International Journal of Mass Spectrometry 190/191 (1999) 145–151

A comparison of overtone and fundamental resonances for mass range extension by resonance ejection in a quadrupole ion trap mass spectrometer

Colin S. Creaser*, James W. Stygall[1]

Department of Chemistry and Physics, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK

Received 3 November 1998; accepted 9 February 1999

Abstract

Mass range extension in a quadrupole ion trap has been investigated using resonant ejection of ions at the fundamental secular frequency (ω_z) and at the Ω-ω_z overtone resonance frequency, where Ω is the drive rf angular frequency. The procedure is demonstrated for two commercial ion trap spectrometers operated at different drive rf frequencies. Higher rf amplitudes were required for ion ejection at low q_z values using the Ω-ω_z resonance than at the fundamental secular frequency, resulting in lower observed mass range enhancements for the Ω-ω_z resonance at the same rf amplitude. Resonance excitation tandem mass spectrometric experiments also show lower energy deposition for the Ω-ω_z resonance, although the effect is less marked at higher q_z values. (Int J Mass Spectrom 190/191 (1999) 145–151) © 1999 Elsevier Science B.V.

Keywords: Quadrupole ion trap; Resonance excitation; Mass range extension

1. Introduction

Resonance excitation is used widely in quadrupole ion trap mass spectrometry to manipulate ions held in stable trajectories and to eject ions from the device [1–4]. Excitation occurs when an auxiliary ac signal, applied to one or both of the endcap electrodes, has a frequency that exactly corresponds to a component of the secular frequency of an ion retained inside the trap. The secular frequency components in the axial direction (ω_z) are given by

$$\omega_z = (n + \beta_z/2)\Omega \qquad (1)$$

where Ω is the angular frequency of the rf drive potential [2], n is an integer, and β_z is determined by the working point of the ion within the stability diagram. In the absence of an applied dc component ($a_z = 0$), β_z is a function of q_z

$$q_z = 8eV/[m(r_o^2 + 2z_o^2)\Omega^2] \qquad (2)$$

where V is the amplitude of the rf drive potential, r_o and z_o are the trap dimensions, m is the mass of the ion, and e is its charge [2]. A number of approximations for the relationship between β_z and q_z have been proposed [3], but for the case where $q_z < 0.4$ (and $a_z = 0$), the contribution of higher harmonics may be ignored and β_z is related to q_z according to Eq. 3.

---

* Corresponding author. E-mail: colin.creaser@ntu.ac.uk

[1] Present address: Drug Discovery Disposition, Rhone-Poulenc Rorer, Rainham Road South, Dagenham, Essex RM10 7XS, UK.

Dedicated to J.F.J. Todd and R.E. March in recognition of their original contributions to quadrupole ion trap mass spectrometry.

PII S1387-3806(99)00022-6

$$\beta_z^2 = q_z^2/2 \quad (3)$$

When $n = 0$, the frequency corresponds to the fundamental frequency $\omega_{z,0}$ $[= (\beta_z\Omega/2)]$ and under these conditions an ion at the $\beta_z = 1$ boundary ($q_z = 0.908$) has a fundamental secular frequency of half the drive frequency applied to the ring electrode.

Resonance excitation is implemented either by tuning the auxiliary ac frequency to the axial component of the ions secular frequency at the appropriate q_z value, or by applying a fixed frequency and increasing the amplitude of the drive rf potential to bring ions into resonance successively. The latter approach is employed in the axial modulation method [5] for enhancing resolution in the mass instability scan, using an applied auxiliary frequency close to the $\beta_z = 1$ boundary of the stability diagram (typically 530 kHz for a drive frequency of 1.1 MHz). Applying the axial modulation at lower frequencies causes resonant ejection of ions at q_z values below the normal $\beta_z = 1$ boundary limit, which has the effect of extending the mass range of the trap for a given maximum amplitude of the rf drive potential [6–9]. Resonance excitation has also been employed in ion excitation for tandem mass spectrometry, ion isolation, and for fundamental ion trajectory studies [4,10–12].

