study of ion/molecule reactions occurring within the ion trap was aided significantly by two important developments in technique: the selective ion reactor (Fulford & March, 1978) and QUISTOR resonance ejection, both of which were developed by the group at Trent University. In the first of these, which was based on an original idea published by Bonner (1977), a single reactant ion species may be isolated by applying appropriate DC pulses to the end-cap electrodes during the ion-creation period, thus rendering unstable the trajectories of all ions except those of the selected precursor.

5. QUISTOR Resonance Ejection

QUISTOR resonance ejection (QRE) (Fulford et al., 1980) utilizes a technique employed originally by Paul, Osberghaus,

and Fischer (1958) and Paul, Reinhard, and Von Zahn (1958) in their use of a quadrupole ion trap for the separation of isotopes, namely, the application of supplementary electric fields to energize ions mass-selectively and thereby render unstable the trajectories of specific ion species. In the case of the QUISTOR, QRE is effected by applying a low-amplitude AC potential between the end-cap electrodes (in fact only one end-cap electrode need be energized because the other is held at earth during the storage period). By this method it has been possible to undertake a number of investigations of different types. For example, the rate constant for partial charge transfer reactions such as $Ar^{2+} \rightarrow Ar^{+\cdot}$ may be found readily by first resonating out primary $Ar^{+\cdot}$ ions formed during the ionization period and then monitoring changes in the Ar^{2+} and $Ar^{+\cdot}$ signal levels as the reaction period is increased. In the same manner the coupling of reactant and product species involved in ion/molecule reactions may be demonstrated (Armitage et al., 1979a, 1980; DeBrou et al., 1978) in a way similar to the ion cyclotron double resonance (ICDR) technique (Anders et al., 1966), and it has proved possible to initiate endothermic ionic processes and to demonstrate a rate dependence upon amplitude of the resonant energy supplied (Fulford et al., 1980). In practice it is found that the precise frequency at which a given ion comes into resonance deviates from that predicted theoretically, and this is analogous to the space-charge-induced shifts in the stability boundaries noted earlier. By studying this effect in detail Fulford et al. (1980) were able to deduce that, under their operating conditions with 2-propanol as the sample, the saturation ion density was $6.4 \times 10^{12} \, m^{-3}$ which compared well with other literature values. This technique of resonant excitation has been applied to the study of collision-induced dissociation processes with the ion trap (Plomley, Londry, & March, 1996) operating in the mass-selective mode (Louris et al., 1987).

C. Theoretical Aspects of Low Pressure Ion Trap Operation

Initial attempts to model the behavior of quadrupole devices relied on the calculation of individual trajectories, assuming specific initial conditions of displacement, velocity and phase angle of the RF drive potential at which the ions were formed. The early work of Paul et al. relied upon finding analytical solutions to the equations of motion (Paul, Osberghaus, & Fischer, 1958; Paul, Reinhard, & Von Zahn, 1958). Subsequently, numerical integration of the Mathieu equation was used together with the fourth-order Runge-Kutta equation (Lever, 1966) and (Dawson & Whetten, 1968a).

1. Phase-Space Dynamics

Two important advances which led to a considerable simplification of the computations were the use of matrix techniques, first applied by Richards, Huey, and Hiller (1973) to the case of a quadrupole analyzer driven by a square wave, and the treatment of the ion motion by the methods of phase-space dynamics, pioneered by Baril and Septier (1974). The detailed derivation of the expressions used in these techniques is beyond the scope of this historical survey, and the reader is referred to other sources (Dawson, 1976a; Waldren & Todd, 1978).

The major advantage of the phase-space representation is that it is easy to envisage the behavior of the ensemble of ions at a specified phase angle with respect to the motion in a given direction. For trajectory stability all the values of the positional and velocity coordinates, $u, \dot{u}$, must lie on or within the appropriate ellipse, and all those ions with values outside the boundary will be rejected. In this case, the ellipse is termed an *acceptance ellipse* and its area, proportional to the acceptance ε, represents the range of initial conditions that the system will accept. An alternative interpretation is that a focusing system will only transmit a beam of particles whose values of u and $\dot{u}$ are bounded by the ellipse, in which case ε is representative of the emergent beam and is called the *emittance* of the *beam ellipse*. Ideally for the QUISTOR-quadrupole combination there should be "phase-space matching" between the two components so that there will be optimum transmission when the emittance of the beam ellipse of ions ejected from the QUISTOR coincides exactly with the acceptance of the ellipse for the quadrupole. Such phase-space matching has not been investigated for the QUISTOR-quadrupole system, although it has been considered for normal ion source-quadrupole mass filter combinations (Dawson, 1975) and for tandem quadrupole systems (Dawson, 1980). Obviously, for a full description of the behavior of the quadrupole ion trap, one must consider ellipses corresponding to the components of motion in the orthogonal x-, y-, and z-directions; the first two are in fact identical, but motion in the z-direction will be out of phase by half a cycle and the value of u_{max} will be given by z_o.

