

# Applications of rf fields and collision dynamics in atomic mass spectrometry†

Dieter Gerlich

Faculty of Natural Science, Technical University, 09107 Chemnitz, Germany.

E-mail: gerlich@physik.tu-chemnitz.de

Received 16th March 2004, Accepted 5th April 2004

First published as an Advance Article on the web 22nd April 2004

Today, inhomogeneous, time dependent electric fields, created with suitable electrode arrangements, are used routinely in sophisticated machines for studying the structure and reactivity of atomic and molecular ions, clusters, and charged nanoparticles. This contribution first illustrates recent progress made in this field by briefly reviewing some fundamental experiments, performed with radiofrequency (rf) based electrode arrangements. The examples have been selected according to their potential relevance for mass spectrometry. They cover the study of integral and differential cross sections in octopoles, the determination of low temperature rate coefficients in multi-electrode systems, and laser induced reactions in traps. In addition to applications in basic research, the past decades have seen many activities in integrating ion guides and traps into instruments developed for analytical purposes. In early applications, rf fields were mainly utilized for confinement, transfer, mass selection, and phase space compression, while currently inelastic or reactive collisions with suitable neutral buffer gases are used in addition for improving the sensitivity and versatility of the instruments. In the field of atomic mass spectrometry the method is called the collision and reaction cell technique or mass spectrometry with a dynamic reaction cell. The strategy is to systematically utilize ion–molecule reactions for changing the mass of isobaric species or polyatomic ions interfering with the element of interest. It is the aim of this paper to tentatively analyze some of the related applications and to evaluate the potential of reaction dynamics and rf-based devices for improving the sensitivity in elemental and isotope analysis. It is concluded that for processes where energy is required (*e.g.*, for collision induced dissociation or endothermic reactions), one should make use of a guided ion beam with well defined kinetic energy, while in the case of exothermic reactions, a thermalized ensemble, especially at cryogenic temperatures, is probably the best choice. Generally applicable methods are the change of mass by deuteration or ternary association reactions with rare gases.

## Introduction

It can be seen in many fields of research that there is a long time from the discovery of a physical effect to its practical implementation in various fields. A typical example is the nuclear magnetic resonance (NMR) method (1952 Nobel prize in physics), on the basis of which powerful analytical instruments have been developed, but it took half a century (Nobel Prizes in Chemistry 1991 and 2002, Nobel Prize 2003 for imaging in medical applications).

It is also more than 50 years ago that researchers realized that charged particles can be confined in inhomogeneous, oscillatory electric fields if these alternate fast enough in time. During those early times the ideas have been stimulated by methods developed in accelerator physics and the search for techniques to confine a plasma. The first instruments utilizing *radiofrequency (rf)* fields were the quadrupole mass spectrometer, the Paul trap and the octopole ion beam guide. The development of this innovative technique and specific applications have been briefly summarized by Gerlich<sup>1</sup> and more thoroughly in a review.<sup>2</sup> In a recent tutorial<sup>3</sup> some newer applications of rf ion guides were referred to. The method of guiding and trapping ions has removed most inherent difficulties encountered by standard electrostatic techniques and it has revolutionized our ability to handle slow charged ions, clusters, and also nanoparticles.<sup>4,5</sup> A selection of typical applications in gas-phase ion chemistry, reaction dynamics and

ion spectroscopy will be summarized below after some remarks on the rf theory and a few hints to typical designs and technical details.

In a similar way to the NMR technique rf ion guides and traps became only slowly integrated into a variety of prototypes of analytical instruments. While quadrupole mass spectrometers had already become commercially available in the 1960s—W. Paul got the Nobel prize in 1989—the potential of multipole ion guides and low temperature ion traps has still not been fully explored in commercial instruments or prototype ones developed in research laboratories. Typical current applications are multi-component trace gas analysis, based on soft ionization *via* low energy proton transfer, or structural analysis of organic molecules by collision induced dissociation in an all fragments collecting octopole. An interesting recent application is high-throughput screening of homogeneous catalysts. This new instrument is based on the integration of an rf 24-pole and an 8-pole, serving as *reaction vessels*, into a tandem mass spectrometer.<sup>6</sup>

In mass spectrometry, applications of so-called *rf-only* or *ac-only rods* became stimulated by the observation that collisions with a buffer gas can significantly increase the detection sensitivity. This empirically discovered improvement, which is incorrectly called *dynamic focusing* in a patent<sup>7</sup> with the title *Mass spectrometer and method with improved ion transmission*, is based on the relaxation of hot ions in collisions with colder neutrals. Indeed, it is of fundamental importance for many applications, such as the storage ion source,<sup>8</sup> that two- and three-dimensional effective potential minima of rf ion guides and traps allow one to compress the six-dimensional (*r* and *v*) phase space of an ion ensemble by the interaction with a

† The opinions expressed in the following article are entirely those of the author and do not necessarily represent the views of the Royal Society of Chemistry, the Editor or the Editorial Board of JAAS.

suitable target. Note that focusing or confinement with electrostatic ion optics is restricted by the Liouville theorem and that collisions in general lead to a dispersion of the beam.

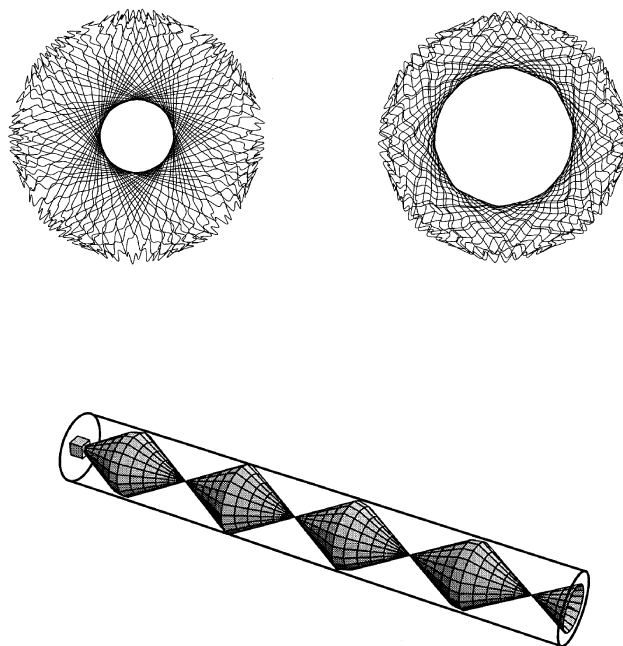
Besides the cooling of the ions created in a suitable ion source, there are various strategies in mass spectrometry to obtain, in addition to the mass, structural information on molecular ions or reduction of disturbing mass overlap in elemental and isotope analysis. In the case of inductively coupled plasma mass spectrometers (ICP-MS) spectral interferences are reduced by the so-called *collision and reaction cell* (CRC) or the *dynamic reaction cell* (DRC) technique.<sup>9</sup> In both instruments the ion beam is, prior to the analyzer quadrupole, guided in an rf-driven multipole through a reaction chamber containing an appropriate target gas. In this region, ion–molecule reactions take place under more or less controlled conditions and they are used to overcome isobaric overlap. Many tests,<sup>10–12</sup> have shown that the specific design of the rf ion guide and its operating conditions significantly affect the efficiency of this chemical filter. However, it is questionable whether the empirically found recipes are optimal or whether there are better strategies in choosing the proper rf device, selecting the best operational parameters and, an almost hopeless task, making the most favorable use of expertise collected in ion–molecule chemistry. It is the aim of this contribution to help to incorporate into the DRC and CRC techniques our knowledge of the development and applications of rf based modules and instruments and to make some—maybe somewhat speculative—proposals originating from our experience in ion–molecule reaction dynamics, laser induced ion processes and low temperature astrochemistry.

## Rf fields: the need to know

### Basic theory

In order to systematically profit from the features of ion guides and traps and to make dedicated use of ion dynamics in such systems, one first needs to understand the motion of a particle under the influence of a time dependent force. Some basics can be found in text-books of classical mechanics;<sup>13</sup> however, one should also be aware that the exact motion of charged particles in an arbitrary time dependent electromagnetic field is an unsolved challenging problem of classical dynamics. The inclusion of dissipative forces, *e.g.*, by inelastic collisions, adds to the mathematical complexity. Many details of the basic theory, numerical calculations and a lot of experimental tests have been thoroughly reviewed by Gerlich.<sup>2</sup> In order to make this contribution not too lengthy we refer often directly to the figures and formulae in this paper. Within the last decade a lot of additional work has been done, some of which has been summarized by Gerlich<sup>3,5,14</sup> and by Armentrout.<sup>15</sup> In the following paper, only a few special hints are given.

