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A retrospective review of the development and application of the quadrupole ion trap prior to the appearance of commercial instruments

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Abstract

An account is given 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. (Int J Mass Spectrom 190/191 (1999) 9–35) © 1999 Elsevier Science B.V.

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1. Introduction

The quadrupole ion trap was first described and investigated in detail by Paul et al. [1] and by Fischer [2]; in this latter work, the detection of ions was achieved by resonance absorption techniques. Subsequently, Rettinghaus reported on the use of the device for residual gas analysis [3] and Dawson and Whetten first conceived the idea for detecting ions by ejecting them from the ion trap [4]. Thus, from these early articles, one is presented with a relatively simple electrodynamic device for the containment of gaseous ions, a resonance absorption method for detecting in situ individual ion species, and the use of the device both as a mass spectrometer and as an accumulator for subsequent detection or examination of ions upon ejection. Not only was the device simple in that it did not require a magnetic field but the major part of the theory of ion trap operation was explicable in terms of the stability regions in a_z, q_z space as derived from the solutions to Mathieu's second-order differential equation; this theoretical treatment, although it encompassed quadrupole mass filters, was novel to the mass spectrometry community. Because the field in a quadrupole device is changing constantly, quadrupole mass spectrometry is referred to as *dynamic* whereas sector mass spectrometry is referred to as *static* because the fundamental parameters providing mass analysis (i.e. magnetic and electric fields) in a sector remain constant in time, except for the slow change required for the purpose of recording a mass spectrum.

In a 1991 review of Ion Trap Mass Spectrometry by Cooks et al. [5], the authors commented that after the discovery and early exploration of the ion trap

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"interest was maintained by only a few research groups, notably those of John Todd at the University of Kent in England and Ray March at Trent University in Canada." One may ponder the question as to why the quadrupole ion trap remained somewhat of a laboratory curiosity in that it did not attract more attention in the 1970s and, furthermore, what chain of events and circumstances led these young (at that time) researchers to labour in this particular vineyard. In the 1960s and 1970s, mass spectrometrists were concerned, in the main, with flow systems such as the flowing afterglow [6], with ion detection using quadrupole mass filters, and ion beam instruments employing magnetic and electric sectors [7]. In addition, there was a dedicated group of researchers who worked with ion cyclotron resonance (ICR) mass spectrometers [8]; yet these instruments were not available commercially at that time. The application of Fourier transform to the ion signals obtained from ICR was demonstrated only in 1974 [9]. Because the theory of ion motion in an ICR cell is unique to such instruments there was little overlapping experience in both ICR and sector mass spectrometry.

This retrospective review affords its authors an opportunity to explain the circumstances that drew them to pursue their early research on the quadrupole ion trap. In preparing this review, we have drawn heavily on an article written by John Todd and published in *Dynamic Mass Spectrometry* [10] in 1981. Because the publication of the article preceded the general awareness of the ion trap that followed the introduction of the first commercial device, and because the article described work that we carried out individually and in collaboration with each other, we thought that it would be appropriate to retrace our early footsteps in this review. In this way, we are able both to describe the various types of research carried out and, in looking ahead over nearly two decades, to comment broadly on that research which has taken place subsequently. The degree of understanding and the variety of applications that we were able to achieve with the crude apparatuses available to us at that time is quite surprising. Throughout this review, we have tried to retain the third person wherever appropriate and we have encountered little problem here; however, the use of tenses in the text has been somewhat more troublesome and we apologise, in advance, for any inconvenience that this may cause the reader.

Both Todd and March were undergraduates at the University of Leeds during the middle to late 1950s and, indeed, each of us appears in a photograph taken around 1956 at the Leeds University School of Chemistry. After the Leeds experience, Todd continued his studies there as a graduate student working with the late Edgar Collinson and the late Fred Dainton on the interactions of metastable excited argon atoms with hydrocarbon molecules (as utilised in the argon ionization detector for gas chromatography, invented by Lovelock [11]). March, on the other hand, moved to Canada as a graduate student to study photochemical kinetics with John Polanyi at the University of Toronto. Todd subsequently spent a period in the U.S. as a postdoctoral fellow with the late Richard Wolfgang at Yale University investigating high energy nuclear recoil atom chemistry. In 1965, both Todd and March obtained university posts, Todd at the University of Kent for its first year of operation and March at Trent University for its second year of operation. Todd became interested in the study of long-lived metastable ions, and devised a means of measuring their decay rates using a combined quadrupole mass filter/time-of-flight technique. For this study, he needed a means of trapping ions for defined periods of time prior to mass analysis, and the quadrupole ion trap appeared to be an ideal way of doing this. Thus an instrument incorporating an ion trap as the ion source for a quadrupole mass filter was constructed by Todd and his first graduate student, Graham Lawson; they also coined the name *Quistor* [12]. Because no reference data on metastable ion decay rates were available, some simple ion/molecule reactions were studied in order to test the potential of this system [13]. In 1972, March read Todd's article on the quadrupole ion trap [14] in *Chemistry in Britain* and envisaged the ion trap as a test tube for ion/molecule reactions and as a reactor for photochemistry; subsequently, he decided to visit Todd's laboratory to learn more about this appealing device.

It is of interest to note that, in the pretransistor days of the 1950s, much postgraduate research was carried out with homemade instruments, power supplies, and electronics; the sole commercial instruments used would have been a jeep or avo-meter and an oscilloscope. In the early 1970s, the synergy between instrument manufacturers and the research community, particularly universities, was very much in evidence, and it became fashionable for postgraduate research in the larger and more affluent universities to be carried out with commercial instruments. Because, at this time, the new universities were far from affluent, the possibility of working with a device that was not available commercially was particularly attractive; clearly, one could build one's own ion trap apparatus relatively cheaply in a new university and use it in research without fear of competition from the established universities. In this way, the ion trap was regarded as an attractive backwater for research.

In 1973 March visited Todd's laboratory at Kent for the first time and worked alongside a young graduate student, Ron Bonner, and gleaned what he could from Graham Lawson who, at that time, had just completed his Ph.D. thesis—the first of many from the Kent group. It says much for Bonner's patience and forebearance that, upon completion of his doctorate, he took up a postdoctoral fellowship with March at Trent and helped in the construction of the first ion trap apparatus at Trent, although it was not the first in Ontario. Mastoris, at the University of Toronto's Institute for Aerospace Studies (UTIAS) had built an ion trap apparatus [15] in the late 1960s but this avenue for research was not pursued further. Parenthetically, Bonner remains active in the mass spectrometry field as an employee of Sciex (an outgrowth of UTIAS) in Concord, Ontario, and Lawson is a member of the academic staff of De Montfort University, Leicester, England.

As noted above, Dawson and Whetten's idea concerning the detection of ions following ejection from an ion trap led to the Kent group mounting the ion trap in place of the ion source of a conventional quadrupole mass filter so as to afford external mass analysis of the ejected ions. Thus the evolutionary process appears to have involved a progressive change from the Quistor being employed as a combined ion source/analyser/detector (Paul [1] and Fischer [2]) to it becoming an ion source/analyser (Dawson and Whetten [4]) and thence an ion source only, albeit one that is capable of storing ions with an optional mass selectivity. It can be argued that it is unreasonable to expect any one piece of equipment to perform more than one function in an optimal way and, therefore, that such a sequence of changes was inevitable. In fact, the idea of limiting the Quistor to the role of an ion source was borne out of requirements for a specific research project, yet it provided a simple means of characterising the instrument in a way that has led to its performance as a mass analyser being improved. To this day, the Quistor finds application as an ion source for a drift cell [16] and for subsequent Fourier transform treatment of ejected ion signals [17]. Two comprehensive reviews of the mass spectrometric applications of the quadrupole ion storage trap were published [18,19] in 1976. Later, two brief reports of particular aspects of ion trap research appeared [20,21].

2. Experimental studies

2.1. Ion/molecule reactions

The earliest systematic studies performed with the Quistor acting as a storage source were directed toward the measurement of ion/molecule reaction rates [13], and included rate constant measurements, in methane, water, ammonia, and in carbon dioxide + hydrogen mixtures [22]. Charge-transfer processes and the unimolecular decay of metastable ions were also reported [23], and the potential use of the Quistor as a low-pressure chemical ionisation source was noted [24]. Comparison of the rate constant data with results of more conventional experiments led to a conclusion that the mean ion kinetic energies within the Quistor are generally quite low (of the order of 1–3 eV under the conditions employed) and this topic has been the subject of further theoretical and experimental investigation, as discussed below.

The Trent group reported upon two developments that are of particular interest in the field of ion/

molecule studies. In the first, the Quistor was operated as a "selective ion reactor" [25], thus the duty cycle consists of an initial period in which the device is operated in a mass-selective mode, to isolate a specific primary ionic species, followed by a reaction period in which the conditions are such that product ions with a range of masses are stored. Analysis was then achieved by ejection into a mass filter. In the second, this group described the technique of "Quistor resonance ejection" (QRE) [26]. This method of operation appeared to be particularly promising in the elucidation of ion/molecule reaction rates and mechanisms and is analogous to ICR "double resonance." Thus an additional low amplitude rf signal was fed to one endcap electrode at an appropriate frequency so as to excite a given ion in its secular oscillation until its trajectory became unstable; the effect on product ion intensities is then monitored. This method of operation promised to be a very powerful extension of the utility of the Quistor for this type of work, and was demonstrated elegantly in the study of the proton affinity and ion chemistry of methylketene [27]. Both of these developments, ion isolation and resonance ejection, are combined today in routine ion trap operation as a tandem mass spectrometer.

The use of the Quistor for chemical ionisation (CI) studies was advanced through the development of a radiofrequency storage source designed to replace the conventional source of an AEI MS902 magnetic sector mass spectrometer [28], and a variety of CI processes were examined. "Spectrum simplification," involving the reduction of the number of peaks appearing in a mass spectrum through "self-chemical ionisation" was also observed [29]. One limitation evident from the CI work was the restricted range of masses that may be stored simultaneously in the Quistor, even in the "total pressure" rf-only mode of operation. This appeared to arise from distortions in the predicted form of the stability diagram (see below), and meant that for a given reactant ion mass there is a limit to the mass of the quasimolecular product ion that can be detected by this method. To a certain extent, this problem could be offset by employing higher molecular weight reagent compounds, and because only low vapour pressures are required ($\sim 10^{-4}$ Torr), substances in the liquid state were acceptable. At that time, CI was carried out conventionally on sector instruments at a CI reagent (e.g. methane) pressure of ~1 Torr; hence the ability to carry out methane CI at a pressure of $\sim 10^{-4}$ Torr, using storage time rather than CI reagent pressure to obtain similar amounts of chemical reaction, was quite novel.

One possible advantage of being able to operate an ion source mass selectively also became apparent from this work. This is "weak peak enhancement" [30] in which the source is set to store ions specifically formed from a component present only as a trace, in order to achieve a direct means of integration and consequent improvement in the signal/noise ratio, while simultaneously eliminating other ions formed from components in excess. A modern version of "weak peak enhancement" using wavebands of selected frequencies for the determination of trace compounds in oils has been reported by Buttrill et al. [31].