It has been shown (Baril & Septier, 1974) that beam ellipse transformation is repeatable periodically due to the periodicity of the equations of ion motion in RF quadrupole fields. It has been found that, for fixed values of RF and DC voltages applied to a quadrupole mass filter (that is, fixed a_u and q_u), when an ion enters at an initial RF phase ξ_0 with certain values of u and $\dot{u}$ then at all phases during subsequent cycles given by

$$\xi = (\xi_0 + k\pi), \quad k = 1, 2, 3, \ldots, \qquad (86)$$

its position and velocity will lie on the same ellipse in phase-space. Therefore, if such an ion spent an infinite time in the quadrupole field, that is $k \to \infty$, its values of u and $\dot{u}$ measured at phase ξ during each cycle would form eventually an ellipse in phase space. Thus, all ions entering the field with initial phase ξ_0 and initial conditions $u(0)$ and $\dot{u}(0)$ lying on the ellipse would, in the long term, have equivalent trajectories. Dawson has shown (Fig. 3 in Dawson, 1974) typical variations of the periodically repeatable ellipse parameters A, B, and Γ over a complete RF cycle for fixed operating conditions.

There are, however, two exceptions to this pattern. First, an ion with an unstable trajectory would have such periodically measured values of u and $\dot{u}$ that lie on a hyperbola rather than an ellipse (Baril & Septier, 1974). For an unstable trajectory the values of u and $\dot{u}$ will continue to diverge with increasing time so that no closed figure could be formed in phase space. Eventually, of course, u would become greater than the physical radius of the device. Second, an ion undergoing motion with a value of β (the well-known constant of secular ion oscillation, see Eq. 78) which is a rational fraction (that is, $\beta = p/d$, where p and d are integers having no common factors) repeats exactly its trajectory after a

certain number of cycles. It should be noted that in such cases, where self-emptying (see Section IV.A.3.e.) and efficient ion ejection in mass-selective axial ejection are observed in the quadrupole ion trap (March & Todd, 2005), the appropriate values of u and $\dot{u}$ would lie only on certain fixed points of an ellipse. It should be remembered that the phase-plane ellipses represent ion motion in only the x- or y-directions and thus the phase transformation described is not only for fixed values of a and q but also for a certain fixed value of β. The phase-space trajectory of such an ion in the mass filter is shown in Figure 10 (Dawson, 1976b) and shows the formation of these ellipses for three different RF phases.

Matrix methods based upon phase-space dynamics were employed by Dawson and Lambert, who performed a detailed study of the behavior of the ion trap operating in the mass-selective storage mode (Dawson & Lambert, 1975). In particular they extended Fischer's earlier work (Fischer, 1959) on the efficiency of trapping under various conditions and showed that radially directed electron beams should be more effective in this regard than axially directed ionization. They demonstrated also how ions formed with significant kinetic energies would be confined less efficiently than those with zero velocity; this work suggested that light ions such as $H_2^{+\cdot}$ and $He^{+\cdot}$ may be very difficult to trap. The efficiency of trapping light ions was investigated also by Baril (1981), and the ability of the trap to confine multiply charged ions formed by sequential ionization was studied by Schwebel and co-workers (Schwebel, Moller, & Manh, 1975; Moller et al., 1976) and by Baril (1981).
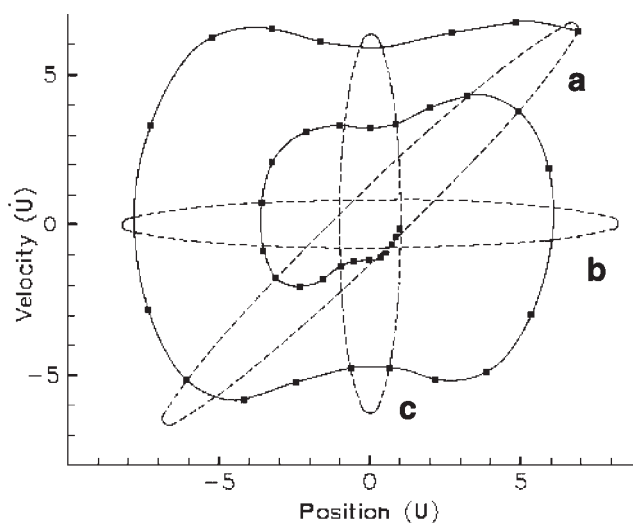
FIGURE 10. The phase-space trajectory of a single ion for the working point $a = 0.230114$, $q = 0.696$ in the mass filter stability diagram. The solid line represents the trajectory during four RF cycles starting with $u_0 = 1$, $\dot{u}_0 = 0$ at the initial phase $\xi_0 = \pi/5$. The points represent the values of u and $\dot{u}$ after each tenth of an RF cycle. Note how the elliptical boundaries for phases (**a**) $\pi/5$, (**b**) 0, (**c**) $\pi/2$, depicted by the broken lines, are built up. Reproduced from Dawson (1976b). Quadrupole Mass Spectrometry and Its Applications Amsterdam, Elsevier, copyright 1976, with permission of Elsevier.