In most applications relevant to mass spectrometry, one uses an inhomogeneous electric field,  $E_0(r) \cos(\Omega t)$ , which oscillates in time with the frequency  $\Omega$ , while the spatial dependence,  $E_0(r)$ , is given by the boundary conditions imposed by suitable electrodes. Note that also nodal points or lines of standing or travelling electromagnetic waves can be of practical interest. It is straightforward to write down the classical equation of motion of a particle with mass  $m$  and charge  $q$  moving in this field. This differential equation can be solved if the field is homogeneous: in most other situations there are no exact analytical solutions. One well-known exception is quadrupolar fields (Mathieu equation), but a less-known special case with an analytical solution is the motion of an electron in a standing plane electromagnetic wave with circular polarization. Computer simulations as shown in Fig. 1 are very useful for getting some feeling for specific properties of certain field geometries and for testing dependences on various parameters;



**Fig. 1** Characteristic ion trajectories, illustrating the transverse motion of an ion in an octopole. It can be seen that the trajectory can be composed of a smooth part  $r_0(t)$  and an oscillating part. Inspection of the direction of the wiggling motion in the turning regions allows one to deduce the location of the electrodes (not shown). Two different initial conditions have been chosen in order to indicate that not only the kinetic energy is conserved in average (outer limitation), but also the orbital angular momentum. Without collisions the ion never reaches the empty inner part. The trajectories in the lower panel indicate the axial motion in an octopole. The angle of a trajectory relative to the axis is conserved (reflection law). This is, among others, important for measuring differential cross sections with the GIB method.<sup>25,27</sup>

however, in order to get a deeper insight, analytical approximations have the advantage that they are more general.

An important criterion for describing motions such as those shown in Fig. 1 is to search, in addition to the rf period  $2\pi/\Omega$ , for other time scales relevant for the dynamic system. Examples include the time needed to traverse the structure or to move from one electrode to the next one in a circular motion; it can also be the time between two collisions with buffer gas. If the velocity of the particles is fast (or the change of the rf field slow) there is the possibility or the risk of resonances. Using suitable geometrical structures and frequencies, oscillating fields can be used for acceleration (*e.g.*, the linear accelerator) or also for deceleration if the phases are properly chosen. If, however, the field oscillates with a sufficiently high frequency  $\Omega$ , fast and slow components of the trajectory can be separated, a well established method in theoretical physics and mathematics. Within such an *adiabatic approximation*, one obtains the important results, that the time averaged kinetic energy of the particle is conserved and that the motion of the particle can be predicted in a much simpler way by using the effective mechanical potential.

$$V^* = q^2 E_0^2 / 4m\Omega^2 \quad (1)$$

In order to get a quantitative measure for the quality of such an approximation, the adiabaticity parameter

$$\eta = 2q|\nabla E_0|/m\Omega^2 \quad (2)$$

has been introduced;  $\eta$  also can be used as a criterion for the stability of the motion and, therefore, is referred to as the stability parameter. Note that both relations are valid for any arbitrary electric field and that  $V^*(r)$  as well as  $\eta(r)$  are usually

functions of the coordinate  $r$ , but independent of time. As explained in detail in ref. 2, one operates within the range of validity of the adiabatic approximation if, along a trajectory,  $\eta(r)$  always remains smaller than 0.3. Under specific conditions, there are also regions of stability for  $\eta > 0.6$ ; however, there are no general rules known.

The effective potential can be used for reflecting, guiding or trapping electrons, ions, clusters and also charged microscopic particles with  $m > 10^{10}$  u using frequencies ranging from GHz (microwaves) via MHz (radiofrequency) to a few Hz (ac, alternating current), respectively. As discussed in detail in ref. 2 it is not difficult, at least in principle, to find operating conditions for simultaneously confining particles with quite different masses in the same electrode arrangement. In the case of very large masses, where the gravitational force must be accounted for, superimposed electrostatic fields are commonly used. Typical applications in this mass range include the electrodynamic balance (see for example work by Davis *et al.*<sup>16</sup>) or the fg-nanoparticle mass spectrometer developed by Schlemmer *et al.*<sup>17</sup>

### Electrode arrangements

There are many possibilities to select special field geometries (see chapter IIC in ref. 2). In the case of any rotationally symmetrical structure, the general potential (see eqn. 34 of ref. 2) can be approximated by ring electrodes. For symmetry reasons, there is no field component in  $\varphi$  direction and the adequate coordinate system uses  $(r, z)$ . In such a device it is possible to superimpose an axial dc field (similar to a drift tube).

Most common are long cylindrical conductors, *i.e.*, no  $z$ -dependence. The general potential, which is given by eqn. 29 of ref. 2, can be approximated by properly formed electrodes, thin wires *etc.* A quadrupole made from 60 thin rods (1 mm diameter) has been described by Mark *et al.*<sup>18</sup> Usually the hyperbolic boundary conditions of the special solutions called multipoles are approximated by circular rods. A first order approximation of the rod diameter  $d$  is  $r_0 = (n - 1) d/2$ , where  $2n$  corresponds to the number of poles and  $r_0$  the inscribed radius (example  $d = 1$  mm,  $r_0 = 5$  mm,  $2n = 22$ ), better approximations have been reported in the literature<sup>2</sup> but are not relevant if one wants to use the electrode arrangement just as an ion guide or trap. The effective potential and the stability parameter of multipoles can be derived from eqn. (1) and eqn. (2),

$$V^* = n^2/4 (q V_0)^2 / (m\Omega^2 r_0^2) (r/r_0)^{2n-2}, \quad (3)$$

$$\eta = 2n (n - 1) (q V_0) / (m\Omega^2 r_0^2) (r/r_0)^{n-2}. \quad (4)$$

There are more complicated electrode structures which are useful in special applications, such as labyrinths or a duodecapole-octopole structure. Common to all such devices is that at those locations, where the effective potential has a minimum, also the stability parameter becomes very small.

### How to choose parameters

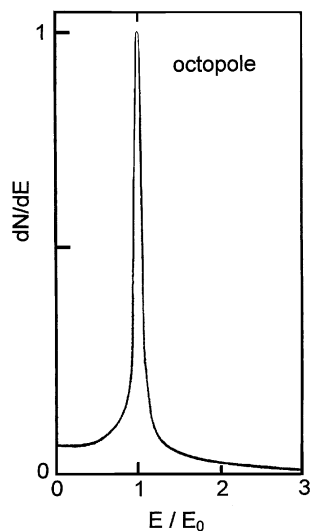
In practice, the two electric potentials applied to two adjacent electrodes (also called RF<sup>+</sup> and RF<sup>-</sup> or RF<sub>1</sub> and RF<sub>2</sub>) are  $\pm \Phi_0 = \pm (U_0 - V_0 \cos\Omega t)$ , where  $U_0$  and  $V_0$  are the dc and rf components, respectively. For a detailed discussion of this convention see ref. 2 on p. 30. The potential difference between two electrodes is  $2U_0 - 2V_0 \cos\Omega t$ . Operating an ion guide or trap in the “rf-only” mode means  $U_0 = 0$ . By this convention, the field axis is set arbitrarily to 0. If, however, externally created ions are injected into an ion guide, it is advantageous to introduce the potential  $U_{FA}$  and to select the reference point of this voltage such that the axial kinetic energy of a guided ion beam is given by  $E_1 = -qU_{FA}$ .  $E_1$  can be determined with meV accuracy by time of flight (see fig. 34 in ref. 2).