2.2. Stability diagram determinations

In order to facilitate the development of the Quistor as a useful instrument in mass spectrometry, it was concluded that further progress would best be achieved by the systematic study of a number of physical characteristics of the device, specifically the observed boundaries of the stability diagrams for the stored ions and the conditions relating to the ejection of the ions. For the determination of stability diagrams, the experimental system illustrated in Fig. 1 was employed [32]. Positive ions were created from a sample by allowing a pulse of electrons to enter a hole in the ring electrode of the Quistor coincident with the radial plane and, after a preset storage time (typically 1 ms), the ions were ejected by applying a negative-going 80 V "suck-out" pulse of 2 μs duration to the endcap nearest to the mass filter. The filter was set to transmit a given ionic species and the arrival of ions at the detector (coincident with the gated "detection pulse") was monitored on an oscilloscope. The appearance of a pulse of ejected ions was taken as an indication that the ions had in fact been stored in

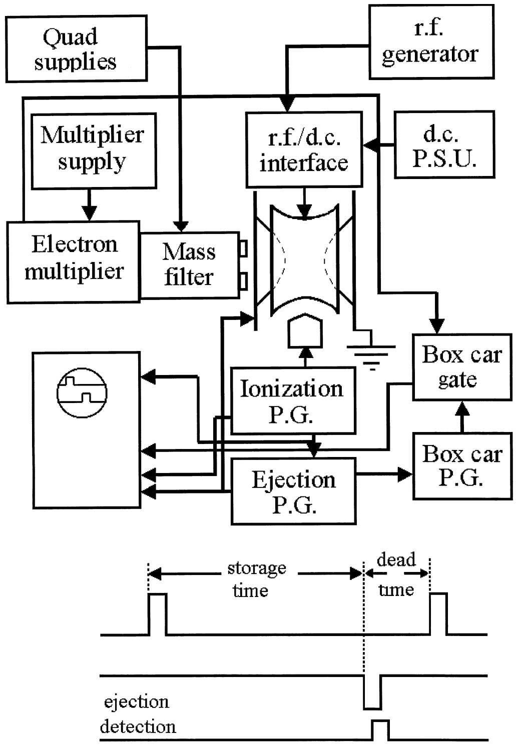

Fig. 1. Schematic representation of the experimental system and timing sequence for Quistor stability diagram determinations.

stable orbits, and the positions of the boundaries of the stability diagrams were then located by varying the rf (V_o) and dc (U) potentials fed to the ring electrode and noting the values at which the stored ion peak just disappeared. In this way, stability diagrams were plotted directly in U–V_o space or in a_z, q_z space (using the relations $a_z = -8eU/mz_o^2\Omega^2$ and $q_z = 4eV_o/mz_o^2\Omega^2$, in which the symbols are those conventionally employed), were built up. This was first achieved for Ar^+ and Ar^{2+} formed from argon in an investigation [33] arising from observations on the effect of storage time on the relative intensities of these species reported by March and co-workers [34] and interpreted in terms of ion migration effects [35]. Extension to a range of masses (Fig. 2) revealed quite significant departures from the theoretically predicted behaviour, particularly for lower mass values as the value of the rf drive frequency is reduced [36]. This behaviour appeared to be attributable to a number of possible effects, including the influence of the thermal velocity of the ions at the moment of creation, and interactions within the ion cloud because of space charge and geometrical imperfections in the electrode structure (see below).

Calculations suggested that, in the limit, initial thermal velocities would indeed show effects in the manner found, but should not cause boundary shifts of the magnitudes observed. A detailed analysis in terms of the various published models on space charge was performed and again indicated departures from the predicted behaviour, manifest as additional destabi-

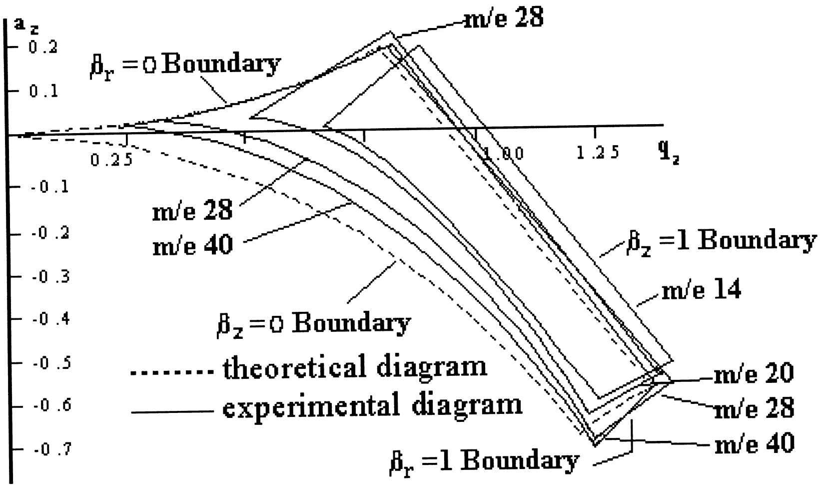

Fig. 2. Experimental stability diagrams for $^{14}N^+$, $^{20}Ne^+$, $^{14}N^{2+}$, and $^{40}Ar^+$ stored for 1 ms at 0.83 MHz.

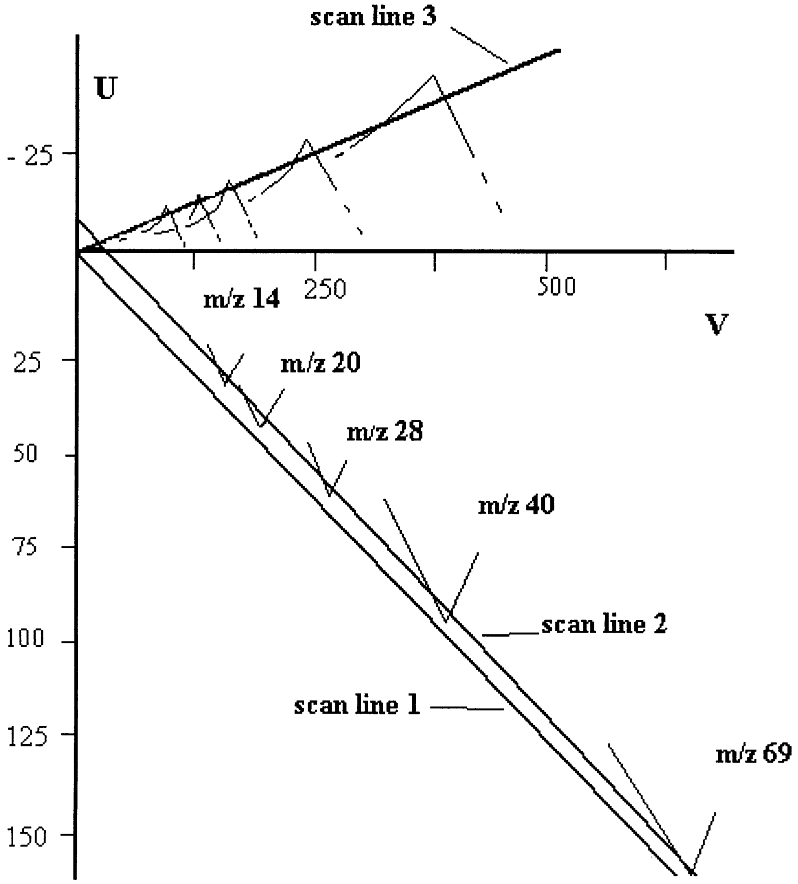

Fig. 3. Upper and lower apexes of experimental stability envelopes for *m/z* 14, 20, 28, 40, and 69 plotted in U–V_o space.

lisation along the z axis of the Quistor. It is possible that this effect arose from the distribution of ions within the Quistor being different from that assumed by the space-charge models (see below).

2.3. The Quistor as a mass spectrometer

The mass-dependent movement of the lower apex of the stability diagram away from the theoretical position has a significant influence on the performance of the Quistor in the mass spectrometric mode [37]. This can be seen from Fig. 3, where the apexes have been replotted in U–V_o space. It is apparent that the ideal scan line (1) completely misses the apexes; however, if the slope of this line were reduced so that transmission were possible across the mass range, then the lower portion of this range would be very much discriminated against. This behaviour contrasts with that of the quadrupole mass filter, where discrimination tends to be against the ions of high mass/charge ratio. However, as seen from Fig. 3, compensation for the shift may be achieved by applying a small constant bias potential between the ring and endcap electrodes, so that the latter are floating with a net positive potential (~4 V), and increasing the gradient of the scan line to give the locus labeled 2. A mass spectrum of n-heptane recorded with the Quistor under optimised conditions is shown in Fig. 4; a resolution of 215 (full width at half maximum) was achieved for *m/z* 43. Fig. 3 also suggested that it should be possible to obtain mass spectra with the Quistor when scanned so as to use the upper apex of

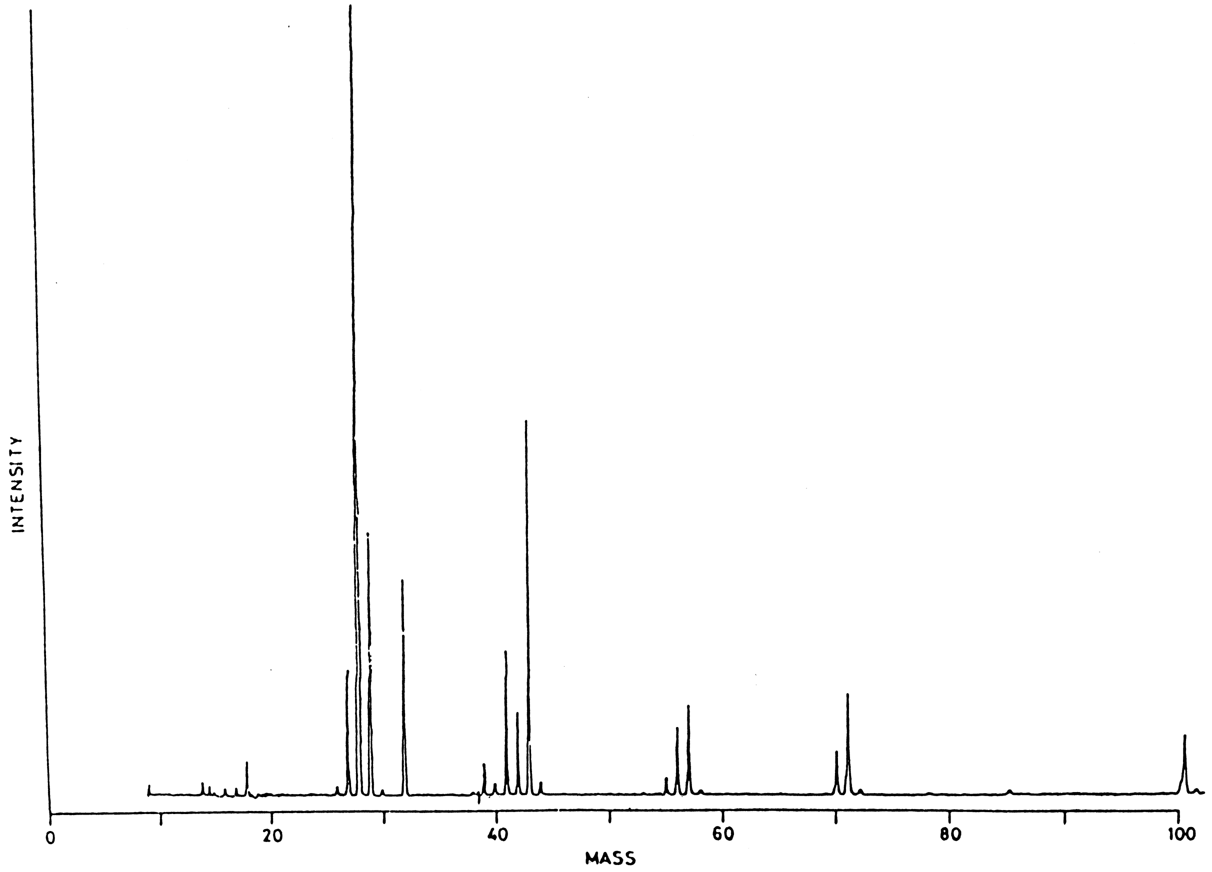

Fig. 4. Mass spectrum of *n*-heptane at a resolution of 215 at *m/z* 43. (Copyright John Wiley and Sons, reproduced with permission from R.E. Mather, R.M. Waldren, and J.F.J. Todd. See [37]).

the stability diagram. The shift of the stability boundaries away from ideality is less marked in this mode but, because these apexes are somewhat broader, the resolution is reduced and the sensitivity is somewhat lower (see below).