Two further important contributions by Dawson included a description of how the phase-space approach could be utilized to determine velocity distributions of the stored ions (Dawson, 1976a), and an analysis of the effects of collisions in terms of ways in which the modified velocity distributions could be represented by changes in the ellipse parameters (Dawson, 1977). In the first of these papers it was assumed that when all points within a given phase-space ellipse are occupied uniformly, then the number of ions having a particular velocity $\dot{u}$ will be proportional to the width of the ellipse at that $\dot{u}$ value; the average velocity may then be found by suitable integration. This treatment was extended subsequently by Todd, Waldren, and Bonner (1980a) and the results compared with calculations of velocities derived from the pseudo-potential well model and one using a smoothed general solution of the Mathieu equation. Todd and co-workers (Todd et al., 1980c) adapted Dawson's velocity distribution approach to the calculation of the spatial distribution of ions (neglecting space-charge and migration effects) and showed how the cylindrical volumes containing the ions varied with the phase angle of the RF drive potential for different values of the parameters a_u and q_u. With this treatment it was possible to offer an explanation for the shape of the "total pressure curve" which is traced out when the ejected ion signal is plotted against the value of q_u at the time at which the ions are created and stored ($a_u = 0$).

2. Pseudopotential Well Model

Other investigations included (1) an appraisal of the accuracy of the pseudopotential well model in terms of phase-space dynamics, where it was shown that only at very low q_u values ($a_u = 0$) did the majority of the $u, \dot{u}$ coordinates lie simultaneously within the relevant ellipses for both models (Todd, Freer, & Waldren, 1980d), and (2) a time-of-flight analysis of ions ejected from the trap by the application of narrow withdrawal pulses which were synchronized with a specific phase angle of the RF drive potential (Waldren & Todd, 1979; Mosburg et al., 1987). In the latter experiments it was shown that the velocities of the fastest ions corresponded to those with the calculated maximum velocity traveling toward the detector at the moment of ejection. Perhaps the most significant result of the phase-synchronized pulse-ejection experiments was to show that the optimum phase angle for ejection of the ions coincides with the time at which the velocities of the bulk of the ions in the radial phase are directed toward the z axis (Todd, Waldren, & Bonner, 1980a). A comparative survey of recent methods (Forbes et al., 1999) employed for the simulation of ion trajectories in the quadrupole ion trap gives an introduction to modeling of ion trajectories for simulation studies.

V. RESEARCH ACTIVITIES WITH THE QUADRUPOLE ION TRAP

Concurrent with the characterization of the quadrupole ion trap, modeling of ion trajectories both with and without collisions with neutrals, the development of theoretical treatments of ion trajectory behavior, and a miscellany of research activities with

the ion trap were being pursued. The variety of these activities was due, in part, to the appreciation of three further aspects of ion trap behavior. First, the number of ion/neutral collisions can be controlled and the effects of such collisions are the quenching of an ion's internal energy and modification of its trajectory, particularly with respect to the maximum excursion from the center of the ion trap. Collisional focusing of the ion ensemble in this manner permitted ready illumination of virtually the entire ion cloud by a laser beam. Second, laser beam irradiation of the ion cloud caused photodissociation of ions whereupon the photoproduct ions were confined within the ion trap. Thus ions created in the trap, either by photodissociation (predominantly by multi-photon absorption thus far) or by unimolecular fragmentation of metastable ions, may be trapped and mass analyzed. Third, while the field at the center of the ion trap is vital for prolonged storage of ions, the shapes of the electrodes to which the field-forming potentials are applied are not so critical. Thus it is possible to create ion-confining fields with a cylindrical ion trap wherein a cylindrical "barrel" electrode and two planar end-cap electrodes are substituted for the hyperboloidal electrodes of the quadrupole ion trap. Todd and March have given a perspective of the developments in the theory, technology, and applications of the QUISTOR in the time window defined broadly as the 1970s and up to the appearance of commercial quadrupole ion trap devices. The circumstances that drew the authors to pursue their research are described also (Todd & March, 1999).

A. Collisional Migration of Ions

The focusing effects of ion-neutral collisions upon a trapped ion ensemble were shown dramatically by Dehmelt and co-workers (Neuhauser et al., 1978a,b), thus supporting the argument of March and co-workers (Bonner, March, & Durup, 1976) for collisional migration of ions. This focusing effect on trapped ions in collision with a light buffer gas was pursued also in great detail by André and co-workers (André, 1976; André, Vedel, & Vedel, 1979) and was vital to the subsequent commercial development of the ion trap (Kelley, Stafford, & Stephens, 1985). In addition to inelastic collisions, reactive ion/molecule collisions were studied with particular emphasis on ion/molecule equilibria for the determination of proton affinities (Kamar, Young, & March, 1986a) and the chemistry of gaseous ions (Fulford, Dupuis, & March, 1978).

B. Laser Irradiation

Laser irradiation has been employed extensively for sideband cooling of trapped ions by the groups of Dehmelt (1983), Wineland (1984), and Wineland et al. (1985c). Though laser cooling, RF spectroscopy, and frequency standards (wherein the frequency of laser-induced light from ions confined in an ion trap may be used as an ultraprecise time standard) are beyond the scope of this volume, the line of demarcation is not firm. We have attempted to acknowledge particularly those contributions from pure physics to our understanding of the ion trap as it is applied to chemical problems. Two examples will serve to illustrate the point: the visible focused ion cloud shown by Dehmelt and co-workers (Neuhauser et al., 1978a,b), and the laser probing of

confined ions by Desaintfuscien and co-workers (Plumelle et al., 1980). The former confirmed the focusing action due to ion collisions with a light gas, while the latter mapped the ion density as a function of working point, both with and without collisions. A knowledge of spatial distribution and ion density is vital to the interpretation of ion signals in chemical applications. Laser-induced fluorescence from trapped ions has been employed in the determination of radiative lifetimes of trapped molecular ions of $HCl^{+\cdot}$ and $HBr^{+\cdot}$ (Martner et al., 1983) and in the investigations by Mahan, O'Keefe, and co-workers (Grieman, Mahan, & O'Keefe, 1980; Grieman et al., 1981a; Grieman, Mahan, & O'Keefe, 1981b; Mahan & O'Keefe, 1982) of fragment ions formed in excited states by electron impact.