For selecting the proper ion guide or trap geometry and for choosing the optimum operating parameters for a special purpose, different criteria have to be taken into account. Parameters, needed in the calculations are, for the ion, the charge  $q$ , the mass  $m$ , and the kinetic energy, and for the rf field the amplitude  $V_0$ , the frequency  $\Omega = 2\pi f$ , and eventually the dc component  $U_0$ . For characterizing the geometry one uses, in the case of multipoles, the number of rods,  $2n$ , and the scale length,  $r_0$ . The geometry of ring electrode arrangements is more flexible, for example one can change the diameter  $r_0$  at a fixed plate-to-plate distance  $\pi z_0$  (see Fig. 7 of ref. 2). If the adiabatic approximation is valid, conservation of energy ensures that transmission or trapping does not depend on the individual initial conditions, but only on  $E_m$ , the maximum transverse kinetic energy of the ions (see III.C.4 in ref. 2). For example, it is easy to show that an rf-only quadrupole ion guide is the best choice if one just wants to confine ions with a single mass and a given value of  $E_m$  to a specific maximum radius  $r_m$  using a minimal amplitude  $V_0$ . If one is interested in collisions with well defined kinetic energies or in the simultaneous confinement of a wide range of masses, it is generally advisable to use so-called “safe operating conditions” (see ref. 2), *i.e.*, fulfil the condition  $\eta < 0.3$  for all ions of interest. This and the possibility of operating rf devices in discriminating modes is discussed below.

Several analytical formulae have been derived that permit one to calculate conditions, which are sufficient for staying always within the adiabatic approximation. Using, for example,  $n = 4$  and  $E_m = 1$  eV, it is found that an amplitude  $V_0 = 48.8$  V is sufficient to guide a singly charged particle. This result is independent of  $m$ , *i.e.*, it holds for electrons, protons, or heavy cluster ions although, of course, different frequencies have to be chosen. For simultaneously guiding ions with  $E_m = 0.1$  eV and masses ranging from  $m_1 = 1$  u to  $m_2 = 100$  u, the values needed are  $V_0 = 105$  V and  $f = 17.8$  MHz for an octopole ( $n = 4$ ,  $r_0 = 0.3$  cm). It also can be shown that for a wider mass range, *e.g.*, a factor of  $10^4$ , a decapole is preferred. More detailed examples can be found in ref. 2.

### Energy impairment

To aid in the interpretation of rf collision cells, it is necessary to understand the time dependent distortion of the ion kinetic energy caused by the confining rf field. As can be seen in Fig. 1 the momentary kinetic energy of an ion oscillates during its reflection from the rf wall. Depending on the initial conditions, it can reach up to three times the initial energy  $E_0$  but only for very short times in multi-electrode arrangements. The distribution  $dN/dE$  shown in Fig. 2 has been calculated by numerical integration of the equation of motion in an octopole. Ion trajectories have been simulated starting near the axis of the octopole. The time averaged probability distribution of  $E(t)$  divided by its initial value  $E_0$  is plotted. It is often disregarded that in most applications of guided ion beams, the motion in the axial direction is not affected at all and only the transverse velocity gets modulated. The energy of a mono-energetic ion beam injected and guided with  $E_1 = 1$  eV at an angle of  $10^\circ$  (see lower panel of Fig. 1) varies only from 0.97 eV to 1.06 eV with a sharp peak at the nominal energy. Using numerical simulations, the influence of collisions with neutral molecules has also been treated in detail in ref. 2. The main conclusion is that one should use electrode structures with wide field-free regions if one needs high energy resolution or if one intends to study reactions at low temperatures. It has to be mentioned that local potential perturbations caused by dirty surfaces which pull the ions towards the electrodes or large space charges (ion number densities above  $10^5$  ions  $\text{cm}^{-3}$ ) which push the ions away from central regions lead to perturbations of the energy distribution of stored or guided ions. In both cases the residence time of the ions in the vicinity of the electrodes becomes longer, as shown



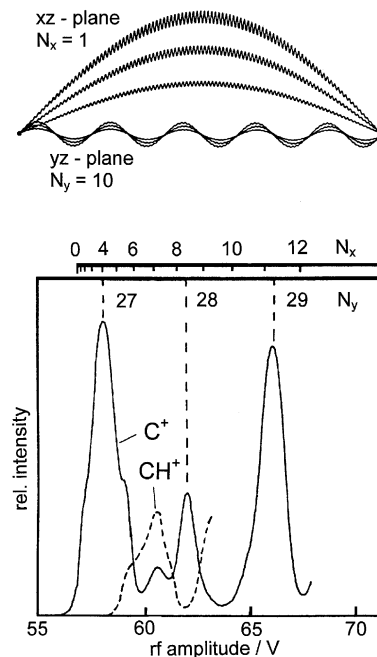
**Fig. 2** Time averaged energy distribution  $dN/dE$  of an ion stored in an octopole. The initial energy the ion has close to the center,  $E_0$ , varies during the reflection between 0 and  $3E_0$ . Note that in this figure linear scales are used in contrast to the lin-log presentations in Figs. 20 and 21 of ref. 2 or the log-log presentation in Fig. 6 of ref. 35.

by numerical calculations (e.g., Fig. 22 in ref. 2). In most low temperature applications, one usually works with a few thousand ions only for keeping the space charge induced potential below the mV level.<sup>14</sup>

#### Differences between $n = 2$ and $n > 2$ multipoles

Very special, and well described in text books<sup>19</sup> are quadrupolar fields, the analytical functions of which can be obtained from the eqns. (28) and (29) in ref. 2 by setting  $n = 2$ . There are many features which are exclusively valid for quadrupole geometries and which should not be extrapolated to higher order multipoles. First of all, the equation of motion can be solved without approximation by transforming it into the well-known Mathieu differential equation. Stable confinement or ion loss is determined, on a sound mathematical basis, by the two characteristic parameters  $a$  and  $q$  (called  $a_2$  and  $q_2$  in III B of ref. 2). If linear quadrupoles are used for mass selection they are operated usually close to  $(a, q) = (0.237\dots, 0.706\dots)$ .

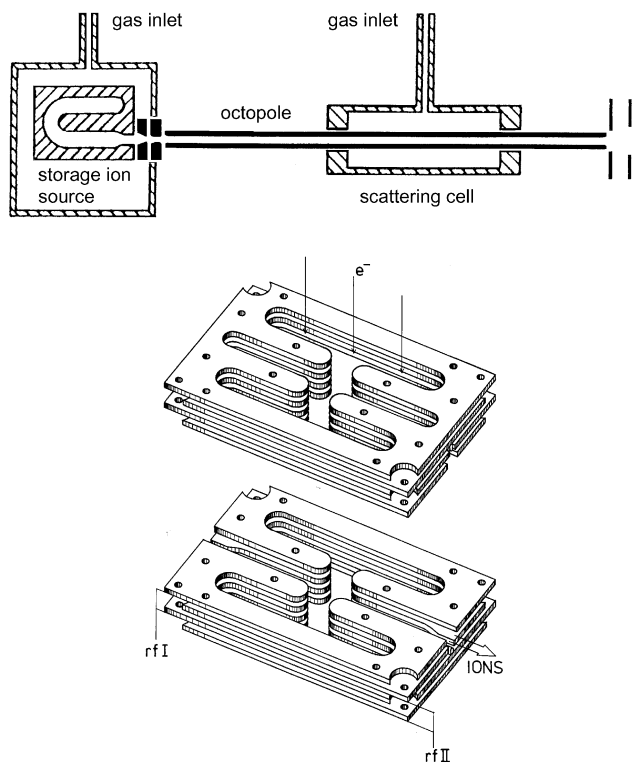
If one intends to use a quadrupole for storing or guiding ions, conservation of the kinetic energy is desirable, i.e., one should select the operating conditions such that  $\eta < 0.3$ . Inspection of eqns. 3 and 4 reveals that for  $n = 2$ , (i) the effective potential  $V^*$  is harmonic, (ii)  $\eta$  does not depend on  $r$  and (iii) one gets the identity  $q = \eta$ . These facts have important consequences such as focusing properties (in the sense of imaging, see Fig. 3) and phase space conserving transmission used, for example, in a photoionization source.<sup>18</sup> The harmonic effective potential also allows for resonant excitation with superimposed auxiliary fields, often called the notch filter mode, or for high mass resolution by recording the secular frequency of trapped nanoparticles.<sup>4</sup> Note that the left boundary of the Mathieu stability triangle,  $a = 1/2 q^2 - 7/128 q^4 + \dots$ , can be derived within the adiabatic approximation. Experimental tests have shown that quadrupoles can have an extremely high band pass mass resolution if one works with very slow ions (kinetic energies  $< 50$  meV) and at  $q < 0.1$ .<sup>18</sup> An example is the preparation of a proton beam with 95% transmission by simultaneously suppressing  $H_2^+$  by 10 orders of magnitude.<sup>20</sup> Also the shifted and very steep onset of  $CH^+$ , which is only indicated in Fig. 3 due to the linear scale, can be used to produce a very clean beam of  $C^+$ . Such a high suppression of the hydrogenated ion is needed for detecting the very few products produced by radiative association, e.g., of  $C^+$  and  $H_2$ .<sup>21</sup>



**Fig. 3** The focusing properties of a quadrupole are illustrated by projecting trajectories with three different starting angles onto the  $xz$  and  $yz$  planes.<sup>1,18</sup> Although the dc difference is very small ( $a = 0.000152$ ), the two frequencies differ significantly. The lower panel shows measured transmission efficiencies for  $C^+$  and  $CH^+$  ions through a focusing quadrupole as a function of the rf amplitude. The scales on top refer to the number of half cycles of  $C^+$  trajectories. Intensity maxima for  $C^+$  are obtained for  $(N_x, N_y) = (27, 4)$  and  $(29, 11)$ . Owing to its larger mass, the onset and the structure of the  $CH^+$  intensity is shifted relative to  $C^+$  to higher amplitudes.