The fundamental secular frequencies in the z and r directions (ω_z and ω_r) are, however, not the only frequency components for ions in stable trajectory (cf. Eq. 1). Vedel and others have used resonance excitation to identify axial frequency components of the type ω_z/n, $n\omega_z$, and $\omega_z + \omega_r$ (where n is an integer) and other linear combinations [13,14]. Linear and nonlinear resonances in a pure quadrupole ion trap and where there are superimposed higher order fields have also been identified [15]. These take the form of weak overtones with frequencies $\nu\Omega + n\omega_z$ and $\nu\Omega - n\omega_z$ (where ν and n are integers) that arise from combinations of the drive rf with the secular frequency. However, whereas the frequency spectrum for pure quadrupolar fields and quadrupolar fields with superimposed higher order components has been investigated both theoretically and experimentally [16–19], reported applications of ion ejection by resonance excitation have employed only the z component of the fundamental secular frequency (ω_z). In this article we report an experimental investigation of mass range extension by resonant ion ejection and collisional activation employing resonances with the ω_z and Ω-ω_z components of the secular frequency spectrum.

2. Experimental

Experiments were carried out using Finnigan ITMS (San Jose, CA) and Teledyne Discovery 2 (Los Gatos Circuits, TN) ion trap mass spectrometers. The ITMS was used in conjunction with the ICMS Ion Trap Software (Version 2.2, © University of Florida). Both instruments were operated using rf-only mass instability scanning with the drive rf frequencies at 1.1 MHz and 900 kHz, respectively. Ion isolation in tandem mass spectrometric experiments was carried out using rf–dc apex isolation at $q_z = 0.708$, with an applied dc voltage of -270 V. The ITMS was maintained at a temperature of 120 °C with helium as buffer gas at a pressure of 1.5×10^{-5} Torr as measured at the ionization gauge (uncorrected). Perfluorotri-*n*-butylamine was introduced into the vacuum chamber through a Megitt Avionics needle valve (Fareham, UK) at a partial pressure of $\sim 5 \times 10^{-6}$ Torr and ionized by electron ionization. The Teledyne trap was operated at a temperature of 100 °C and the helium buffer gas and perfluorotri-*n*-butylamine pressures were 4.0×10^{-5} and 5×10^{-6} Torr, respectively (uncorrected).

In a typical resonance excitation experiment, the low mass cutoff was set to eject ions of $m/z < 50$ and the instrument was calibrated using perfluorotri-*n*-butylamine with axial modulation applied. The auxiliary ac potential was then set to preselected values in the range ~100–900 kHz (6–24 V_{p-p}) for the Finnigan ITMS and ~100–600 kHz (1.2 V_{p-p} + 200 μV_{p-p}/DAC) for the Teledyne spectrometer. Voltages were measured at the balun circuit output. The perfluorotri-*n*-butylamine ions were ejected using a standard mass-instability scan in both cases (scan rate

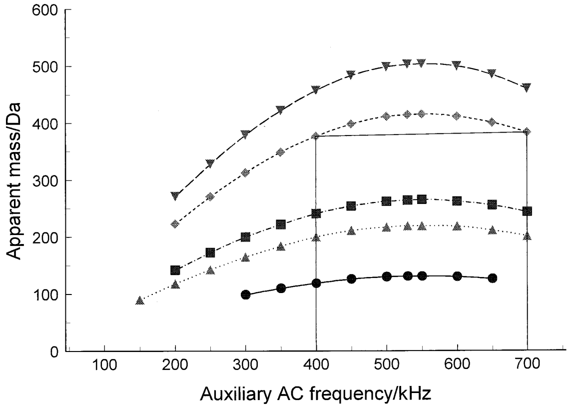

Fig. 1. Variation of apparent mass with applied auxiliary ac frequency (6 V_{p-p}) for the perfluorotri-*n*-butylamine ions at *m/z* 502 (upside down triangles), 414 (diamonds), 264 (squares), 219 (triangles) and 131 (circles) recorded using the Finnigan ITMS spectrometer ($\Omega = 1.1$ MHz).

5555 Da/s for the Finnigan ITMS and 12 000 DA/s for the Teledyne Discovery instrument) [20].

3. Results and discussion

The results for a resonant ejection experiment carried out on the Finnigan ITMS spectrometer are shown in Fig. 1. The data are presented in the form of a plot of auxiliary ac frequency applied to the endcap electrodes in dipolar mode (at an amplitude of 6 V_{p-p}) against "apparent mass"—the mass observed using the mass calibration for ion ejection with standard axial modulation. Mass range extension by resonant ejection is therefore reflected in a decrease in the apparent mass of the ion; the extended mass range being given by

$$\text{Extended mass range} = (m_{\text{ax}}/m_{\text{ap}}) \cdot M_R \qquad (4)$$

where m_{ax} is the mass of the ion calibrated using the axial modulation mode of operation, m_{ap} is the observed apparent mass, and M_R is the standard mass range of the ion trap.