As might be expected, the storage time affects both the resolution and the sensitivity of the mass spectra recorded with the Quistor, as well as the relative intensities within the actual mass spectrum. Results obtained for *n*-heptane are listed in Table 1, and a plot showing the variation of relative intensities of ions from *n*-hexane with storage time is shown in Fig. 5.

The *n*-hexane results were recorded with an ion trap having cylindrical geometry [38,39], and it is seen that one group of ions (*m/z* 43, 57, 71, and 86) tends to increase with storage time whereas a second (*m/z* 27, 29, 39, 40, 41, and 55) decreases with time and a third (*m/z* 42 and 56) remains approximately constant. Because, in the mass spectrometric mode, only one type of ionic species is stable at a time, those that decrease are assumed to be dissociating to other products, either unimolecularly or through collisional

Table 1
Effect of storage time on *m/z* 43 from *n*-heptane

Storage time (μs)	Resolution ($m/\Delta m$), FWHM[a]	Relative sensitivity
80	52	20
150	72	7
250	120	4
500	185	1

[a] Full width at half maximum.

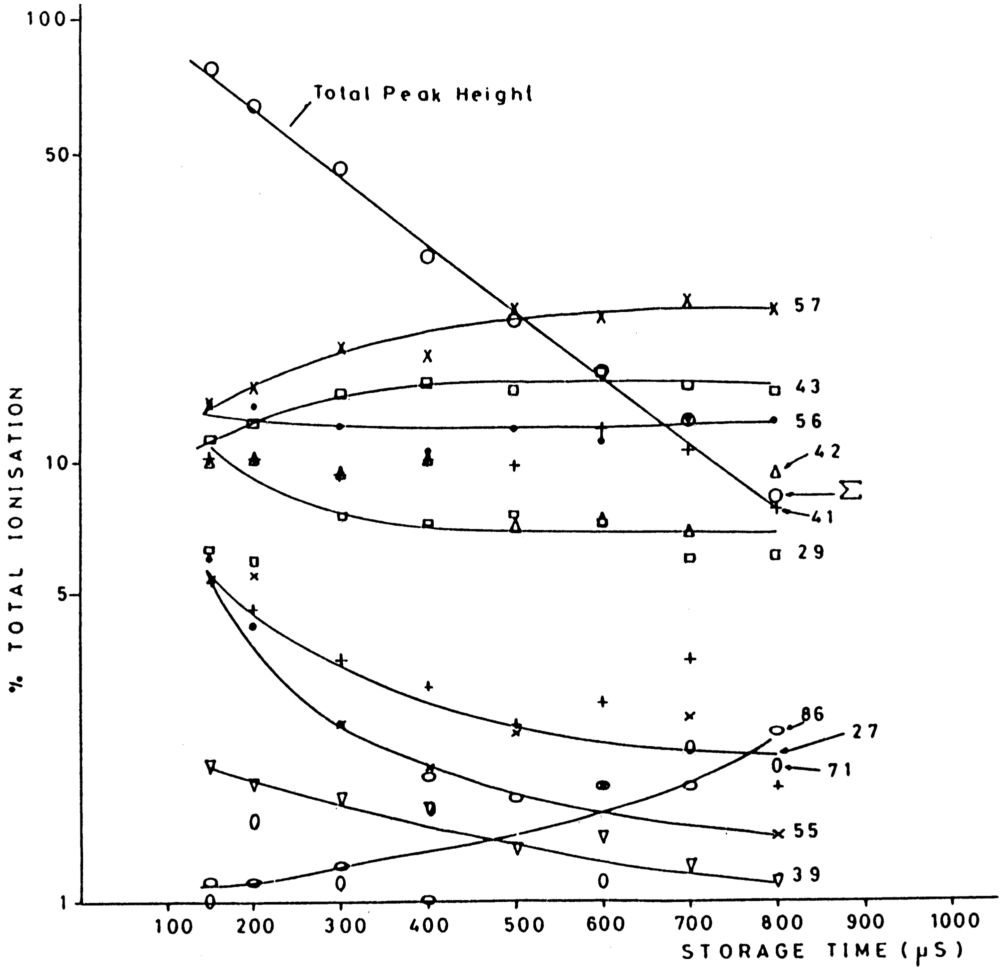

Fig. 5. Plots of peak intensities (expressed as a percentage of total ionisation) vs. storage time for principal ions in the mass spectra of *n*-hexane recorded with a cylindrical ion trap. Copyright Elsevier Science, reproduced with permission from R.E. Mather, R.M. Waldren, J.F.J. Todd, and R.E. March. See [39].

activation, whereas those whose relative abundances increase are presumably being collisionally stabilised. The ions whose relative abundances remain constant are assumed to be stable, low energy species.

A series of cylindrical ion traps of slightly differing geometries was subjected to quite intensive investigation in a collaborative project between the groups at Kent University and at Trent University, with particular emphasis on the determination of stability diagrams and on achieving a comparison with theoretical predictions made by Benilan and Audoin [40]. The electrodes for our homemade quadrupole ion traps had been fabricated carefully in the machine shop and polished to a mirror finish, yet we were curious as to the need for such precise electrodes, especially because Dawson had shown that ion storage could be realised in a device where the electrodes were constructed from wire mesh! Hence, three cylindrical ion traps were constructed. It was found that the stability diagrams obtained for the cylindrical ion traps were similar to those of the quadrupole device: ion/molecule reactions could be carried out, resonant excitation could be effected, and our calculated field within the cylindrical device was essentially quadrupolar. A more precise theoretical calculation of the field in cylindrical devices carried out nearly 20 years later [41] was virtually indistinguishable from that obtained from the original calculation.

2.4. Phase-synchronised ion ejection

In all of the experiments described so far, the timing of the ion ejection pulse was quite random in respect to the phase angle of the rf drive potential applied to the ring electrode. Brief accounts of the possible importance of synchronising the ejection pulse in this way had been given by Harden and Wagner [42], by Mastoris (loc. cit.) and by Dawson and Lambert [43], who concluded that the relative efficiencies of ejecting different masses would itself be phase dependent. For this reason, a comprehensive program was undertaken at Kent in which the effects of phase-synchronised ion ejection on the performance of the Quistor both as an ion source ("total pressure mode") and as a mass spectrometer were investigated.

Details of the experimental system employed in this work have been published [44–46]. Essentially two types of experiment were performed. In both cases, a "pulse/rf synchronisation circuit" sampled the rf potential fed to the ring electrode, and this provided an output trigger pulse gated to a specified phase angle of the drive potential. In one series of experiments, this trigger pulse activated the ejection pulse generator and the phase angle was swept over several complete cycles so that a recording was made of the ejected ion signal. Typical results obtained for Ar^+ ions at $a_z = 0$, $q_z = 0.64$ at a drive frequency of 0.83 MHz with suck-out (attractive) ejection are shown in Fig. 6. The numbers on the traces refer to the duration of the ejection pulse in microseconds, and the traces clearly indicate that there is both a very marked dependence upon phase angle, and also that the dependency becomes more complex for pulse widths equal to or greater than half the period of the drive potential. The minimum signal corresponds approximately to the point where the potential on the ring is zero, passing from positive to negative ($\Psi_r = \pi$) and the maximum ($\Psi_r = 0, 2\pi$) when it is zero and passing from negative to positive. With this type of experimental arrangement, it was possible to confirm the observation reported by Dawson and Lambert [43] in which ions were seen to be ejected from the ion trap in the "wrong direction." This effect is shown in Fig. 7. The Quistor was mounted between a multiplier and a mass filter + multiplier so that ions could be detected directly or mass analysed before detection. Curve (1) shows a normal trace for Ar^+ ions at $a_z = 0$, $q_z = 0.91$ ejected by applying a negative 1 μs pulse to endcap electrode B. Curve (2) shows the response obtained from the mass filter when endcap B was earthed, and endcap A was pulsed negative to draw ions out into the multiplier, whereas curve (3) shows the mass filter response when endcap B was pulsed positive with A earthed so as to repel

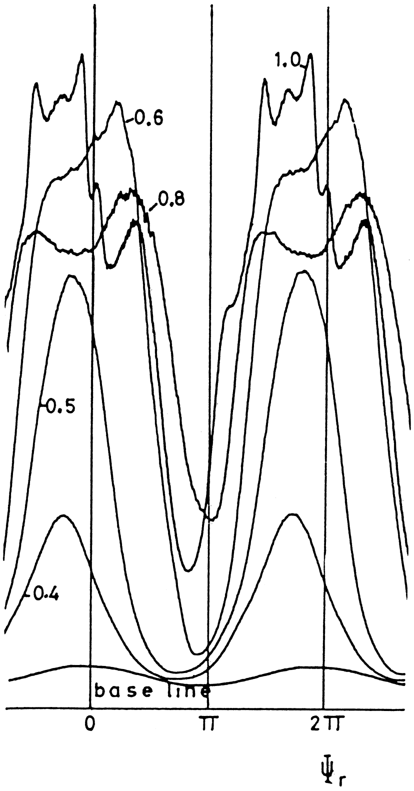

Fig. 6. Scan of the ejected Ar^+ ion signal vs. phase (Ψ_r) of the rf drive potential applied to the ring electrode for stated ejection pulse widths (μs) at $a_z = 0$, $q_z = 0.64$. Copyright Elsevier Science, reproduced with permission from J.F.J. Todd and R.M. Waldren. See [44].

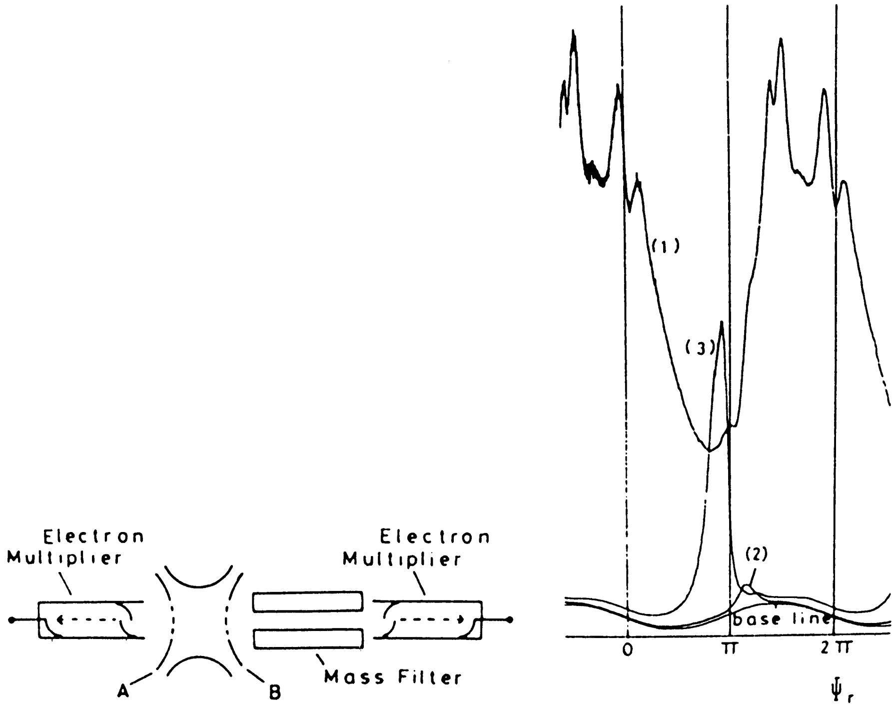

Fig. 7. Experimental arrangement affording ejection of ions from the Quistor into either the mass filter or multiplier, together with scans showing the ejection of Ar^+ ions in the "wrong direction" (for details see text). Copyright Elsevier Science, reproduced with permission from J.F.J. Todd and R.M. Waldren. See [44].

ions into the multiplier. It is this effect that permits one to carry out simultaneous positive/negative ion mass spectrometry with the Quistor (see below).