Higher order multipoles, i.e.,  $n > 2$ , are very different from the quadrupole for a variety of reasons. Very important is that the stability parameter  $\eta$  does depend on  $r$  and it goes to zero in the limit of  $r \rightarrow 0$ . This means that the adiabatic approximation is the better the closer the trajectory gets restricted to the center line. Therefore, collisional relaxation becomes very efficient in hexa- and higher order multipoles! Another obviously important fact is that the effective potential becomes steeper with increasing  $n$ . Therefore, in many applications, the linear 22-pole guide is superior to the octopole. Some of the discussed features of an octopole are illustrated in Fig. 1. In the inner part of the guide, the ion moves rather unperturbed on straight trajectories. If the ion comes close to a rod or approaches one in a gap, the oscillatory motion is longitudinal or transverse, respectively. The trajectory remains restricted, a consequence of the adiabatic conservation of energy. Another adiabatic constant of the motion is the orbital angular momentum of the ion motion relative to the octopole axis, leading to the hole in the picture. For details, see ref. 2.

Although some authors have tried to find empirically stability diagrams for multipoles (see, for example, Fig. 14 in ref. 11, which shows an attempt to present an  $(a_3, q_3)$  diagram), numerically determined boundaries are most probably ill-defined. The question whether there is a general  $(a_n, q_n)$ -diagram, has been discussed in II.D.3 of ref. 2. So far, well-defined mass selective properties of multipole ion guides have been derived within the adiabatic approximation. The result can be expressed in analogy of the left boundary of the Mathieu  $(a, q)$  diagram,  $a_n = 1/n q_n$  where  $a_n$  and  $q_n$  are given by eqn. 65 of ref. 2. This means that one obtains, for  $U_0 > 0$ , a very sharp cut-off for masses larger than  $m_{\max} = qV_0^2/(\Omega^2 r_0^2 U_0)$ . It is certainly possible to operate multipoles at frequencies where for small masses the parameter  $\eta$  becomes so large that these ions are often excited by the rf field and finally lost. It is an open question whether one can use the



**Fig. 4** Schematic view of the first GIB instrument.<sup>3,23</sup> Inhomogeneous rf fields have been used for storing and thermalizing ions in the storage source as well as for guiding primary and product ions in the octopole (stainless steel rods,  $d = 1.4$  mm,  $r_0 = 2$  mm, length 24.3 cm). Note the location of the scattering cell (effective length 8.8 cm). A magnetic mass spectrometer and an electron multiplier were used to count both primary and product ions. Lower panel: labyrinth ion source used in the universal guided ion beam machine.<sup>1</sup> There are exits on both sides which have also been used to inject externally created ions for relaxation.

adiabaticity parameter  $\eta$  simultaneously as a stability parameter (*i.e.*, instability for  $\eta > 0.52\dots$ , see the example in Fig. 4 of ref. 2). Experimentally it has been shown that  $H^+$  can be suppressed efficiently while  $H_3^+$  is safely confined in the storage ion source if one operates at a frequency where  $\eta$  is just 0.3 for mass 3. This method may also be suitable in collision cell applications when one intends to eject low mass ions produced by CID. If, on the other hand, unwanted ions are converted in a collision cell into larger mass products by reactions, the superposition of a dc field can help to discriminate against them.

## Specific instruments

On the basis of the rf technique, which allows one to create two- and three-dimensional effective potential minima, a variety of innovative instruments has been developed. Many of these are dedicated to studying low energy collision dynamics but the confinement of ions by the effective potential has also been proved to be extremely useful in photofragmentation, photoionization, and ion spectroscopy, where one often needs elongated overlapping volumes between the ions and a laser beam, long interaction times or cold ions.

## Guided ion beams

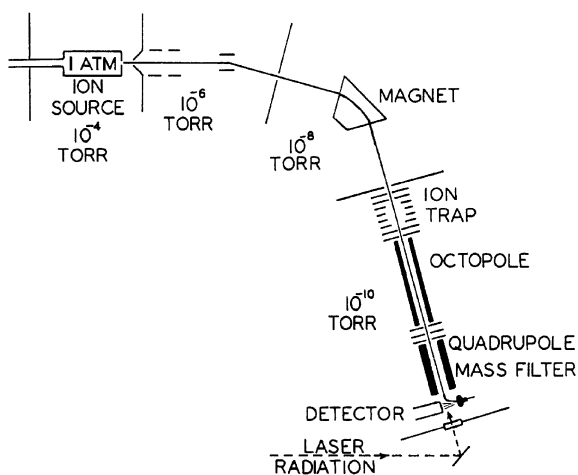
As was mentioned in the introduction, the use of rf fields for confining charged particles started about fifty years ago. One early published experimental study in which an rf quadrupole was used to guide an ion beam which was slow enough to observe the decay of metastable ions, was reported in the 1960s.<sup>22</sup> The first apparatus in which an octopole was used for

studying ion molecule reactions became operational thirty years ago.<sup>23</sup> The name *guided ion beam* technique (GIB) was introduced by M. Henschman<sup>24</sup> in an early review: a detailed description of this apparatus was published by Teloy and Gerlich.<sup>8</sup> This instrument has already demonstrated several outstanding capabilities of the GIB technique, including a wide range of collision energies, extreme sensitivity, and high accuracy for the determination of integral cross sections. For example, the cross section for the reaction,  $Ar^+ + D_2 \rightarrow ArD^+ + D$ , reported in ref. 8, became the reference standard for comparing absolute values determined with different ion beam experiments.

The first GIB apparatus, which is shown schematically in Fig. 4, had important features which are still of general importance for similar applications. In this case, ions were created by electron bombardment and for thermalization and phase space compression, a *U-shaped trap* and sufficiently high gas pressure was used. With a special lens electrode system the source could be operated in a pulsed mode. The geometry was such that ions were injected close to the center line of the octopole. For creating an intense and rather pure beam of rare gas ions or molecular ions such as  $H_3^+$ , no mass filter was required. A later version of such a storage ion source used in the *universal guided ion beam* machine<sup>1</sup> is shown in the lower panel of Fig. 4. Suitable trapping volumes, *e.g.* labyrinth like ones, can be formed by a stack of electrodes. There are situations where storage of the ions in the source has not only been used for relaxation but also for chemical suppression of unwanted species. An example (see fig. 39 in ref. 2) is the preparation of a very clean beam of  $^{12}C_2H_2^+$  ions. By adding hydrogen gas, ions such as  $^{12}C_2H^+$ ,  $^{13}C^{12}CH^+$  and  $^{12}C_2D^+$  have been almost completely eliminated *via* hydrogen abstraction reactions. As can be seen from Fig. 4, the length and the location of the scattering cell has been chosen such that most collisions occur in the middle part of the octopole and not in the entrance or exit transition regions. Using suitable apertures, distances and pumps, the influence of the two gases in the source and in the scattering cell can be minimized.