1. Infra-Red Multiphoton Dissociation

An alternative method resonance excitation for the dissociation of mass-selected ions is infra-red multiphoton dissociation (IRMPD) with an infra-red laser. When nascent ions are allowed to undergo multiple collisions with helium buffer gas, the ions become focused into a small cloud at the center of the ion trap that can be subjected to infra-red radiation. Because the ions are confined within a sphere of radius *ca.* 1 mm, they can be bathed in the laser beam for relatively long periods; during irradiation, internal energy in the ions increases to the point where the dissociation channel of lowest activation energy is accessed. Product ions can be mass analyzed subsequently. In the first IRMPD experiments in an ion trap using a CO_2 continuous wave laser, March and co-workers pursued studies of protonated aliphatic alcohol dimers, and their deuterated analogs were formed, isolated, and irradiated (Hughes, March, & Young, 1982; Hughes, March, & Young, 1983a,b,c). Subsequently, the dissociation rates of protonated aliphatic alcohol dimers were studied (Young, March, & Hughes, 1985), and the technique was extended to photodissociation of protonated species for isomer differentiation (Kamar, Young, & March, 1986b).

C. Cylindrical Ion Traps

The development of cylindrical ion traps (Langmuir et al., 1962; Benilan & Audoin, 1973; Gabrielse & MacKintosh, 1984) and the characterization of such devices (Bonner et al., 1977; Nassiopoulos, Moller, & Septier, 1980a,b; Mather et al., 1980) was followed rapidly by the utilization of these ion traps for RF spectroscopy (Houssin, Jardino, & Desaintfuscien, 1987). Micro-traps of modified geometry (Bergquist et al., 1985; Beaty, 1987; Wineland et al., 1987) have been used also for RF spectroscopy. Lifshitz and co-workers, in their studies of metastable ions fragmenting in the millisecond time range, have employed an ion trap with cylindrical geometry combined with a quadrupole mass filter as a means of obtaining time-resolved photoionization mass spectra (Lifshitz et al., 1982; Lifshitz and Malinovich, 1984).

In tracing this history of the ion trap, we have seen that the interplay of theory and experiment has led to a greater understanding of the chemical and physical processes that take place within the device. Indeed, these studies have continued with extensive theoretical work on the means by which one may trap, in the QUISTOR, ions generated externally and injected into the

QUISTOR (Kishore and Ghosh, 1979; Todd, Freer, & Waldren, 1980e; O and Schuessler, 1981, 1982) and experimental studies (Ho et al., 1984; Curtis et al., 1987) which include conversion of an ion to a Rydberg state so that as a neutral species the ion may enter the ion trap wherein it is reionized (Vedel et al., 1984). Wanczek and co-workers used a cylindrical QUISTOR to trap ions formed by electron ionization of carbon dioxide clusters present in a supersonic beam (Gabling, Romanowski, & Wanczek, 1986; Romanowski, Gabling, & Wanczek, 1986, 1987) and, using a mass-selective technique, investigated cluster ion decay in the millisecond time range. However, as noted above, it is perhaps significant that up to this point in time the ion trap had still not been developed commercially. A detailed account of recent research utilizing cylindrical ion traps and micro-traps is given in Chapter 6 of March and Todd (2005).

D. Quadrupole Ion Trap as a Detector for Gas Chromatography

Although there had been early thoughts about the viability of the ion trap as a commercial mass spectrometer (Finnigan & Todd, personal communication), and there was evidence that the trap could be employed for the enhancement of weak mass spectral peaks (Lawson & Todd, 1977) and as a successful mass detector for use with a gas chromatograph (Armitage, 1979), there were several factors working against its adoption as a routine analytical instrument. Specifically, it did not appear to offer any marked advantages over the existing instrumentation in relation to applications that were current in the mid-1970s. In addition, the technology was relatively unknown and appeared to be complex, especially regarding the efficient ejection of ions from the trap and the associated control systems for optimizing the performance of the electronic circuits. However, the QUISTOR-quadrupole mass filter combination permitted the observation of both electron ionization and chemical ionization of compounds eluting from a gas chromatograph (Armitage, 1979). In 1980 and 1981 the position changed dramatically with the discovery at Finnigan MAT (Kelley, Stafford, & Stephens, 1985) of an alternative means of generating mass spectra, that is, by ramping the RF voltage amplitude so as to eject ions mass selectively into a detector, and the advent of relatively inexpensive microcomputers such as the IBM PC and its successors (see Section VI).