In the second series of experiments, the phase angle for ejection of the ions was fixed, and the delay between the "ejection" pulse and "detection" pulse was scanned (see Fig. 1). In this way, arrival time distributions were obtained, as shown in Fig. 8. These data were obtained for Ar^+ ions stored at $a_z = 0$, $q_z = 0.64$ and ejected by a suck-out (attractive) pulse of 0.75 μs duration at the stated phases. The marked variation in the widths of the velocity distributions suggested that under certain conditions the ions are bunched quite tightly and that the positioning of the detection pulse may be quite critical. The observed mass dependence in the flight time of ions through the quadrupole (the "dead" period between the ejection pulse and the arrival of the fastest ions in Fig. 8) was verified by making a comparison between data obtained for Ne^+ ions and for Ar^+ ions under identical conditions. An interpretation of these results was provided making use of the results of the phase-space treatment (see below), and it was possible to find a consistency between the observed velocities of the fastest ions and corresponding calculated velocities [47].

The relationship between the extent of mass discrimination and phase angle of ejection with the Quistor operating in the mass spectrometric mode may be seen in Table 2, where the intensities of the ions *m/z* 29 and *m/z* 43 from *n*-heptane are recorded. Compared to *m/z* 29, the *m/z* 43 ion was found to be much more dependent upon phase angle, both with respect to intensity and resolution. This suggested that synchronisation of the ejection pulse with the rf phase may be quite critical in optimising the performance of the device as a mass spectrometer, and certainly the observations were consistent with the results of experiments designed to show the relative positions of the mass spectrometric apexes for stability diagrams obtained with different phase angles of ejection (Fig. 9).

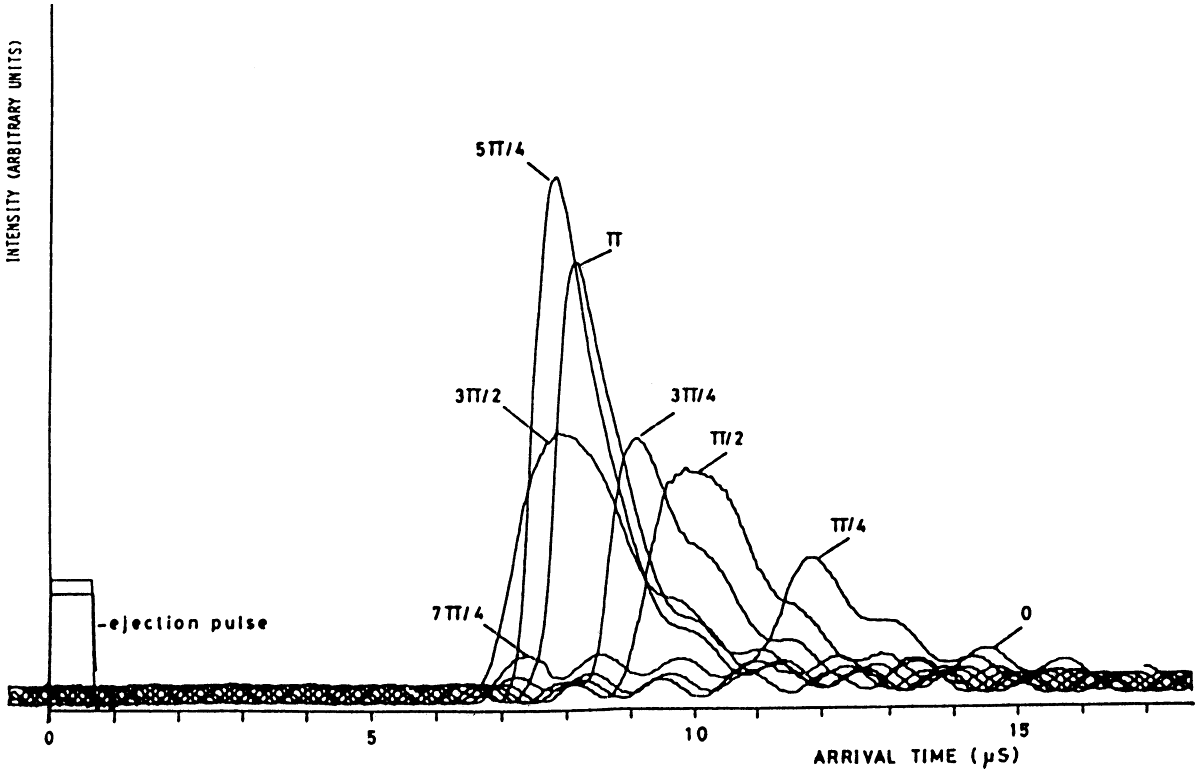

Fig. 8. Arrival time profiles for Ar^+ ions ejected with 90 V "suck-out" pulses of width 0.75 μs at the phase angles stated and $a_z = 0$, $q_z = 0.64$. Copyright Elsevier Science, reproduced with permission from J.F.J. Todd and R.M. Waldren. See [44].

Three other articles appeared on ion ejection from the Quistor in which the ejection pulse was not synchronised to the phase angle of the drive potential but was free running. Two virtually simultaneous publications [48,49] dealt with attempts to characterise the depth of the potential well, but led to somewhat differing conclusions about the magnitude of the ejection potential required. Each investigation em-

Table 2
The effect of phase-synchronised ejection of ions *m/z* 29 and *m/z* 43 formed from *n*-heptane

	m/z 29		*m/z* 43		Ratio of peak heights
Ψ	Peak height[a]	Resolution[a]	Peak height[a]	Resolution[a]	$I_{m/z\ 29}/I_{m/z\ 43}$[b]
0	4.62	58	0.69	82	6.70
π/4	4.75	60	0.69	93	6.90
π/2	15.60	62	11.53	69	1.35
3π/4	13.13	66	18.36	110	0.72
π	15.09	61	20.85	106	0.72
5π/4	12.52	70	17.80	113	0.70
3π/2	13.11	69	18.29	87	0.72
7π/4	10.34	62	6.43	66	1.61
2π	4.62	58	0.69	32	6.70

[a] Peak heights in cm, resolution FWHM.

[b] Ratio of intensities, $I_{m/z\ 29}/I_{m/z\ 42}$, obtained from 70 eV mass spectrum recorded on an AEI MS902 double focusing sector mass spectrometer = 0.32.

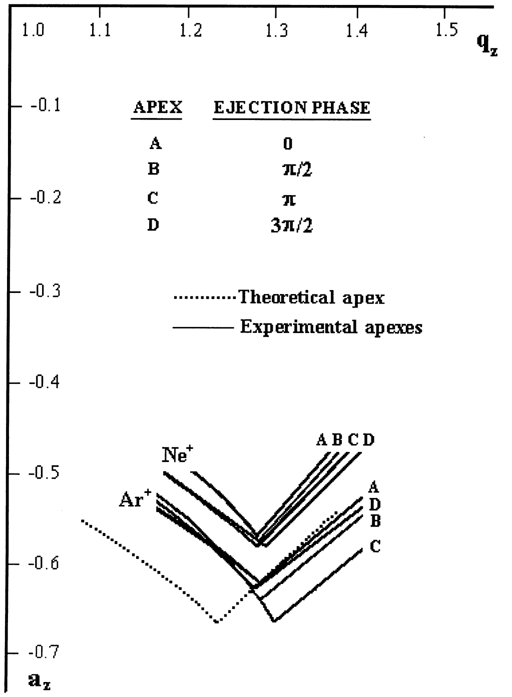

Fig. 9. Partial stability diagrams showing the theoretical and experimentally observed boundaries at the lower apex for Ne^+ ions and Ar^+ ions ejected at different phase angles, Ψ_r.

ployed a double-pulsing method, with the second extraction pulse providing a means of assessing the efficiency of the first in the ejection of ions. Thus Fulford and March concluded that a pulse amplitude of the same magnitude as the depth of the pseudopotential well (see below) was sufficient to ensure ejection, whereas Mather and Todd observed that a potential of some two to three times this magnitude was required. That one might expect a somewhat larger potential is apparent from the model shown in Fig. 10, which suggests that an ejection pulse of four times the well depth would be required to empty the ion trap completely. However, the real situation is extremely complex, and the validity of the well model is open to question (see below). This difference between the two sets of results has yet to be rationalised, although it would appear that the duration of the ejection pulse employed by Fulford and March (50 μs) was 2.5 times that used by Mather and Todd. It may well be that one should consider the area of the ejection pulse; certainly for the narrow pulses employed in the phase-synchronised studies, even with very high amplitudes, ion ejection was not complete. The third publication [50] reported upon a series of experiments in which the rf drive potential was gated in such a way that the amplitude was reduced rapidly to zero during the ejection pulses. The results seem to suggest that there is some increase in signal level and reduction in noise with this refinement.

2.5. Simultaneous positive/negative ion mass spectrometry

It has already been noted that the application of ejection pulses to the endcap electrodes of the Quistor may lead to the ejection of ions in the opposite direction to that expected. One consequence of this behaviour is that, with a sample from which both positive ions and negative ions may be formed, pulsing the electrodes to eject negative ions will also lead to the simultaneous ejection of positive ions in the same direction. Because the mass filter transmits ions of either sign and uses a detector system that is capable of responding to both positive ions and negative ions, it is possible to record a "mixed" spectrum [51], such as that obtained from dichloromethane and shown in Fig. 11. The simultaneous storage of positive and negative ions is possible only over the region of overlap between the stability diagram and its mirror image obtained by reflection through the q axis (Fig. 12), so that choosing a suitable dc bias potential affords a means of storing charges of one sign only. The mass spectrum shown in Fig. 13 was recorded under identical conditions to those employed in obtaining Fig. 11 but with a dc bias chosen to store negative ions only.