Combinations of ion guides with collision cells are now used routinely for measuring integral and differential cross sections at kinetic energies ranging from meV to keV.<sup>25–27</sup> By studying the onset of endothermic reactions and collision-induced dissociation of ions in the threshold region, the GIB method has been established as a reliable tool for getting thermochemical data.<sup>15,28</sup> One example, which is interesting in the context of this paper, is the endothermic charge transfer reaction of  $N^+ + N_2$ .<sup>29</sup> Interferences with traces of  $N_2^{2+}$  which were present in the  $m/q = 14$  *ule* beam have been detected in different ways and efficiently suppressed by the operating conditions of the ion source. Another example is the separation of primary and product ions in the resonant charge transfer  $^{40}Ar^+ + ^{40}Ar$  on the basis of their different velocities.<sup>30</sup> It is common to derive from endothermic cross sections such as  $N^+ + N_2$  or  $C^+ + H_2$ , measured with the guided ion beam technique or, with higher resolution, with the crossed and merged beam technique,<sup>3</sup> “thermal” rate coefficients for astrochemical applications<sup>31</sup> or calibrations of the “temperature” of ions stored in Paul traps.<sup>32</sup>

In many mass spectrometers, the ion source is operated at high pressure, whereas in the rest of the machine high and ultra-high vacuum is required. Fig. 5 shows an early version of a guided ion beam molecular ion spectrometer constructed in the 1970s in Berkeley.<sup>33</sup> In this instrument, an atmospheric pressure ion source was used to prepare weakly bound cluster ions. After passing a magnetic sector field, the ions were accumulated in a special trap made from a stack of plates alternately connected to opposite phases of an rf oscillator circuit. In order to avoid conservation of angular momentum (see Fig. 1) and for finally extracting the ions along the center line, a stadium like storage volume was used instead of circular



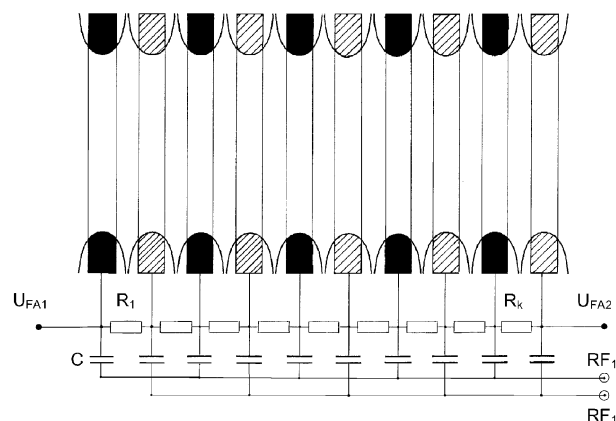
**Fig. 5** Molecular ion spectrometer developed in Berkeley.<sup>33</sup> This early construction of a tandem mass spectrometer, which was constructed for infrared fragmentation of cluster ions, illustrates the combination of a high pressure ion source with a ring electrode trap designed for ion accumulation and a long octopole, where the primary ions interact with the laser and which confines the photo-fragment ions.

holes. In the long octopole, finally, the ions interacted with a pulsed coaxial laser. The operating conditions of this ion guide were adjusted for efficient collection of all photo fragment ions.

### Multielectrode traps

The development of special multi-electrode temperature-variable rf traps with wide field free regions was motivated by the goal to construct an ion source with *in situ* phase space compression via inelastic buffer gas collisions, to study collision processes at very low energies, to produce internally cold ions for spectroscopy, and to synthesize specific ions at low temperatures which cannot be produced otherwise. Applications of low temperature ring electrode traps already have a rather long history: results measured with a liquid nitrogen cooled device have been reported by Gerlich and Kaefer.<sup>34</sup> Best tested is meanwhile the 22-pole trap, the effective potential of which increases with the 20th power towards the walls. The effective potential of the ring-electrode trap increases exponentially. A detailed comparison of these two traps can be found in a special article discussing its applications for studying radiative association (p. 1517 of ref. 35). One fundamental difference between rod and ring sets is that one has only one free scaling parameter for multipoles,  $r_0$ , while there are two independent ones for rings,  $r_0$ ,  $z_0$  (see Fig. 7 of ref. 2). For injection and extraction of ions, multipoles are superior since they have a field-free region close to the center line. During and after their injection into the trap, ions are usually cooled with an intense pulse of buffer gas, in most cases He.

With the exception of the dc entrance and exit electrodes, these traps have normally vanishing field components along the axis. However, there are applications where one needs axial acceleration, *e.g.*, for fast extraction of the ion cloud. In the 22-pole, a set of five thin electrodes is used to have some control over the axial potential (with sub-mV accuracy). They can be used to create very small potential wells or barriers. Also, mass selective ejection of ions is, in principle, possible by tuning the axial field to a harmonic potential and resonant excitation of oscillatory motions of ions. Better control of axial fields can be obtained with ring electrodes, as indicated in Fig. 6. Using a stationary potential gradient and gas, the rf trap can be operated like a drift tube. Superimposing fields with a specific time dependence, this device can be used for acceleration, deceleration, or compression. An interesting related rf device is the so-called electrodynamic ion funnel in which a series of ring electrodes of decreasing hole size is used in combination with



**Fig. 6** Rotationally symmetrical ring electrode trap. The indicated equipotential lines, which are defined in eqn. (34) of ref. 2, are approximated by a stack of plates the shape and dimensions of which can be taken from the graph. The capacitors and resistors indicate schematically the possibility of creating potential gradients in the axial direction or superimposing in a pulsed mode a suitable electric field for TOF-MS extraction.

both rf and dc potentials.<sup>36</sup> In the presence of gas, this combination improves the collection of ions. This is again an example of *phase space compression* in a trap: maybe the term funnel is somewhat misleading. A trapping configuration such as is shown in Fig. 5 is probably more efficient for ion gathering since those which turn around can come back again.

The combination of an rf ring electrode trap and a time-of-flight mass spectrometer (TOF-MS) has been described recently by Luca *et al.*<sup>37</sup> By simultaneously detecting the masses of all ions contained in the trap, the statistical errors are significantly reduced, especially in cases where many different masses are produced in the trap. Several strategies have been tested to transform the initial phase space volume, which is extremely small for low temperature multipole or ring electrode traps, to the acceptance of a suitable TOF detector. In conclusion, avoiding ion compression by pulses is recommended because of space charge effects. An alternative solution is to extract the ions from the whole storage volume by using suitable starting conditions, *e.g.*, by applying proper potentials to the electrodes shown in Fig. 6, and by imaging the trap content on a large position and time sensitive detector. Note that for these applications, buffer and reactant gases have to be introduced in a pulsed mode and, during extraction, the densities have to be already sufficiently low.

## Selected results

### Energy dependence of integral cross sections

It is not straightforward to identify reactions which can be used in ICP-MS collision cells for removing unwanted species or for transferring the isotope of interest to another mass, *e.g.*, by oxidation. Therefore, we give here only a few examples and a few hints have already been given above in the experimental section. A recent example which illustrates both the power of the technique and also the thermochemistry is the activation of  $\text{CH}_4$  by  $\text{Zr}^+$ , which has been studied in a guided ion beam mass spectrometer.<sup>28</sup> At energies below 1 eV, the only process observed is dehydrogenation, which is also slightly endothermic and which shows a strong isotope effect when  $\text{CD}_4$  is used. At higher energies products resulting from C-H cleavage processes become appreciable, while above 3 eV, formation of  $\text{ZrH}^+$  prevails. Note that such processes are not very efficient since the cross sections are all  $1 \text{ \AA}^2$  or smaller.

Another example illustrating the sensitivity of the GIB method and its application in anion chemistry (note that the effective potential depends on  $q^2$ ) is the exchange reaction

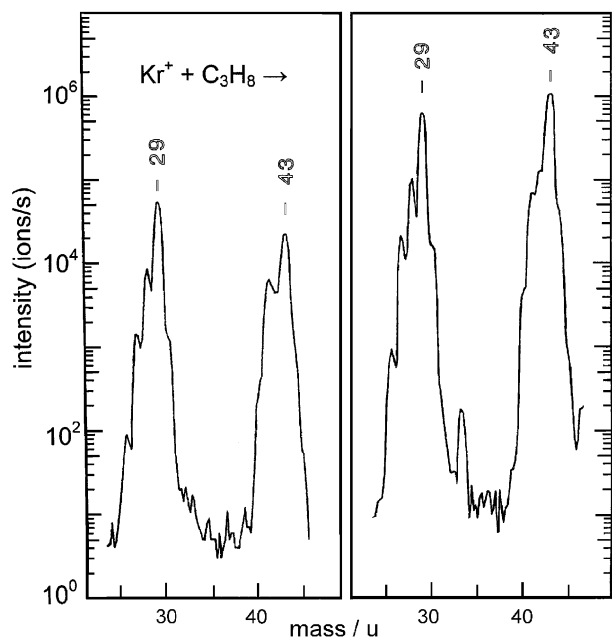
$H^- + D_2 \rightarrow D^- + HD$ .<sup>38</sup> Similar to the neutral analogue, this reaction is hindered by a barrier, the height of which has been determined experimentally. For this cross sections as low as  $0.01 \text{ \AA}^2$  were determined. The mentioned paper also describes a rather complicated ion beam-trapping machine where several modules have been assembled for specific purposes, *e.g.*, chemical probing of products from radiative association.