The commercialization of the quadrupole ion trap has been described in detail elsewhere (Syka, 1992; Syka, 1995). The linkage between university research and an industrial, entrepreneurial corporation was made at the 27th Annual Conference of the American Society for Mass Spectrometry held in Seattle, Washington, in 1979. George Stafford of Finnigan MAT Corporation attended a lecture given by Ray March on the characterization and application of the quadrupole ion trap (Armitage et al., 1979b). Among the applications discussed in this lecture were the use of the quadrupole ion trap as a detector for a gas chromatograph (Armitage, 1979) and the use of resonant ion ejection for the study of ion/molecule reactions in a quadrupole ion trap (Armitage et al., 1979a). Stafford became interested in ion traps and, after some reflection, had an idea that

represented an entirely new strategy for the use of the quadrupole ion trap in mass analysis, that of mass-selective axial ejection.

VI. MASS-SELECTIVE AXIAL EJECTION

In its most basic form the operation of the ion trap in the mass-selective ejection mode employs the remarkably simple idea that if the working point (a_z, q_z) lying within the stability diagram (that is, corresponding to a trapped ion) is moved along a "scan line" which intercepts either the $\beta_z = 0$ or $\beta_z = 1$ boundary, then the trapped ion will rapidly develop axial instability and be ejected from the ion trap into a suitably positioned detector. In practice, the easiest way of achieving axial instability is to supply the ring electrode of the trap with RF power only so that the scan line becomes coincident with the q_z axis (Stafford et al., 1984). The cycle of operation commences by creating ions with a pulse of electrons while the RF amplitude is held at a constant value; the RF amplitude is then ramped linearly so that the a_z, q_z values of the ions are moved to the $\beta_z = 1$ boundary, whereupon the ions are ejected in order of increasing m/z value (see Fig. 6).

While the quality of the mass spectrum thus obtained is generally tolerable, it emerges that the presence of a light buffer gas, for example helium, within the trap has a considerably beneficial effect upon the mass spectrum in terms of resolution and sensitivity. Theoretical modeling (Todd, Bexon, & Smith, 1987a,b) suggests that this is because the moderating collisions cause the ions to migrate toward the center of the trap in a manner similar to the effects associated with charge-transfer processes discussed earlier (see Section V.A.), so that on ejection they are better "bunched," both axially which improves the resolution, and radially which improves the ejection efficiency and hence the sensitivity. A further benefit of ion migration to the center of the ion trap is that the motion of the ions is less susceptible to field imperfections near the electrodes, so that the manufacturing tolerances are less stringent than those necessary for quadrupole mass analyzers. The migration effect and mass-selective axial ejection, together with the small size and the use of sophisticated software, has led to a veritable explosion in the use of ion trap mass spectrometers especially in GC/MS and LC/MS applications where multiple stages of MS/MS using the tandem-in-time methodology have provided uniquely useful information. It was revealed later that the commercial ion trap had been stretched such that the separation of the end-cap electrodes had been increased by 10.7% (March et al., 1992a). New generations of commercial ion traps, based upon the electrode configuration of the linear quadrupole mass filter have begun to appear, offering mass spectrometrists a bewildering choice of technology and variety of experimentation.

A. Tandem Mass Spectrometry (MS/MS)

The first MS/MS studies using a commercial ion trap system (the ITMS™) were reported in 1987 by Louris et al. (1987). This brief description of the development of the quadrupole ion trap for tandem mass spectrometry is illustrated by reference to the determination of dioxins and furans. The power and limitation of the ion trap using but a single scan function are discussed.

1. MS/MS Determination of Dioxins, Furans, and Polychlorinated Biphenyls

Determination of dioxins and furans requires the utilization of many scan functions not only for isolation of molecular ions from the various congener groups (tetrachloro-, pentachloro-, etc.), but also for the isolation of co-eluting isotopically labeled compounds added to the original sample. The demand for multiple scan functions was met through rapid development of appropriate software. Much of the new software that came on line in the 1990s could be loaded and used on quadrupole ion trap instruments with little modification, if any, of ion trap hardware. The original ITD™ could be shown to be extremely versatile given appropriate software.

The molecular ion cluster for, say, 2,3,7,8-tetrachorodibenzo-p-dioxin (2,3,7,8-T₄CDD) is composed of several peaks due to the presence of naturally occurring ^{13}C and ^{37}Cl isotopes. The molecular ion of greatest ion signal intensity is m/z 322, $[C_{12}H_4Cl_3^{37}ClO_2]^{+\cdot}$. Upon CID this ion species loses the radical COCl˙ to form a product ion of m/z 259 as shown in Eq. (87):

$$[C_{12}H_4Cl_3^{37}ClO_2]^{+\cdot} \rightarrow [C_{11}H_4Cl_2^{37}ClO]^+ + COCl^\cdot \quad (87)$$
$$\scriptsize (m/z\,322) \qquad\qquad (m/z\,259)$$

There are fifteen isomeric T₄CDDs and, in each molecular ion cluster, the ion of greatest signal intensity is m/z 322. Initially with a modified ITD™ it was possible to use *only one scan function* for the determination of a single congener group (i.e., tetra) in a single chromatographic run. Any congener group could be selected but, once selected, that congener group was the only group examined with the scan function. In 1994 a rapid screening technique, carried out with a quadrupole ion trap operated tandem mass spectrometrically (MS/MS), was reported for the detection and quantitation of T₄CDDs (Plomley, Koester, & March, 1994b). One microliter of a clam extract was injected onto a DB-5 fused silica capillary column (J&W Scientific, Folsom, CA) and the single scan function appropriate to Eq. (87) was used repeatedly throughout the GC run.