3. Theoretical studies

3.1. Phase-space methods: optimum phase for ion ejection

Until 1980 there had been little advance in the theoretical understanding of the behaviour of ions in

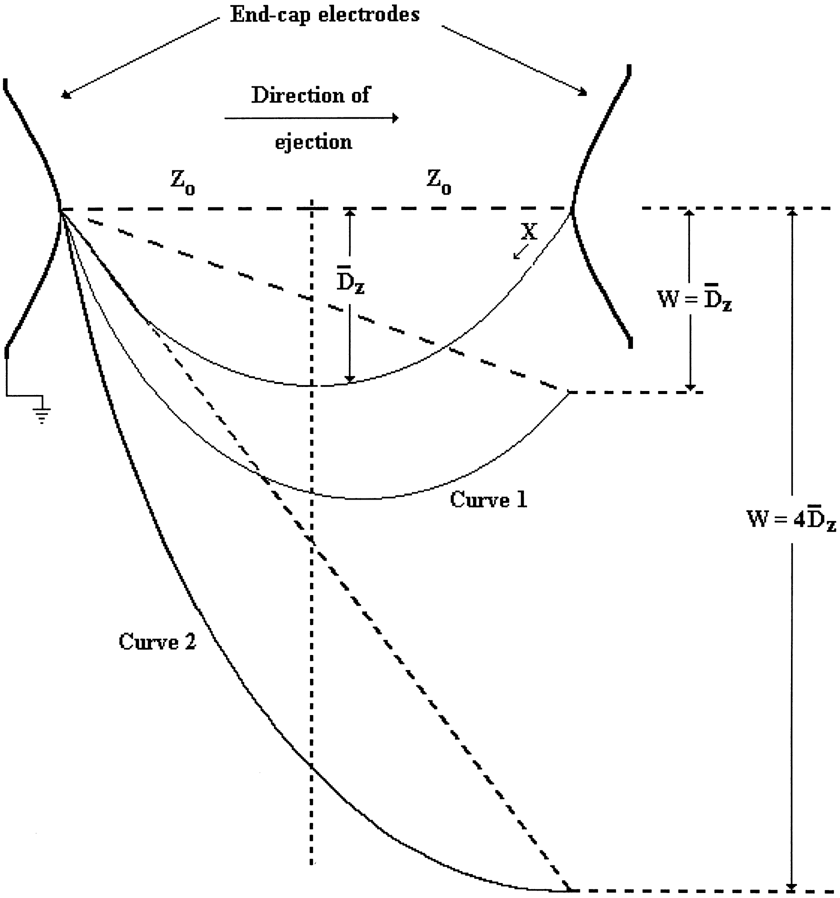

Fig. 10. Representation of the potential along the z axis of the Quistor when a pulse of magnitude $-$W is applied to one endcap electrode.

the Quistor since the early publications of Paul and of Fischer. In 1974, however, Baril and Septier [52] showed how matrix methods and phase-space dynamics, used in accelerator design, could be applied to the motion of ions in radiofrequency quadrupole electric fields. This approach was used extensively by Dawson and co-workers [53,54] and, later, by the Kent group to investigate the motion of ions both within quadrupole mass filters and within the Quistor.

The basis of the phase-space method is that for any given phase angle of the drive potential an elliptical relationship of the form

$$\Gamma u^2 + 2Au\dot{u} + B\dot{u}^2 = \epsilon \qquad (1)$$

exists between the displacement u and velocity $\dot{u}$ of an ion in a one-dimensional quadrupole field. ϵ is a constant, known as the emittance of the ion, and is independent of phase angle, whereas the coefficients A, B, and Γ are phase angle dependent, and may be derived from the Mathieu equation by matrix algebra or from a knowledge of the appropriate C_{2n} coefficients and the Wronskian determinant [55]. If A, B, and Γ are scaled so that $B\Gamma - A^2 = 1$ then the area of the ellipse defined by Eq. (1) equals ϵ/π and, therefore, the motion of the ion may be represented by a family of ellipses with a common centre, each ellipse having the same area but a different orientation. Two sets of ellipses representing, respectively, the radial and axial motion of ions within the Quistor are shown in Fig. 14. The axes are plotted in units of the radius dimension r_o, and the phase angles, γ_r, refer to the canonical time variable in the Mathieu

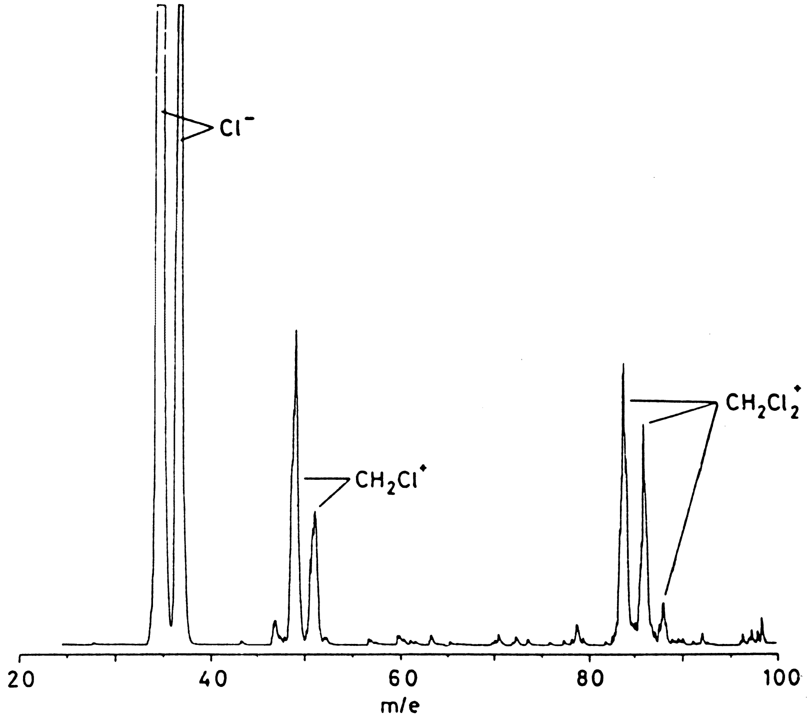

Fig. 11. Positive/negative ion mass spectrum of dichloromethane at 10 ms storage time. Copyright Elsevier Science, reproduced with permission from R.E. Mather and J.F.J. Todd. See [51].

equation for the *r* direction, which is related to the phase angle of the rf drive potential, coupled to the ring electrode by $\gamma_r = (\Psi_r/2 - \pi/4)$. When the maximum possible displacement is equal to r_o or z_o ($0.707\ r_o$) then the emittance is equal to the acceptance of the device and, under these circumstances, the ion trajectories will be stable within the Quistor only when the $(r,\ \dot{r})$ and $(z,\ \dot{z})$ coordinates lie on or within the respective ellipse at every phase angle. The results of the experiments with phase-synchronised ejection were explained in terms of the radial and axial components of motion, as represented by the ellipses in Fig. 14. Thus the *z* motion appears to determine the arrival time of the ions, whereas the *r* motion determines whether, on application of the ejection pulse, ions will be directed toward or away from the exit holes in the endcap electrode. For example, at $\gamma_r = 3\pi/4$ ($\Psi_r = 0$), most ions (corresponding to the ratios in the bounded areas) lie within the quadrants $(+r,\ +\dot{r})$, $(-r,\ -\dot{r})$ so that an impulse in the *z* direction would cause the ions to be lost between electrodes (see Fig. 15). At $\gamma_r = \pi/4$ ($\Psi_r = \pi$), the radial velocity vectors are directed toward the origin so that the ejection pulse will focus ions through the exit holes, toward the mass filter, giving a much enhanced ion signal.

3.2. Ion kinetic energies

We have already seen that evidence derived from the determination of the rate constants for ion/molecule reactions has suggested that the mean ion kinetic energies are of the order of 1–3 eV. Several attempts have been made to derive the mean ion kinetic energies theoretically, making certain assumptions about the nature of the motion of ions within the Quistor. The simplest approach is that based on the model of the ion oscillating sinusoidally in a pseudopotential well, which results from the inhomogeneity of the radiofrequency electric field, as developed

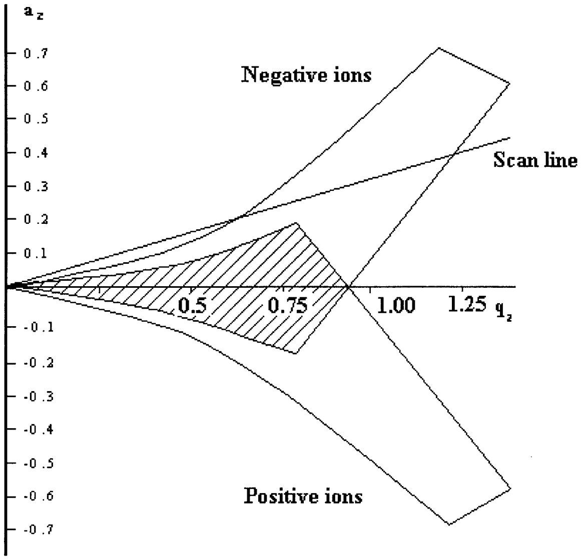

Fig. 12. Superimposed stability diagrams for the Quistor for positive and negative ions showing the common area of overlap (simultaneous trajectory stability) and the scan line for the selective storage of negative ions.

originally by Wuerker et al. [56] and by Major and Dehmelt [57]. In this treatment of ion motion, the contribution made by the high frequency oscillation resulting from the rf drive potential is neglected by averaging over the period of the drive; this approximation is valid only at low values of $q_z = (<0.4)$. A similar limitation applies to an alternative simple treatment proposed by the Kent group in 1976 that utilises a smoothed version of the general solution of the Mathieu equation to describe the motion of the ions. In the same year, Dawson [58] had shown how the phase-space ellipses of the type described above may be utilised to determine the distribution of ion velocities at a given phase angle and, hence, to find average velocities. In fact, two kinds of average must be considered: the average velocity at a given phase angle and the mean of the averages taken over a cycle of the rf drive potential. The method may also be employed to evaluate the maximum velocity and the rms (root mean square) velocity at each phase angle, and the cycle average of these quantities. A detailed comparative study of this field was published by the Kent group [59] in 1980, and a typical comparative plot of kinetic energies calculated by the various methods is shown in Fig. 16, plotted in terms of an "energy factor" E^f versus q_z. To determine the kinetic energy (in eV) at a given value of q_z, the value of E^f was taken from the appropriate curve and multiplied by the value of the operating potential, V_0 (in volts). Evidently the smoothed general solution [curve (B)] and the phase-space method [curve (D)] gave similar

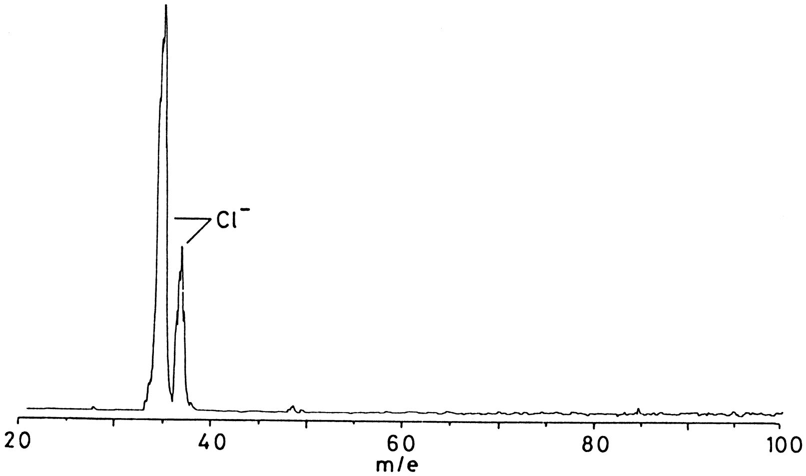

Fig. 13. Mass spectrum as in Fig. 11 but with a dc/rf ratio of ~0.11 set to store negative ions selectively (cf. Fig. 12). Copyright Elsevier Science, reproduced with permission from R.E. Mather and J.F.J. Todd. See [51].