In general, it may be better for ICP-MS to use near thermoneutral reactions for chemical quenching. Operating at low energies usually avoids fragmentation and in many cases the cross sections steeply increase with decreasing energy. In order to illustrate this, Fig. 7 shows results from a  $Kr^+ + C_3H_8$  collision. These unpublished experiments have been performed for testing the potential of a universal GIB apparatus<sup>1</sup> for atmospheric trace gas analysis using electron transfer ionization. The gas sample used was 2000 ppm  $C_3H_8$  in  $N_2$ . At kinetic energies of  $E_1 = 0.15 \text{ eV}$  and higher, fragmentation prevails while operating the octopole at the lowest possible energy a significant increase of the signal is obtained.

### Temperature variable trapping experiment

Ion traps are also used in ICP-MS for removing interferences *via* high energy collisions,<sup>10</sup> *e.g.* based on collision induced dissociation or endothermic processes, but also using exothermic ion-molecule reactions under the collision conditions defined by the quadrupolar field. The results from our low temperature experiments may provide evidence that exothermic processes such as ternary association may lead to an additional improvement of the reaction cell based mass spectrometers. Selections of experimental results measured with ring electrode and 22-pole ion traps have been reviewed by Gerlich.<sup>14,39,40</sup>

Based on the process of laser induced reactions in a 22-pole ion trap, a sensitive experimental method has been developed for ion spectroscopy and state specific reaction dynamics.<sup>41</sup> For example, the H-atom transfer reaction  $C_2H_2^+ + hv_3 + H_2 \rightarrow C_2H_3^+ + H$  has been used to monitor the infrared excitation of acetylene ions. Vibrational excitation of the ions increases the

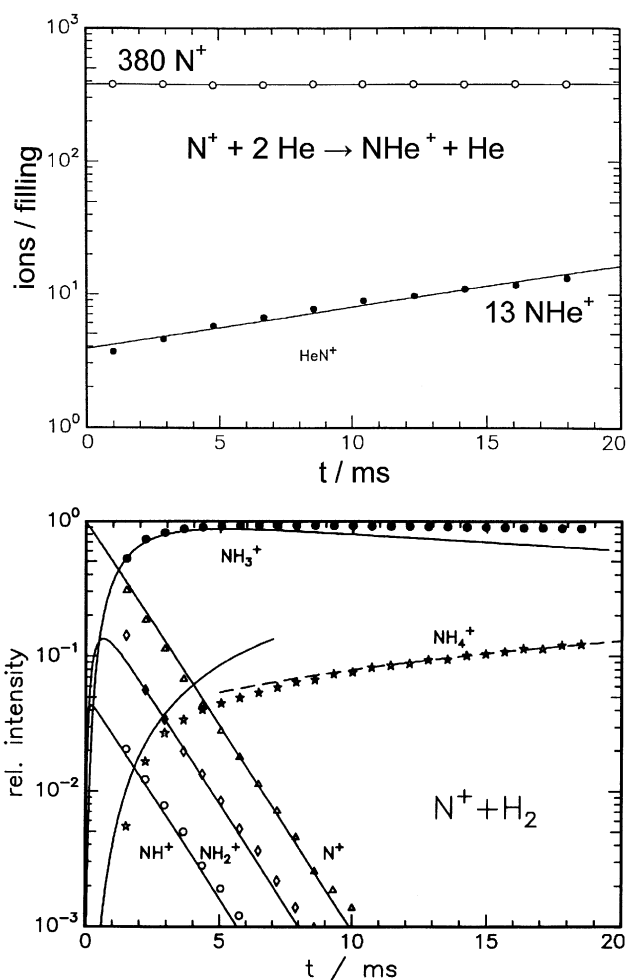


**Fig. 7** Chemical ionization of propane *via* electron transfer to  $Kr^+$  ions. The gas sample used was 2000 ppm  $C_3H_8$  in  $N_2$ . At a kinetic energy of  $E_1 = 0.15 \text{ eV}$  (left panel) mainly  $C_2H_5^+$  fragments are formed. Operating the octopole at the lowest possible energy a significant increase of the signal is obtained and less fragmentation (right panel). Under these conditions, collisions occur mainly at 300 K. In addition, trapping of some of the primary ions increases the residence time in the scattering cell and the reaction probability.

rate of the reaction by more than three orders of magnitude, while rotation slightly hinders the reaction. The same machine has been used to distinguish between the  $HCO^+$  and  $HOC^+$  isomers formed under conditions similar to interstellar clouds. In this case, chemical probing with a gas pulse containing either  $CH_4$  or  $NO$  has been used to separate the isomers and to determine the  $HOC^+ + H_2$  isomerization rate.<sup>42</sup>

Other examples demonstrating the outstanding sensitivity of the multi-electrode rf trap and the wide range of densities that it can be operated under, are the systematic studies performed on radiative and ternary association. One of the first studies was association of  $CH_3^+$  and  $CD_3^+$  in collisions with *n*- $H_2$ , *p*- $H_2$ ,  $D_2$  and  $He$  at 80 K.<sup>34</sup> The dynamics of the growth of hydrogen ion clusters and their deuteration has been reported in two papers by Paul *et al.*<sup>43,44</sup> A recently published example is the growth and fragmentation of  $(CO)_n^+$ , which was studied systematically as a function of temperature by Schlemmer *et al.*<sup>45</sup> The results gave direct hints that the formation of metastable isomers can be controlled by experimental parameters such as temperature or density of non-reactive buffer gas for cooling intermediate products.

Storage of an elemental ion,  $N^+$ , in a 22-pole ion trap at 15 K is illustrated in Fig. 8. The use of pure helium target gas at a



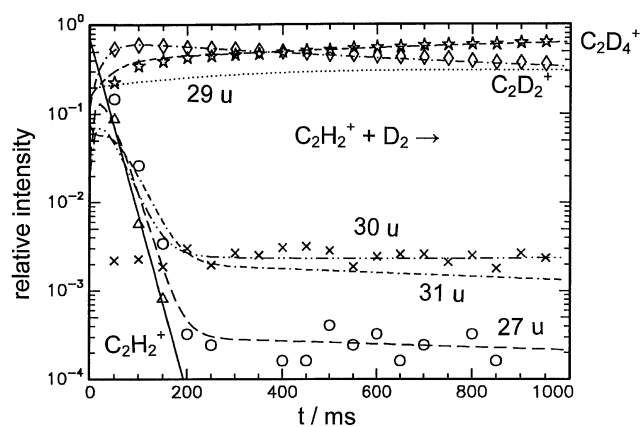
**Fig. 8** Reactions of  $N^+$  ions stored at 15 K in a 22-pole ion trap. Upper panel: ternary formation of  $NHe^+$  ions in collision with two He atoms. Despite the rather high number density of  $[He] = 1.9 \times 10^{15} \text{ cm}^{-3}$ , three-body association is very slow. In this experiment the apparent second-order rate coefficient is  $8.7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ . Lower panel: collisions with hydrogen ( $[H_2] = 1.4 \times 10^{13} \text{ cm}^{-3}$ ) convert  $N^+$  very quickly into  $NH_3^+$  *via*  $NH^+$  and  $NH_2^+$  intermediates. Finally the  $NH_3^+$  ions react to  $NH_4^+$ , but very slowly. The lines are solutions of a simplified rate equation approach. The deviations are due to the fact that the intermediate products are formed with internal and translational excitation.

rather high number density ( $[\text{He}] = 1.9 \times 10^{15} \text{ cm}^{-3}$ ) leads to almost no perturbation of the primary ions (upper panel). In 20 ms, of a total of 13  $\text{NHe}^+$  ions have been formed from 380  $\text{N}^+$  ions initially injected. From these numbers, an apparent second-order rate coefficient of  $8.7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$  can be calculated. The situation is completely different if one uses hydrogen (Fig. 8, lower panel). Although the number density was two orders of magnitude lower than the helium one ( $[\text{H}_2] = 1.4 \times 10^{13} \text{ cm}^{-3}$ ), and although the formation of  $\text{NH}^+$  is slightly endothermic, the  $\text{N}^+$  ions disappear so quickly that only  $10^{-3}$  of the initially injected ions are left after 10 ms. Already at 3 ms most ions have been converted into  $\text{NH}_3^+$  via sequential hydrogen abstraction. The reaction from  $\text{NH}_3^+$  to  $\text{NH}_4^+$  is, although exothermic, very slow. It is hindered by a barrier and, therefore, can occur only via tunnelling at low energies. For more details see ref. 40.