The perfluorotri-*n*-butylamine ions at *m/z* 131, 219, 264, 414, and 502 all gave apparent masses that coincide with their true masses when the tickle frequency was set to 530 kHz, the normal value for axial modulation on the instrument. However, the apparent masses of all these ions decreased as the auxiliary ac frequency was reduced because the ions were ejected at lower q_z values. This corresponds to the normal mode of operation for mass range extension by resonant ion ejection in the ion trap [6]. Low mass ions with secular frequencies (ω_z) always greater than the applied auxiliary ac frequency were ejected at the $\beta_z = 1$ boundary ($q_z = 0.908$) during the rf scan as a result of mass instability rather than resonance ejection. These low mass ions were therefore observed close to their correct mass in the spectrum.

Increasing the auxiliary ac voltage frequency above 530 kHz also resulted in a decrease in the apparent mass of the perfluorotri-*n*-butylamine ions (Fig. 1), even though the fundamental secular frequencies of the ions are all less than half the drive rf frequency (550 kHz from Eq. 1 for the ITMS instrument). Resonant ejection at higher frequencies must arise from coincidence of the applied auxiliary frequency with a component of the frequency spectrum other than the fundamental frequency (ω_z) during the mass-instability scan. This is assigned to the Ω-ω_z component of the spectrum from the shape of the curves in Fig. 1. The relationship is illustrated in Fig. 2 for the spectra of perfluorotri-*n*-butylamine obtained by resonant ejection with applied auxiliary frequencies at 400 kHz and 700 kHz (amplitude 24 V_{p-p}). The apparent masses of the major perfluorotri-*n*-butylamine ions are very similar in these two spectra. For example, at 400 kHz (ω_z) the apparent mass of the *m/z* 414 ion is 375, and at 700 kHz (Ω-$\omega_z = 1100 - 400$ kHz) the apparent mass is 377 (see Fig. 1). The observed difference in the apparent mass is attributed to mass assignment errors associated with peak centroiding, which is affected by resolution and data acquisition rate, and to a slight delay in the time of ion ejection for the weaker Ω-ω_z resonance compared to the ω_z resonance.

The mass range extension archived at the auxiliary ac voltage amplitude of 6 V_{p-p} used in this resonance ejection experiment was significantly less for all of the perflourotri-*n*-butylamine ions using the Ω-ω_z frequency than for resonant ejection of ions at their