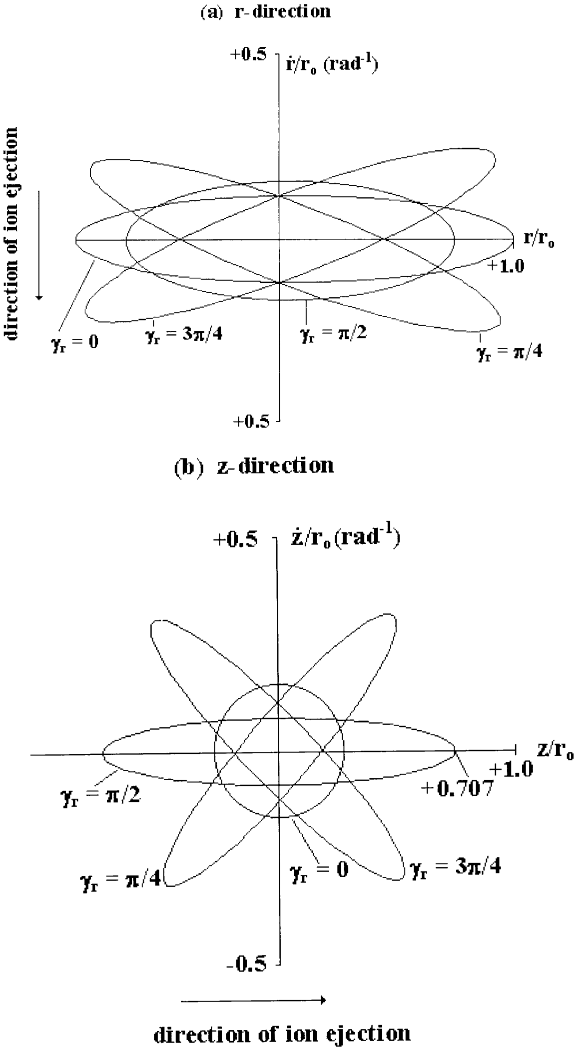

Fig. 14. Phase-space ellipses for the Quistor operating at $a_z = 0$, $q_z = 0.64$ corresponding to (a) $\beta_r = 0.23$ and (b) $\beta_z = 0.50$. [Note: (1) the ellipses in (b) are scaled according to $z_0 = 0.707r_0$; (2) the phase angles are all quoted in terms of the canonical variable γ_r.]

results for the average energy over the entire range of q_z, whereas the well model [curve (A)] and the average rms energy [curve (C)] follow each other up to $q_z = 0.3$, beyond which average energies derived from the well model appear to be overestimated. The cycle averages of the maximum, rms, and average kinetic energies derived from the phase-space treatment have been subjected to curve fitting to obtain the following relationships:

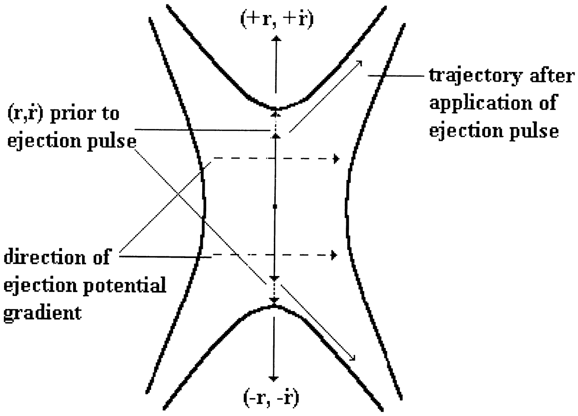

Fig. 15. Possible consequences of the application of an ion ejection pulse at an "unfavourable" phase, e.g. $\gamma_r = 0$ or $3\pi/4$.

$$\{E_{\mathrm{max}}\} = 0.3059\ V_0 \ln(1.662q_z + 1) \tag{2}$$

$$\{E_{\mathrm{rms}}\} = 0.0765\ V_0 \ln(1.662q_z + 1) \tag{3}$$

$$\{E_{\mathrm{av}}\} = 0.0551\ V_0 \ln(1.662q_z + 1) \tag{4}$$

There was little direct evidence with which to compare these calculated kinetic energies; two such investigations involved the measurement of the Doppler shifts in the spectra of stored Ba^+ [60] and Hg^+

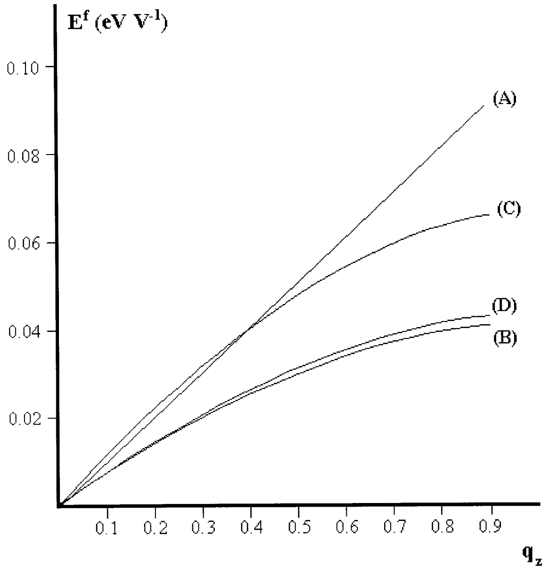

Fig. 16. Plots of the "energy factor," E^f vs. q_z for average kinetic energies calculated by different models (for key, see text).

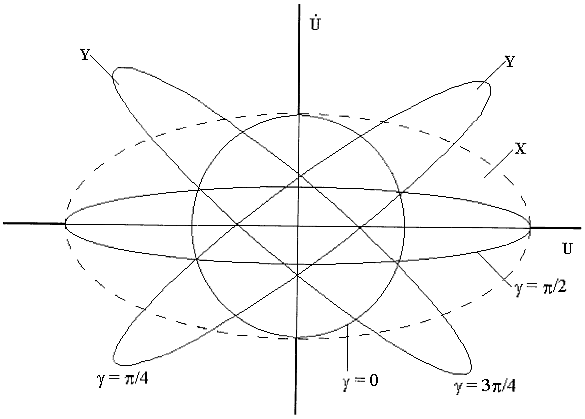

Fig. 17. Phase-space ellipses corresponding to motion along the z axis plotted for the working point $a_z = 0$, $q_z = 0.64$.

[61] ions, where the average ion kinetic energies were found to be approximately one-tenth the depth of the pseudopotential well, a somewhat lower value than that calculated. In these experiments, which were conducted at pressures of $\sim 10^{-9}$ Torr, the storage time was of the order of minutes, thus giving an opportunity for collisional moderation of the ions that is assumed not to have occurred in the theoretical calculations. The validity of the well model was examined in 1980 by Todd et al. [62], who made use of the fact that the maximum kinetic energy along the z axis calculated by the phase-space method at a phase angle of $\gamma_r = 0$ is equal to the depth of the corresponding potential well $\bar{D}_z$. Thus one can draw a composite set of ellipses, as shown in Fig. 17, where the dashed curve shows the phase-space ellipse for the pseudopotential well, which is invariant with phase. The acceptance, ϵ', of the well ellipse is approximately equal to the characteristic quantity β for low values of q. Two types of areas, marked X and Y, denote regions where the two descriptions of ion motion are incompatible. In the case of region X, ions are stable at some point during a cycle of the drive potential, whereas in Y ions possess u, $\dot{u}$ coordinates that are always inaccessible in the well model. The results of this work confirm the statement made earlier, namely that the well model gives a reasonably close approximation to reality at low values of q_z.

3.3. Ion distributions

The approach developed by Dawson for the calculation of velocity distributions from the phase-space parameters was adapted by the Kent group to the calculation of theoretical ion distributions in rf quadrupole fields in one, two, and three dimensions [63]. The basis of the method is depicted in Fig. 18, where, assuming that all the available regions of phase space are equally occupied, the height of the ellipse $|\dot{u}_1 - \dot{u}_2|$ at some displacement u' is taken as a relative measure of the number of ions in that region (neglecting space charge). This idea was extended to the two-dimensional case of the mass filter by noting the independence of motion in the x and y directions and obtaining a three-dimensional probability plot as shown in Fig. 19. In this way it is seen that, for a given phase angle, all the ions are contained within a rectangular boundary, but with a distribution represented by a contour diagram, as in Fig. 20. This is, of course, for one phase angle, and when the ion distributions are summed over a complete cycle, the contour diagram shown in Fig. 21 is obtained. This pattern corresponds closely to the sort of distribution obtained experimentally for the mass filter [64]. For the Quistor, we invoked the cylindrical symmetry around the z axis and obtained a three-dimensional probability function, making the implicit assumption that there was no initial component of angular momentum about this axis. At any phase angle, the ions within the Quistor are contained within a cylindrical volume, typically having distributions in the radial ($z = 0$) and vertical (r–z) planes, as shown in Fig. 22. When summed over a cycle of the drive potential, contour diagrams of the type shown in Fig. 23 are obtained.

This treatment was applied to eight working points within the stability diagram for the Quistor and, by normalising the distributions of the kind shown in Fig. 23, it was possible to gain an idea of how the ions could be accommodated within the Quistor under different conditions. In this way, it appeared that the upper apex should be much less suitable for mass spectrometric operation than the lower apex because of both the smaller ion density and the distribution

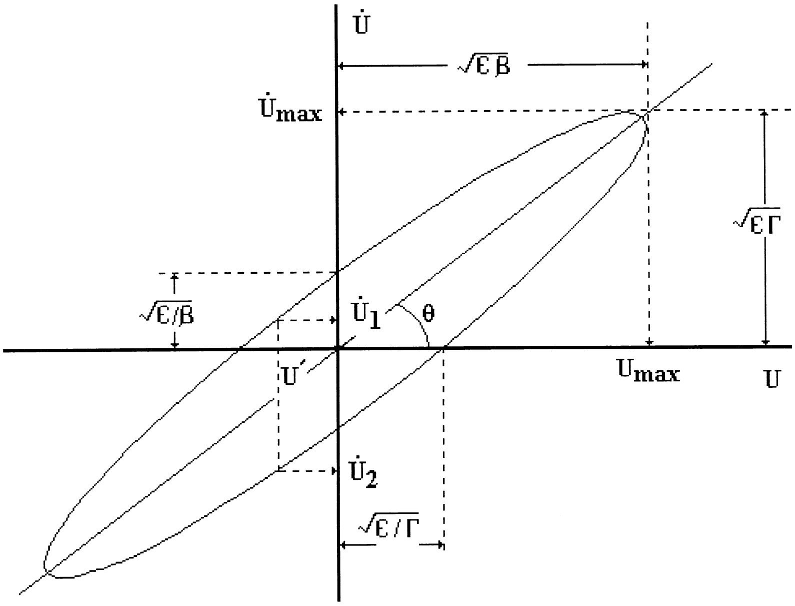

Fig. 18. Phase-space ellipse showing certain critical dimensions.

being more extended in the radial plane for the former; experimental confirmation of the superiority of the lower apex as a working point has already been noted. A further correspondence between observation and theory was the success with which the above model follows the envelope of the "total pressure curve" for the Quistor, obtained by tracing the ejected ion signal for a given species as a function of the value of q_z (i.e. applied potential) along the $a_z = 0$ line. Fig. 24 shows such a curve for $^{84}Kr^+$ ions together with the results of three different theoretical plots; the dotted trace labeled (c) was derived according to the foregoing model.

3.4. Injection of ions from an external source

The idea of trapping injected ions with a Quistor was proposed by Dawson and Whetten in 1970 [65],

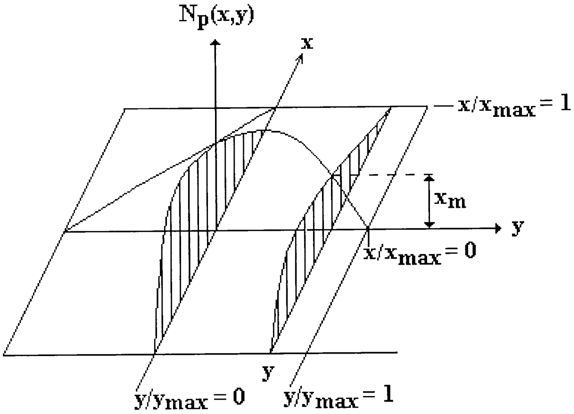

Fig. 19. Form of the probability function $n_p(x, y)$ describing the ion distribution in two dimensions.