Stable isotopes of several elements, D,  $^{13}\text{C}$ ,  $^{15}\text{N}$  and others, have been detected in interstellar molecules, and it is known that isotope fractionation is an important reactive process at the low temperatures prevailing in dense interstellar clouds.<sup>46</sup> The H–D exchange in a collision between a hydrogen containing molecular ion and HD or  $\text{D}_2$  is usually exothermic due to a net gain in zero point energy. Isotopic rearrangement may also be used to reduce isobaric interferences with hydrogenated ions. In Fig. 9 two effects are illustrated, deuteration and ternary association. If acetylene ions,  $\text{C}_2\text{H}_2^+$ , are stored in deuterium at rather low density  $[\text{D}_2] = 5 \times 10^{10} \text{ cm}^{-3}$ , they are quickly converted into  $\text{C}_2\text{D}_2^+$ . The rate coefficient is close to the Langevin limit. In addition, these product ions are converted into  $\text{C}_2\text{D}_4^+$ , with a ternary rate coefficient of  $k_3 = 2 \times 10^{-24} \text{ cm}^6 \text{ s}^{-1}$ . Another recent result is the reaction and deuteration of  $\text{CH}_4^+$  ions in collisions with  $\text{H}_2$ , HD and  $\text{D}_2$ . A surprising negative temperature dependence has been observed in the experiment and significant isotope effects.<sup>47</sup>

### ICP-MS: a personal view

Basic information about the history, design, operation and application of inductively coupled plasma mass spectrometers (ICP-MS) can be found in several recent surveys ranging from ‘‘A Beginner’s Guide’’<sup>48</sup> via a tutorial review<sup>11</sup> to detailed information in the handbook of elemental speciation.<sup>9</sup> It is obvious, that ICP-MS is a powerful technique for (ultra)trace element determination. In recent years, the sensitivity of these instruments has been significantly improved by adding a ‘‘Collision and Reaction Cell’’ (CRC) or a ‘‘Dynamic Reaction



**Fig. 9** The mass of hydrogenated ions can be quickly changed by deuteration, especially at low temperatures. In this example acetylene ions,  $\text{C}_2\text{H}_2^+$ , are stored in deuterium at a rather low number density  $[\text{D}_2] = 5 \times 10^{10} \text{ cm}^{-3}$ . The conversion into  $\text{C}_2\text{D}_2^+$  occurs rather fast with a rate coefficient close to the Langevin limit ( $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ). In subsequent three-body reactions, these product ions are converted into  $\text{C}_2\text{D}_4^+$  with a ternary rate coefficient of  $k_3 = 2 \times 10^{-24} \text{ cm}^6 \text{ s}^{-1}$ .

Cell’’ (DRC). This new generation of instruments profits from the removal of spectral interferences, long associated with the ICP-MS, via inelastic or reactive collisions. In the CRC technology a gas filled rf-hexapole or –octopole is used while the DRC technology uses a quadrupole ion guide which can be operated in various mass selective modes. For example, unwanted species can be ejected via resonant excitation, such that they neither give rise to a signal in the mass spectrum nor take part in further reactions.<sup>11</sup> Also, an rf quadrupole ion trap is used in an elemental and isotopic ICP-MS instrument.<sup>10</sup> In this case resonant excitation is used for heating certain ions in the trap with the aim of dissociating molecular ions or initiating endothermic ion-molecule reactions. This instrument also employed an octopole ion guide and a collision cell. Both the ion trap and collision cell could be used to carry out chemical reactions to alleviate isobaric and polyatomic interferences.

### Critical evaluation

ICP-MS instruments are very complex systems and it seems to be impossible to understand all the developments and tricks used in elemental analysis. In such situations, improvements are often based on trial and error. Oversimplified models, which should describe the complicated influence of the various operating parameters, are also not very efficient in finding the optimal operating conditions of an individual instrument.

The simultaneous use of a quadrupole as ion cooler, reactor and mass selector is necessarily a compromise. It is not possible to operate a quadrupole simultaneously as a mass filter and as a guide of an ion beam with well-defined kinetic energy if the masses of interest are close to each other. A typical example is the use of non-adiabatic heating of  $\text{Zn}^+$  ions in a quadrupole filled with oxygen gas, reported by Hattendorf and Günther.<sup>12</sup> The increase of the  $q$ -value way above 0.3 certainly affects the kinetic energy of the  $\text{Zn}^+$  ions. Apparently they reach the several eV needed for forming the endothermic product  $^{66}\text{ZnO}^+$ . On the other hand, the lighter ions (including  $^{66}\text{Zn}^+$ ) already start to become unstable and get lost. A huge problem in such operational modes is the transfer of the ions emerging from the reaction cell to the detector since axial rf fields accelerate the ions in the transition region due to the focusing properties of quadrupoles (see Fig. 3). A better strategy for the DRC technology may be to operate the quadrupole within the adiabatic limit and to use resonant excitation of the secular motion (notch filter).

In general, it seems to be advisable to clearly separate in space or in time (e.g. in a trap) ion preparation, chemical reactions and detection. First one has to remove uncertainties in the kinetic and internal energy of the ions produced in the ICP configuration by thermalizing them in a suitable trap containing a non-reactive buffer gas such as He or Ne. In this way, one also becomes independent of the temperature and the electrostatic potential of the plasma. For making controlled use of endothermic reactions as the next step, the relaxed ions have to be accelerated by a defined potential difference to the desired kinetic energy  $E_1$  and injected into the collision cell, preferably a hexapole or octopole ion guide. A problem is that the transit time gets rather short and one may not get enough collisions to sufficiently eliminate the ions interfering with the elemental ion. A compensating increase of the number density is not always possible, especially if elastic and inelastic collisions lead to a widening of the phase space of the ion beam. If one intends to completely eliminate the perturbing ions without affecting the ions of interest, the useful properties of the guided ion beam method mentioned above are probably not really applicable in ICP-MS. A better strategy seems to be to use exothermic reactions at low energies or also at low temperatures.

## The potential of ion chemistry

It is a general question whether ion chemistry offers a strategy for monitoring heavy metals, toxic pollutants and radionuclides, to determine elements such as Fe, Ni, Co, Cu or Zn, Pb isotopes or to look for the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio in wine. How can one remove polyatomic molecules having the same mass as the elemental ions of interest? Examples mentioned in the literature are the efficient reactions  $\text{Ar}^+ + \text{H}_2 \rightarrow \text{Ar}^+ + \text{H}$  and  $\text{ArH}^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{Ar}$  which remove  $^{40}\text{Ar}^+$  interfering with  $^{40}\text{Ca}^+$  and  $^{38}\text{ArH}^+$  interfering with  $^{39}\text{K}^+$ . Hydrogen gas does not react with the potassium. Also, other Ar-containing molecular ions, such as  $\text{ArC}^+$ ,  $\text{ArO}^+$ ,  $\text{ArCl}^+$  and  $\text{Ar}_2^+$ , can be significantly suppressed by reactions with hydrogen, such that trace levels of Cr, Fe, As and Se can be accurately determined. Spectral overlap due to the occurrence of oxide ions may be avoided by converting them into a dioxide.

In addition to the usually used classes of ion–molecule reactions such as charge transfer, atom or proton transfer, or collision induced dissociation (see ref. 11) it is proposed here to use deuteration and, in contrast to general opinion, ternary association, predominantly with rare gases but also with hydrogen. The efficiency of deuteration in the case of hydrogenated molecules is obvious and easy to test. Rate coefficients for ternary association are strongly dependent on the number of degrees of freedom of the intermediate collision complex and they vary by many orders of magnitude from the atom–atom collision to large collision complexes. This means that the atomic ion can remain more or less unperturbed, while the polyatomic ions add much faster the target gas. Further growth to larger agglomerates can usually be controlled by choosing an adequate temperature. In this context it is interesting to note that many rate coefficients of ion molecule reactions change by several orders of magnitude, going from 300 K to 10 K.