Figure 11 shows a comparison of two chromatograms of TCDD isomers from a clam extract; the chromatograms were obtained by a QIT and by high resolution mass spectrometry (HRMS). The upper chromatogram shows the original ion signals for m/z 259 obtained by MS/MS with the QIT where m/z 322 was isolated initially; the lower chromatogram (HRMS) shows the original ion signals as obtained in the single ion monitoring (SIM) mode for $[M+2]^{+\cdot}$ molecular ions of m/z 321.8936. The variations in relative peak signal intensities of 12 T₄CDDs in each chromatogram are seen to be remarkably similar; this observation was quite extraordinary considering the significant differences between the two types of instrument and, particularly, with respect to the CID process in the QIT. From inspection of Figure 11 it could be concluded either that the available CID energy exceeded the highest activation energy for loss of COCl˙ from amongst the congeners, or that the T₄CDDs have a common activation energy for loss of COCl˙ from each T₄CDD congener. This observation made possible the use of a single QIT scan function (with constant resonant excitation conditions) for the CID of each congener group.

The success of this first tandem mass spectrometric determination of dioxins with an ion trap was followed by
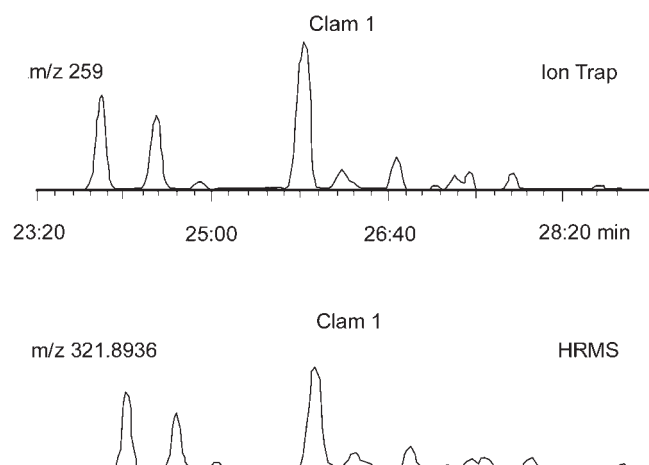
FIGURE 11. Two chromatograms for tetrachlorodibenzo-*p*-dioxins obtained from a clam extract. The upper chromatogram shows the original ion signals for *m/z* 259 obtained by MS/MS with the QIT; the lower chromatogram (HRMS) shows the original ion signals as obtained in the single ion monitoring (SIM) mode for $[M + 2]^{+\cdot}$ molecular ions of *m/z* 321.8936. The variations in relative abundances of T₄CDDs in each chromatogram are seen to be remarkably similar. Chromatographic retention times (min) correspond to ion trap data. Reproduced from March and Todd (2005, Fig. 7.8 of QITMS), copyright 2005, with permission of John Wiley & Sons, Ltd.

further work using advanced software (Lausevic, Splendore, & March, 1996; Plomley, March, & Mercer, 1996; Carette et al., 2000; March et al., 2000a,b). This last reference was the first of our publications for which copies of figures were transmitted electronically to the publisher; the article was published without a single figure. The paper was republished, subsequently, as (March et al., 2000b). A similar MS/MS technique had been applied to the determination of polychlorinated biphenyls (Lausevic et al., 1995a,b; Vasiljevic, Lausevic, & March, 2000) and, in 2000, a review of ion trap research on dioxins, furans, and polychlorinated biphenyls was published (Plomley, Lausevic, & March, 2000).

B. High Mass-Resolution and Mass Range Extension

The early commercial ion trap instruments were scanned during mass-selective mass analysis at the rate of 5,550 Th sec⁻¹ using axial modulation, which is a form of resonant excitation as the working points of ions approach the $\beta_z = 1$ boundary. Under these conditions unit mass resolution was achieved. Once electrospray ionization (ESI) became available and was found to be compatible with the quadrupole ion trap, the inadequacy of the relatively low mass resolution of the quadrupole ion trap for the investigation of ESI mass spectra was a spur to further research.

There is a high degree of interdependence of resonant excitation, high mass-resolution, scanning rate, mass range extension, utilization of higher-order fields for rapid ion ejection, and compatibility of the ion trap with ESI and liquid chromatography.

1. High Mass-Resolution

The landmark publication of Schwartz, Syka, and Jardine (1991) concerning high mass resolution in a quadrupole ion trap mass spectrometer opened the door to the investigation of ESI at high mass resolution. Briefly, the mass resolving power of a quadrupole ion trap is inversely proportional to the mass-scanning rate; when the mass-scanning rate is reduced, the observed mass resolving power is increased, thus permitting a "zoom" operation, see Williams, Cox, and Schwartz (1995) and Chapter 8 of (March & Todd, 2005). A resolution in excess of 10^6 has been demonstrated on a CsI cluster ion (Cooks et al., 1991) using very slow scans, and resolution in excess of 10^7 for *m/z* 614 from the calibration compound perfluorotributylamine (FC-43) using even slower scans have been reported (Londry, Wells, & March, 1993a,b; Londry & March, 1995; Wells et al., 1995).