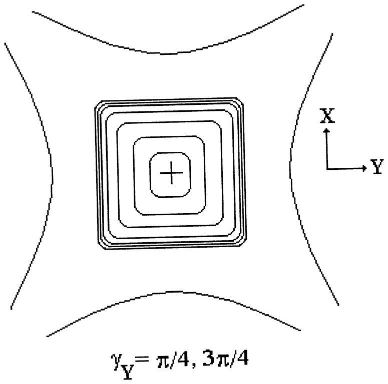

Fig. 20. Contours [values of $n_p(x, y)$] showing the distribution in an ion beam traversing a quadrupole mass filter ($a = 0$, $q = 0.9$) at the stated phase angles.

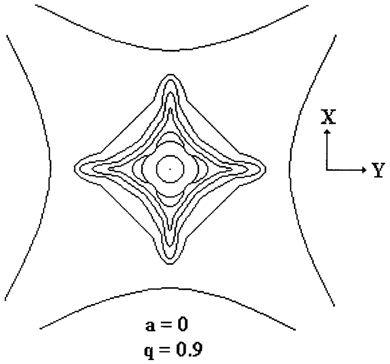

Fig. 21. Contour diagram of the time-averaged distribution of traversing a quadrupole mass filter ($a = 0$, $q = 0.9$).

yet there appears to have been no published report at that time of such a proposal being implemented successfully. In fact, it is evident from the phase-space approach and from the work on ion distributions just described that unless both the phase of injection and the ion velocity were carefully controlled, many injected ions would immediately, on entering the electric field, adopt unstable trajectories and be lost from the trap. In 1976, however, Kishore and Ghosh [66], using conventional trajectory calculations, suggested a method of operation whereby a bunch of ions is injected from an external source with the rf drive potential attenuated to zero, the latter then being brought to full power at a suitable phase angle after an appropriate time delay. The aim of this work was to determine the optimum time delay and phase angle of application of the rf power for the efficient trapping of ions injected along an asymptote between an endcap and the ring electrode. Subsequently, a more extensive treatment of the problem was given by the Kent group [67] who employed the phase-space method to compare the efficiency of trapping for this means of injection with those for radially- and axially-injected ion beams.

The basis of the method is shown in Fig. 25. A bunch of ions emitted from a source *S* traveling with a radial component of velocity $\dot{r}(\leq(\epsilon\Gamma)^{1/2}$ must lie between radial displacements r_1 and r_2 after a delay time in order to remain stable upon the application of rf power with an initial phase angle corresponding to

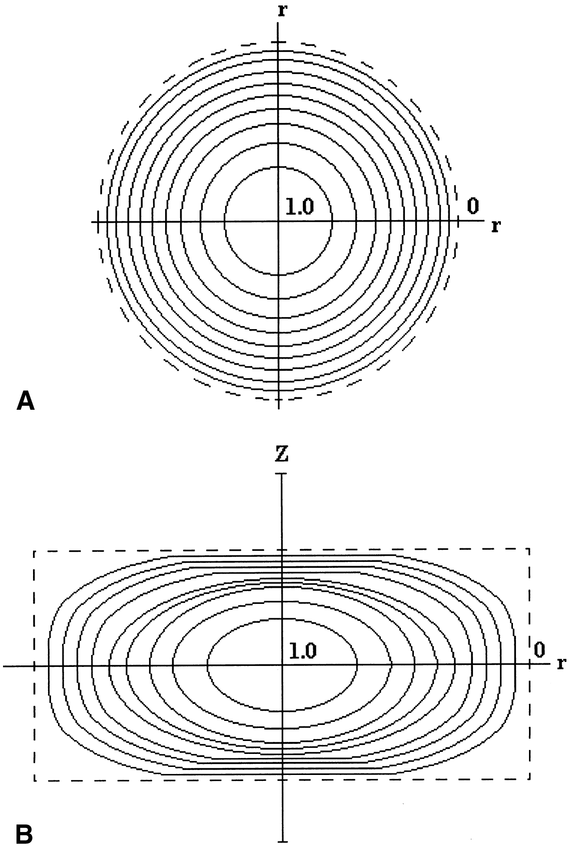

Fig. 22. Contour diagrams for ion distribution in the Quistor at $a_z = -0.667$, $q_z = 1.236$ and $\gamma_r = 0$. Upper: radial plane ($z = 0$); lower: r–z plane.

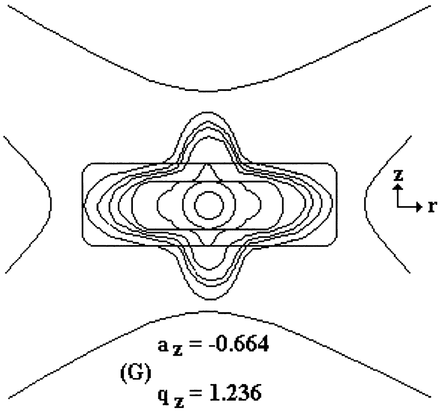

Fig. 23. Contour diagram of the time-averaged distribution (r–z plane) of ions in the Quistor at $a_z = -0.667$, $q_z = 1.236$ (lower mass spectrometric apex).

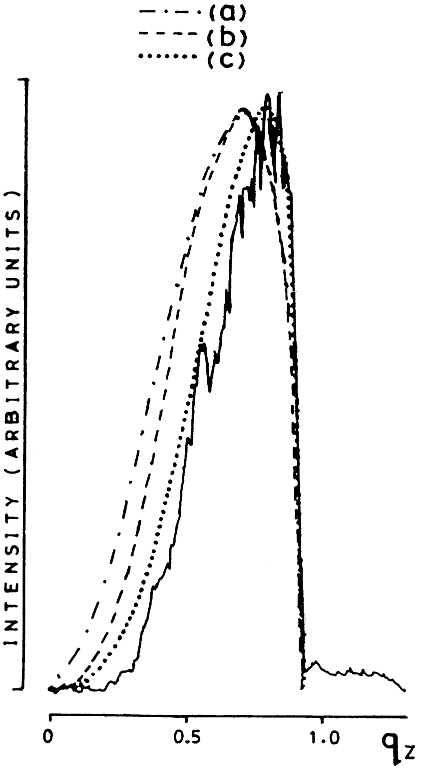

Fig. 24. Total pressure plots for the Quistor. Continuous line: experimental data for Kr^+ ions (*m/z* 84) at 0.8 MHz. Broken lines: curves calculated according to various models. The plot labeled (c) was derived according to the model described in the text. Copyright Elsevier Science, reproduced with permission from J.F.J. Todd, R.M. Waldren, D.A. Freer, and R.B. Turner. See [63].

the ellipse shown. For stability, similar considerations must apply to the *r* and *z* directions simultaneously. In this way, it was verified that the trajectory and phase-space treatments give essentially the same results but, for the conditions selected, the most efficient trapping should be obtained with radial injection through the ring electrode.

The first report of mass-selected injection of ions into an rf ion trap was by March and co-workers [68]. In their experiment, ions were injected from an EB sector instrument into the trap through the gap between ring and endcap electrodes at an angle of 125°. Ions were injected at their full 4 keV acceleration energy. A collision gas was admitted into the trap through a pulsed valve. Stored ions were extracted through a hole in one endcap electrode of the ion trap and mass analysed by an attached quadrupole mass filter. The aim of that experimental setup was to study high energy collision-induced dissociation (CID) processes that result in larger scattering angles and are, therefore, discriminated against in conventional CID collision cell experiments. A Monte Carlo simulation study had indicated that about 2% of the parent ions may be trapped intact after having undergone 15 collisions, whereas greater than 4% of the fragment ions were collected. Two operating modes of the trap were reported: in mode I, the trap was used as an integrating detector for the sector instrument exploiting the fact that injected ions can be accumulated in the trap; in mode II, the ion trap and quadrupole mass filter served as the second stage for MS/MS analysis.

In an improved version of the instrument [69], collision gas addition through a pulsed valve was replaced by a constant collision gas flow and a collision cell in front of the trap. The collision cell served as a deceleration stage, whereas the "thermalization" step (ion energy less than 10 eV) had to occur within the trap in order to store an injected ion. An estimated 0.5–3% of the total injected ions could be trapped. It was observed that a fraction of the molecular ions survived collisional thermalization intact. It was also observed that the ion beam injected at an angle of 125° could be deflected and transmitted through the endcap electrode of the trap and the quadrupole by applying a large negative dc potential to the bottom endcap electrode. Control over the kinetic energy of the injected ions has been achieved in the BE/Quistor/quadrupole instrument described by Schlunegger and co-workers [70], whereas the coupling of a commercial quadrupole ion trap to a BE mass spectrometer has been described by Cooks and co-workers [71]. Commercial ion traps such as the LCQ, GCQ (Finnigan, San Jose, CA), and ESQUIRE (Bruker Daltonic, Bremen, Germany) now employ injection of ions generated externally.

3.5. Monte Carlo calculations

It is possible to calculate the trajectory of a charged species in the quadrupole ion trap by numerical integration of the Mathieu equation. However, it is not

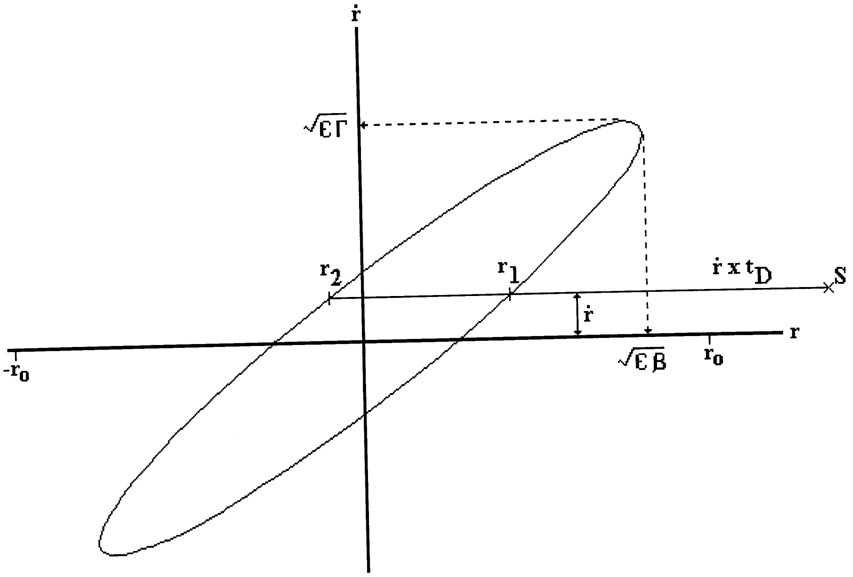

Fig. 25. Phase-space ellipse for motion in the r direction showing values of $r_{\max}[= (\epsilon B)^{1/2}]$ and $\dot{r}_{\max}[= (\epsilon\Gamma)^{1/2}]$. For stability, a bunch of ions with velocity $\dot{r}$ must leave a source S and reach a point between r_1 and r_2 within the time delay t_D.

necessary to follow the motion of the ion continuously; integration of the Mathieu equation offers the advantage that the details of an ion's trajectory can be calculated directly at any given point in time with great accuracy. The majority of such simulation studies has been carried out with the rf drive potential applied to the ring electrode and with the endcap electrodes grounded. In this case, and for the case of resonance excitation in the quadrupolar mode, ion trajectories may be calculated directly by integration of the Mathieu equation.