## Conclusions

It has been shown in many applications that confinement of charged particles in oscillating fields allows one to construct very versatile tools and, due to their high sensitivity and the energy and temperature range, today's applications are not only restricted to fundamental ion–molecule reaction dynamics and spectroscopy but they extend into fields such as biology, aerosol research, astrochemistry and modern material science. An innovative development is the new nanoparticle mass spectrometer, which has a very high mass resolution in a mass range not accessible to any other existing techniques.<sup>4,17</sup>

There is no doubt that all this know-how and the technologies emerging in different applications can also be used to further improve the instrumentation in trace elemental analysis. This, however, requires a rather interdisciplinary effort and the development of new prototypes in research laboratories since the commercial systems are in general not flexible enough and usually used in routine work. From our experience, a promising solution is a temperature variable multipole trap, operated with suitable timing sequences and with pulsed valves (e.g., small pumps), and maybe with pulsed lasers and a TOF-MS. In addition to the reactions mentioned above, also electron–ion recombination may be used for primarily removing the polyatomic ions, a process well-known from interstellar chemistry.

It may be allowable to make final remarks relating to further developments of the use of rf fields. In applications such as ion–molecule reactions it is recommended that one works in the range of the validity of the adiabatic approximation;<sup>2</sup> however, more mathematical work is needed to explore other features of these devices and applications in mass selection or dedicated ion heating. Similar to the notch filter, the applicability of rf devices has been and can be further extended by adding other temporal or spatial varying fields. Also, the superposition

of a magnetic field could be very useful for mass specific resonant excitation, as can be seen from the versatility of ICR instruments.

## References

- 1 D. Gerlich, in *Electronic and Atomic Collisions*, eds. D. C. Lorents, W. E. Meyerhof and J. R. Peterson, Elsevier, Amsterdam, 1986, pp. 541–553.
- 2 D. Gerlich, *Adv. Chem. Phys.*, 1992, **82**, 1–176.
- 3 D. Gerlich, in *The Encyclopedia of Mass Spectrometry*, ed. P. B. Armentrout, Elsevier, 2003, pp. 182–194.
- 4 S. Schlemmer, S. Wellert, F. Windisch, M. Grimm, S. Barth and D. Gerlich, *Appl. Phys. A*, 2004, **78**, 629–639.
- 5 D. Gerlich, *Hyperfine Interactions*, 2003, **146**(147), 293–306.
- 6 P. Chen, *Angew. Chem. Int. Ed.*, 2003, **42**, 2832–2847.
- 7 D. J. Douglas and J. B. French, US Patent 4963736: *Mass spectrometer and method with improved ion transmission*, 1990.
- 8 E. Tely and D. Gerlich, *Chem. Phys.*, 1974, **4**, 417–427.
- 9 F. Vanhaecke and G. Köllensperger, in *Handbook of Elemental Speciation: Techniques and Methodology*, eds. R. Cornelis, H. Crews, J. Caruso and K. Heumann, Wiley, Chichester, 2003, pp. 281–312.
- 10 G. C. Eiden, C. J. Barinaga and D. W. Koppenaal, *J. Anal. At. Spectrom.*, 1999, **14**, 1129–1132.
- 11 S. D. Tanner, V. I. Baranov and D. R. Bandura, *Spectrochim. Acta, Part B*, 2002, **57**, 1361–1452.
- 12 B. Hattendorf and D. Günther, *Spectrochim. Acta, Part B*, 2003, **58**, 1–13.
- 13 L. D. Landau and E. M. Lifschitz, in *Theoretical Physics*, Pergamon, Oxford, 1960, vol. 1, p. 93.
- 14 D. Gerlich, *Phys. Scr.*, 1995, **T59**, 256–263.
- 15 P. B. Armentrout, *Int. J. Mass Spectrom.*, 2000, **200**, 219–241.
- 16 F. Zheng, X. Qu and E. J. Davis, *Rev. Sci. Instrum.*, 2001, **72**, 3380–3385.
- 17 S. Schlemmer, J. Illeemann, S. Wellert and D. Gerlich, *J. Appl. Phys.*, 2001, **90**, 5410–5418.
- 18 S. Mark, T. Glenewinkel-Meyer and D. Gerlich, *Phys. Chem.*, 1996, **15**, 283–298.
- 19 *Quadrupole Mass Spectrometry and its Applications*, ed. P. H. Dawson, Elsevier Scientific Publishing, Amsterdam, 1976.
- 20 D. Müller, Diplomarbeit, University of Freiburg, Germany, 1983.
- 21 D. Gerlich, in *Molecules and Grains in Space*, ed. I. Nenner, AIP Press, New York, 1994, 489–500.
- 22 H. Tatarczyk and U. von Zahn, *Z. Naturforsch.*, 1965, **20a**, 1708–1710.
- 23 D. Gerlich, Diplomarbeit, University of Freiburg, Germany, 1971.
- 24 M. Henschman, in *Ion-molecule Reactions*, ed. J. L. Franklin, Plenum, New York, 1972, vol. 1, 101–105.
- 25 S. Mark and D. Gerlich, *Chem. Phys.*, 1996, **209**, 235–257.
- 26 S. L. Anderson, *Acc. Chem. Res.*, 1997, **30**, 28–36.
- 27 F. Muntean and P. B. Armentrout, *J. Chem. Phys.*, 2001, **115**, 1213–1228.
- 28 P. B. Armentrout and M. R. Sievers, *J. Phys. Chem. A*, 2003, **107**, 4396–4406.
- 29 J. Glosik, A. Luca, S. Mark and D. Gerlich, *J. Chem. Phys.*, 2000, **112**, 7011–7021.
- 30 S. Pullins, R. A. Dressler, R. Torrents and D. Gerlich, *Z. Phys. Chem.*, 2000, **214**, 1279–1297.
- 31 D. Gerlich, R. Disch and S. Scherbarth, *J. Chem. Phys.*, 1987, **87**, 350–359.
- 32 M. Vedel, J. Rocher, M. Knopp and F. Vedel, *Int. J. Mass Spectrom. Ion Processes*, 1999, **190**(191), 37–45.
- 33 D. Gerlich, S. W. Bustamente, L. R. Carlson and H. S. Kwok, *Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Annual Report, LBL 8580*, 1978, pp. 331–332.
- 34 D. Gerlich and G. Kaefer, *Ap. J.*, 1989, **347**, 849–854.
- 35 D. Gerlich and S. Horning, *Chem. Rev.*, 1992, **92**, 1509–1539.
- 36 A. V. Tolmachev, T. Kim, H. R. Udseth, R. D. Smith, T. H. Bailey and J. H. Futrell, *Int. J. Mass Spectrom.*, 2000, **203**, 31–47.
- 37 A. Luca, S. Schlemmer, I. Cermak and D. Gerlich, *Rev. Sci. Instrum.*, 2001, **72**, 2900–2908.
- 38 E. Haufler, S. Schlemmer and D. Gerlich, *J. Phys. Chem.*, 1997, **101**, 6441–6447.
- 39 D. Gerlich, in *XVIII. International Conference on Physics of Electronic and Atomic Collisions*, eds. T. Andersen, B. Fastrup, F. Folkmann and H. Knudsen, AIP, New York, 1993, pp. 607–622.
- 40 D. Gerlich, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 2199–2208.

- 
- 41 S. Schlemmer, E. Lescop, J. von Richthofen, D. Gerlich and M. Smith, *J. Chem. Phys.*, 2002, **117**, 2068–2075.
- 42 M. A. Smith, S. Schlemmer, J. von Richthofen and D. Gerlich, *Astrophys. J. Lett.*, 2002, **578**, 87–90.
- 43 W. Paul, B. Lücke, S. Schlemmer and D. Gerlich, *Int. J. Mass Spectrom. Ion Process.*, 1995, **150**, 373–387.
- 44 W. Paul, S. Schlemmer, B. Lücke and D. Gerlich, *Chem. Phys.*, 1996, **209**, 265–274.
- 45 S. Schlemmer, A. Luca, J. Glosik and D. Gerlich, *J. Chem. Phys.*, 2002, **116**, 4508–4516.
- 46 D. Gerlich and S. Schlemmer, *Planet. Space Sci.*, 2002, **50**, 1287–1297.
- 47 O. Asvany, I. Savic, S. Schlemmer and D. Gerlich, *Chem. Phys.*, 2004, **298**, 97–105.
- 48 R. Thomas, *Spectroscopy*, 2002, **17**, 42–48.