2. Extension of Mass Range

Three methods for mass range extension have been explored: (i) reduction of the dimensions of the ion trap (Kaiser et al., 1989); (ii) reduction of the main RF drive frequency (Kaiser et al., 1991); and (iii) resonant ion ejection using an AC potential of appropriate frequency applied across the end-cap electrodes either in dipolar (Kaiser et al., 1991) or monopolar mode (Wang, Bohme, & March, 1993). These early studies showed a mass range extension to 72,000 Th.

VII. RESONANT EXCITATION

The tinkling of glass in a chandelier induced by high notes from a soprano is a well-known example in the physical world of resonant excitation. Another example is the regularly repeated application of a force on a bridge such that the structure becomes excited and, ultimately, unstable; hence the necessity for soldiers to break step when marching across a bridge. Similarly, the application of an oscillating potential of the order of *ca.* 1 V to either or both end-cap electrodes of a quadrupole ion trap can rapidly excite trapped ions of a given species when the oscillating frequency of the potential coincides with the secular frequency of the ions.

A. Experimental Studies

Resonance excitation is a powerful method for ion excitation, ion isolation, ion dissociation, and ion ejection. Among the many aspects of resonance excitation that have been examined are (i) are the influence of cooling time on the excitation of ions (Liere et al., 1994), (ii) pressure effects on resonance excitation (Liere et al., 1995), (iii) modification of competing dissociative channel yields (Liere et al., 1996), (iv) a comparison of resonant excitation modes (Plomley, March, & Mercer, 1996), and (v) resonance excitation in DC and RF fields (Splendore et al., 1997).

B. Resonant Ejection

Resonant ejection is practiced now in virtually all quadrupole ion traps. Illustrative publications of Canadian contributions in this area are given in Vedel, Vedel, and March (1990, 1991).

C. Resonance Theory

A series of publications during the 1990s dealt with the study of resonance theory and culminated in an introduction to the field interpolation simulation method (March et al., 1989, 1990, 1991; Alfred, Londry, & March, 1993).

D. Boundary-Activated Dissociation

An alternative method to resonance excitation for the dissociation of mass-selected ions is boundary-activated dissociation. Here, the working point of a precursor ion is taken close to a boundary of the stability diagram whereupon the ion gains kinetic energy rapidly (March et al., 1984) and, in collisions with helium buffer gas, dissociates. When the $\beta_z = 0$ boundary of the stability diagram is chosen, product ions can remain in the ion trap for subsequent mass analysis (Londry, March, & Catinella, 1995). The influences of collisional cooling (March et al., 1993a) and controlled variation of fragmentation processes (March et al., 1994) have been investigated.

E. Simulation Studies

A series of simulation studies was carried out once powerful bench-top computers became readily available. This series of studies led to the development of simulation programs for the calculation of ion trajectories and, eventually, to the simulation of mass spectra. The series started with a study of resonance excitation in a quadrupole ion trap (March et al., 1989, 1990, 1991), then moved to mass-selective isolation of ions (March et al., 1992b, 1993b), kinetic energy effects of resonantly excited ions (March et al., 1993b), computer simulation of single ion trajectories (Londry, Alfred, & March, 1993), and a simulation study of ion kinetic energies during resonant excitation in a stretched ion trap (Splendore et al., 1996).

F. Chemistry Applications

There are myriad chemical systems to which the ion trap has been applied in addition to the dioxins, furans, and PCBs discussed above. Some illustrative examples of Canadian studies are: (i) an investigation of the structures of isomeric ions derived from acetone, diacetone alcohol and mesityl oxide (March & Young, 1988); (ii) determination of n-nitrosodimethylamine in complex environmental matrices (Plomley, Koester, & March, 1994); (iii) study of protonated phosphonates in the ion trap under electron impact conditions (Mechin et al., 1995); and (iv) the collision-induced dissociation of 2- and 3-dimensional polycyclic aromatic hydrocarbon cations (Wang et al., 1997).

The influence of ion activation and thermalization effects on reaction rate constants in an ion trap have been reported (Liere et al., 1997). The behavior of negative ions in ion traps has been investigated also (Catinella et al., 1995; Gregoire et al., 1998).

VIII. COMPARISON OF QUADRUPOLE ION TRAP PERFORMANCE

It is no simple matter to compare the performance of one mass spectrometer with that of another, and only two comparisons are

presented here. A comparison is presented of the performances of three mass spectrometers of high specificity in the determination of dioxin/furan congeners (March et al., 2000b). The three instruments used in this study were a triple-sector EBE mass spectrometer operated at high mass resolution (HRMS), a quadrupole ion trap (QIT) mass spectrometer, and a triple-stage quadrupole (TSQ) mass spectrometer. The QIT and TSQ instruments were operated in tandem mass spectrometric mode. A mixture of tetra- to octa-chlorodibenzo-p-dioxins (T-4-O8CDD) containing in all seven dioxin congeners was used for much of this study. The factors considered in this comparison were the tuning of each instrument, the preparation and comparison of calibration curves, the 2,3,7,8-T4CDD detection limit for each instrument, ion signals due to H(6)CDDs obtained with each instrument from two real samples (air and pyrolysed polychlorinated phenols), average relative response factors, and ionization cross sections. This comparison was carried out with the cooperation of the Ministry of the Environment (MOE) of the Province of Ontario.