When a buffer gas is added to the ion trap so that collisions occur between ions and buffer gas atoms, the trajectory between successive collisions may be calculated directly by integration of the Mathieu equation. For the calculation of trajectories of ions subjected to resonance excitation in the dipolar and monopolar modes, integration of the Mathieu equation is no longer valid, and a field interpolation or other method must be used. Approximation methods have also been applied to the calculation of ion trajectories. In the calculation of the trajectory of an ion within a quadrupole ion trap of known r_o, it is necessary to define the initial conditions of ion position and velocity, that is, x, y, z, $\dot{x}$, $\dot{y}$, $\dot{z}$, the rf drive amplitude V_o of phase ξ_o and radial frequency Ω, and the mass m of the assumed singly charged ion. Once the initial conditions have been selected, all of the relevant ionic parameters may be calculated.

The first application of numerical methods to the analysis of single ion trajectories in the quadrupole ion trap was reported some 30 years ago by Dawson and Whetten [4]. At that time, application was limited to the use of the ion trap as a storage device for specific ions, that is, as a mass spectrometer [72,73]. These early studies were extended by Dawson and Whetten [74] to an examination of ion ejection where a range of ion masses was confined simultaneously. André and Schermann [75] had studied earlier the spatial and velocity distribution of a population of ions stored in an ion trap and subjected to collisions with rare gas atoms. The application of Monte Carlo methods by the Trent group permitted the investigation of ion motion with the ions undergoing momentum-dissipating collisions and charge exchange; these studies indicated that ions migrate to the center of the ion trap with an accompanying diminution in ion kinetic energy, and from which the ions can be extracted with increased efficiency [76,77]. The use of Monte Carlo methods was extended subsequently to the study of an ensemble of two ion species [78].

The Trent group, in collaboration with the Kent group and the Provence group (Fernande and Michel Vedel), have published a series of some 20 ion trajectory simulation articles during the past two decades in what has been a fruitful and memorable association. This series of articles was initiated by the visit to Trent of Jean Durup, of Orsay. In 1973, computer calculations required the use of batches of punched cards and an unseen computer at a distance; this situation is a far cry from the powerful desktop computers that are ubiquitous today. The initial task of the Durup initiative was to attempt to explain a series of mass spectra of Ar^+ and Ar^{2+} recorded as a function of storage time. The task was accomplished by showing that the doubly charged ions were focused collisionally on the centre of the Quistor at a greater rate than were the singly charged ions, and that ions were sampled preferentially from the central axial cylinder within the Quistor.

A mathematical formalism of temporal invariance, developed by Vedel et al. [79], was applied to the study of the statistical spatial and energy distributions of trapped ions subjected to collisional cooling. These studies were extended to the space charge case by Vedel and André [80,81]. Early applications of numerical and analytical methods to the analysis of trapped ion behaviour have been reviewed previously [82].

Representative trajectories for trapped ions of three different masses, with working points on the q_z axis and in a collision-free and resonance-free system, have been calculated by Louris et al. [83] by integration of the Mathieu equation. Lunney et al. [84] have applied finite element analysis to the calculation of fields within the ion trap from which trajectories were calculated. Their interpolation method lacked sufficient accuracy and has been superceded by a field modeling process developed by Lunney and Moore [85], in which the field was reconstructed using a summation of multipole potentials.

Some unpublished trajectory plots by Bexon and Todd and by Fies Jr., for ions stored within the ion trap and subjected to collisions with helium buffer gas, appeared in a fairly recent publication by Todd [86]. Bexon and Todd calculated one-dimensional (axial) trajectories of *m/z* 25 ions showing the effect of regular collisions with helium atoms; the motion of *m/z* 69 ions in the *r–z* space plane both with and without helium buffer gas was calculated by Fies Jr.

3.6. *Infrared multiphoton dissociation (IRMPD) in the Quistor*

As with the ICR technique, the Quistor is capable of storing ions for long periods of time, and this facility makes the ion trap compatible with a wide range of experiments using light. One of the first successful uses of the ion trap in conjunction with photodissociation involved the study of the proton-bound dimer of 2-propanol utilizing a cw infrared CO_2 laser [87]. 2-Propanol was chosen for study because its gas-phase ion chemistry is well known, and the formation of the protonated dimer is easily accomplished. Because it had been shown earlier, by experiment and by Monte Carlo calculations, that ions in the Quistor appeared to become focused at the centre of the device as a result of momentum-dissipating collisions with buffer gas or parent neutrals, it was argued that the entire cloud of ions could be irradiated by an infrared laser beam. Unfortunately, the Trent group did not possess such a laser. However, Dr. Clive Willis of the National Research Council (NRC) of Canada, offered the loan of such a laser provided that infrared multiphoton dissociation (IRMPD) could be demonstrated in the NRC laboratory. Thus, the entire ion trap apparatus at Trent was dismantled, transported by truck to Ottawa, and reassembled. Although the demonstration of IRMPD was not entirely convincing, Dr. Willis arranged for transportation of the laser to Trent and its installation.

The instrumental configuration employed differed from the normal Quistor/quadrupole mass filter in that the Quistor was connected directly to the ion source of a quadrupole mass filter. The ion source located between the ion trap and the quadrupole mass filter was used for mass calibration purposes with perfluorokerosene. The ion optics of the mass filter ion source allowed for transmission of ions from the ion trap to the mass filter. The Quistor was operated exclusively in mode II, with the endcap electrodes held at ground and a radiofrequency potential ϕ_0 applied to the ring electrode. A detailed description of the optimization of ion trapping characteristics for studies of ion photodissociation in a Quistor can be found in a publication by March, Hughes, and Young [88].

The ring electrode of the Quistor was modified with a 3-mm-diameter hole on the center axis that functioned as the entrance aperture for a low power cw CO_2 laser beam directed through a NaCl window. Upon reaching the other side of the ring electrode, the laser beam was partially reflected throughout the Quistor, but a portion of the beam passed through a 0.8-mm-diameter hole on the opposite side of the ring electrode and through another NaCl window where it was monitored externally. The pressure of 2-propanol was adjusted to 5 mPa so that photodissociation of the proton-bound dimer, $(2M + H)^+$, at *m/z* 121 could occur at an appreciable rate. At pressures optimum for the formation of the proton-bound dimer (13 mPa), no laser-induced dissociation was observed due to collisional deactivation of the vibrationally-excited proton-bound dimer. At the low pressures used in these experiments, the dissociation rate constant k_D was proportional to the product of the phenomenologically defined cross section σ_D and the photon flux ϕ. The highest absorption cross section for 2-propanol was found to be at 944 cm^{-1}, with the corresponding absorption of 10 photons. The dissociation rate constant k_D was determined to be 2.2 s^{-1}, assuming first-order dependence on photon flux. Photodissociation followed by subsequent mass analysis showed three different photoreaction channels open with IRMPD of the proton-bound dimer of 2-propanol [89,90].

The same experimental apparatus was also used to investigate the gas-phase ion chemistry of ethanethiol, 1- and 2-propanethiol, and 2-hydroxyethanethiol [91,92]. The collisionally cooled proton-bound dimers of ethanethiol, 1-propanethiol, and 2-propanethiol were unaffected by laser irradiation at 944 cm^{-1}. However, the proton-bound dimer of 2-hydroxyethanethiol was photodissociated completely at the same wavelength. The proposed structure for the proton-bound dimer of 2-hydroxyethanethiol was thought to contain a $S–H^+–O$ linkage that absorbs readily at 944 cm^{-1}, as opposed to the $S–H^+–S$ linkage that was shown to be transparent at the same wavelength. Isomer differentiation by multiphoton dissociation of the proton-bound dimers of propanone (*m/z* 117) and protonated diacetone alcohol (*m/z* 117) was also demonstrated in that the former ions dissociated to protonated propanone whereas the latter ions fragmented to yield ions of *m/z* 99 [93–95]. Investigation of the wavelength dependence of IRMPD photodissociation efficiency of the proton-bound dimer of ethanol using the Quistor demonstrated the observable frequency shifts of the C–O stretch in the IR region [96]. Application of the Quistor technique to the study of photodissociation rates by varying relaxation time, buffer gas pressure, and analyte pressure yielded data for the proton-bound dimers of isopropanol, 2-d_1-2-propanol, and ethanol. The effect of collision rate on the defined photodissociation cross section was studied also. The results obtained for the fully relaxed proton-bound dimer population showed access to only the lowest E_a pathway, thus demonstrating the only variable observed was that of the collisional deactivation process (corresponding to higher collision rates $\geq$5 ms^{-1}).

4. Nonmass spectrometric applications of the Quistor

In parallel with the mass spectrometric development of the Quistor described above, there has been extensive work involving the application of the ion trap to other areas, some of which have been reviewed previously [97]. Mainly, it is in the field of atomic spectroscopy where advances have been made, although publications have described the use of the ion trap as a source for an accelerator for microparticles [98–100]. The spectroscopic applications stem essentially from the work of Dehmelt and collaborators [101–103] and have been reviewed recently by Schuessler [104]. Thus, stored $^{135}Ba^+$ and $^{137}Ba^+$

ions have been detected by the observation of fluorescence radiation [105] and the hyperfine spectrum of $^{199}Hg^{+}$ ions was characterised [106]. In a particularly interesting publication, Schermann and Major [107] described a series of experiments in which Tl^{+} and I^{-} ions formed by photodissociation of thallium iodide were stored simultaneously and the plasma characterised. It was possible to observe decay through ion recombination over a period of 10 s and, under the conditions of the experiment, the absolute ion density was found to be 1.1×10^{-7} cm^{-3}, with a maximum energy of the order of 5 eV. Evidently, the presence of oppositely charged ions led to a significant increase in the density of ions that could be stored.

In a later publication, Schuessler and Holder [108] described a detailed study in which the cross sections for the electron impact ionisation of a beam of helium atoms with 350 eV and 500 eV electron beams were measured. The trap was operated in the “symmetric storage” mode, whereby a dc potential is applied between the endcap electrodes and the ring electrode so that the depths of the two pseudopotential wells, $\bar{D}_r$ and $\bar{D}_z$, were equal. The ions were detected by means of a tuned circuit and, at a pressure of 5×10^{-10} Torr, a half life of 72 s was observed for the decay of the stored helium ions. The values for the ionisation cross sections agreed well with those measured by other techniques, and the possible application to the study of the production of multiply charged ions was suggested. In a further article from the same laboratory, O and Schuessler described an ion storage trap with semispherical electrodes [109]. The particular advantage of this geometry was the device’s ease of fabrication to small dimensions, such as the trap employed by Neuhauser et al. [110] for the laser cooling of stored ions, but which was of hyperbolic geometry. From calculations of the potential distribution and equations of motion of the ions, the authors concluded that the field nearest the centre of the trap is closest to that of an ideal trap of the same dimensions when the radii of the endcap electrodes and the ring electrode are 2.60 z_o and 0.55 r_o, respectively. The calculated stability diagram is closely similar to that published by Benilan and Audoin for the cylindrical trap of diameter r_o and height $2z_o$, and, as with the cylindrical trap, the calculated ion storage capacity is greater than that of the hyperbolic trap operated under the same conditions. However, because of anharmonicity in the ion motion arising from the higher-order field components in the semispherical trap, ion losses were greater, leading to shorter storage times.

5. Conclusion

In this retrospective review, we have attempted to provide both an explanation of the circumstances that drew us to the early research described here and a summary of developments in the theory, technology, and applications of the Quistor during the 1970s. In 1981, it was evident that the emergence of this device as a mass spectrometer, as a mass-selective ion source, as an ion/molecule reactor, and as an essential tool in atomic spectroscopy was still continuing, and that the potential contributions that ion storage techniques may make had yet to be fully realised. Today, it is evident to us that, with some 5000 commercial ion trap instruments in laboratories throughout the world, quadrupole ion trap mass spectrometry is serving a multitude of needs in a wide variety of applications. Even so, we would venture that there still remain many potential contributions that ion storage techniques may make but have yet to be fully realised.

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