In a second comparison, product ion mass spectra of a series of nine protonated flavonoids were observed by (i) electrospray ionization combined with quadrupole/time-of-flight (ESI QTOF) and (ii) matrix-assisted laser desorption ionization combined with a quadrupole ion trap (MALDI QIT) tandem mass spectrometer (March et al., 2007). The center-of-mass energies in ESI QTOF and MALDI QIT were similar (1–4 eV) and their product ion mass spectra were virtually identical.

IX. SURVEYS OF THE FIELD

It is of value, from time to time, to survey the field of ion trap mass spectrometry so as to recognize the progress that has been made, rather like viewing the wake of a boat and, if one has courage, to comment on future directions for research. In 1991, the prospects for future application of the quadrupole ion trap were presented as "A musing on the present state of the ion trap and prospects for future applications" (March, 1991). This musing was followed by a review of the years 1989–1991 during which great progress had been made with respect to both the mass range of the ion trap and mass resolution (March, 1992). In 1997, an introduction to ion trap mass spectrometry was presented (March, 1997) followed by further general reviews in 1998 (March, 1998a,b), environmental applications of the quadrupole ion trap (March, 1999), a retrospective review (Todd and March, 1999), a view at the turn of the century (March, 2000), and another survey in 2001 (Hao and March, 2001).

X. CONCLUSIONS

The quadrupole ion trap is an extraordinary device that functions both as an ion store, in which gaseous ions can be confined for a period of time, and as a mass spectrometer of considerable mass range and variable mass resolution. As a storage device the ion trap acts as an "electric field test-tube" for the confinement of gaseous ions, either positively charged or negatively charged, in the absence of solvent; the confining capacity arises from the

formation of a trapping potential well when appropriate potentials are applied to the electrodes of the ion trap. In is simplest form an ion trap permits the study of the spectroscopy and the chemistry of trapped ions; as a mass spectrometer, when combined with various ion selection and scanning techniques, the elucidation of ion structures by the use of repeated stages of mass analysis known as tandem mass spectrometry has added a new dimension to the armory of analytical techniques, especially in the biosciences. Quadrupole ion trap mass spectrometry has been a continuously growing technology since its invention in 1953 and, over the past two decades since its commercialization, has developed to be a work-horse instrumental technique in many analytical laboratories. With the advent of new methods by which ions can be formed in the gas phase, from polar as well as from covalent molecules, and introduced subsequently into an ion trap, the range of applications of the quadrupole ion trap mass spectrometer has increased enormously. So much so that quadrupole devices have wrought a revolution in the field of mass spectrometry during the past twenty years that has seen, in large measure, the demise of sector instruments. A compilation of Canadian scientists and Visiting Students/Professors whose contributions to the study of quadrupole ion traps have been recognized here is shown in Table 3.

Quadrupole instruments have appeared that are concatenations of quadrupole mass filters together with modified quadrupole rod sets that function as highly efficient ion pipes for the transmission of ions through various pressure regimes. Such concatenations, when combined with a quadrupole

TABLE 3. Compilation of Canadian scientists and Visiting Students/Professors whose contributions to the study of quadrupole ion traps have been recognized here

R. L. Alfred	M.A. Armitage
E.T. Allinson	M. Baril
H. Becker	D.K. Bohme
R.F. Bonner	M. Carette
T. Croley	J.E. Curtis
P.H. Dawson	G.B. DeBrou
M.C. Doran	J.W. Dupuis
J. Durup	M.W. Forbes
J.E. Fulford	G.F. Hamilton
M.J. Higgins	C.Y. Hao
M. Ho	D.-N. Hoa
A.C. Hopkinson	R.J. Hughes
W.B. Jacobs	X.W. Jiang
A. Kamar	E.M. Kazdan
C.J. Koester	C. Lambert
M. Lausevic	Z. Lausevic
E.G. Lewars	H.X. Li
P. Liere	P.J. Matthews
C.D. Metcalfe	Y. Morita
R.J.S. Morrison	P. Perrier
J.B. Plomley	E.J. Reiner
U.P. Schlunegger	L.T. Scott
A. Septier	M. Sharifi
M. Splendore	J.A. Stone
J.F.J. Todd	M. Tkacyzk
F. Vedel	D.S. Waddell
X.M. Wang	M.R. Weir
G.J. Wells	G.J. Wong

collision cell, constitute tandem mass spectrometers of high sensitivity. In the early stages of development of triple-stage quadrupole mass spectrometer, the ion beam moved continuously in the *z*-direction. However, with the development of quadrupole linear ion traps, the forward motion of the ion beam can be arrested and, when required, can be reversed for ion manipulation then reversed once again before being directed to the detector.

The quadrupole linear ion trap is one of a number of new ion trapping instruments has evolved recently; these include the high-capacity trap, the Orbitrap, the digital ion trap, the rectilinear ion trap, the toroidal RF ion trap, ion clocks, and arrays of cylindrical ion traps. March and Todd have prepared a presentation of new ion trapping devices under the title of *Practical Aspects of Trapped Ion Mass Spectrometry*, volumes 4 and 5 (March & Todd, 2009).

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