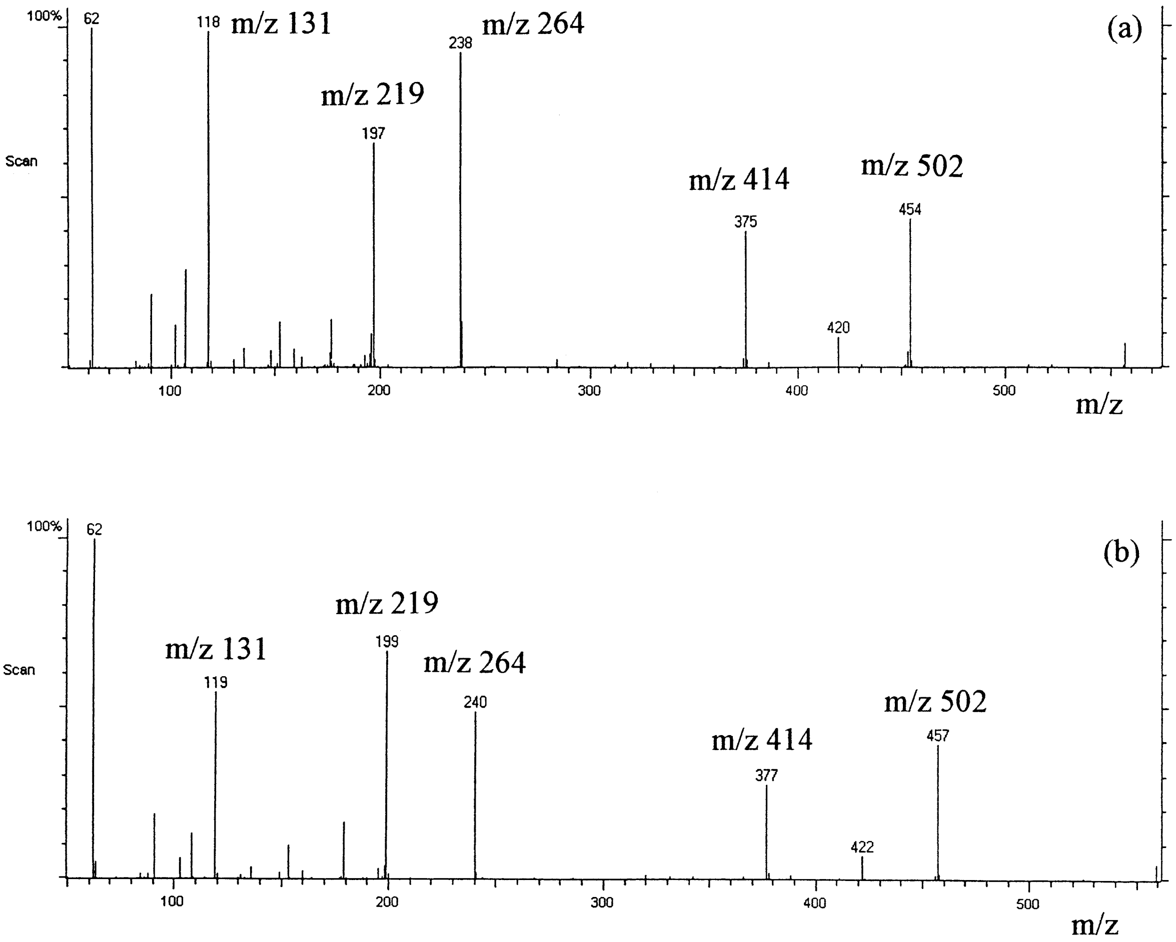

Fig. 2. Electron ionization mass spectra of perfluorotri-*n*-butylamine obtained by resonant ejection with applied auxiliary frequencies at (a) 400 kHz and (b) 700 kHz on the Finnigan ITMS instrument.

fundamental secular frequencies. This suggests that the Ω-ω_z band in the frequency spectrum is weaker than the secular frequency; an observation that is supported by both theoretical and experimental data for pure quadrupole traps and those containing superimposed higher order fields [15,16]. The range of frequencies leading to resonant ejection of perfluorotri-*n*-butylamine ions is restricted both at low and high auxiliary ac frequencies because the ions gain insufficient kinetic energy from the applied auxiliary field to exit the trap. The auxiliary ac amplitude required for resonant ejection of an ion is dependent upon the pseudopotential well depth at the q_z working point of the ion [3]. Higher amplitudes are required to eject ions with q_z values in the range 0.35–0.4 (e.g. *m/z* 131) than those with q_z values <0.2 and this determines the mass range extension possible under a given set of operating conditions.

The effect of increasing the auxiliary ac voltage amplitude to 24 V_{p-p} is shown in Fig. 3. Raising the amplitude of the auxiliary frequency increased the mass range extension at both ends of the applied frequency scale. The mass range increased from 1200 Da/charge at 200 kHz to above 1600 Da/charge for an applied ω_z frequency at 150 kHz, and from ~700 Da/charge to ~1200 Da/charge for the Ω-ω_z reso-

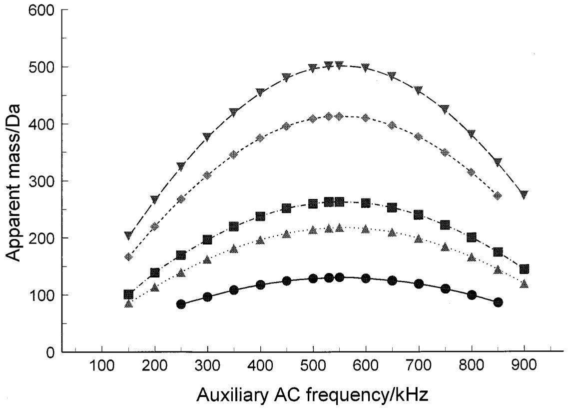

Fig. 3. Variation of apparent mass with applied auxiliary ac frequency (24 V_{p-p}) for the perfluorotri-*n*-butylamine ions at *m/z* 502 (upside down triangles), 414 (diamonds), 264 (squares), 219 (triangles) and 131 (circles) recorded using the Finnigan ITMS spectrometer ($\Omega = 1.1$ MHz).

nance at 900 kHz. Increasing the auxiliary voltage amplitude therefore has the same effect on mass range extension as that established for the fundamental secular frequency. It appears from these observations that resonant ejection using the $\Omega\text{-}\omega_z$ overtone is a viable alternative to ejection at the fundamental secular frequencies provided that the amplitude of the applied field is increased to compensate for the weaker overtone resonance.

A similar effect was observed in the MS/MS product spectra of the *m/z* 264 ion of perfluorotri-*n*-butylamine, obtained by collisionally activated dissociation with resonance excitation using the ω_z and $\Omega\text{-}\omega_z$ frequencies at a working point of $q_z = 0.344$ (corresponding to a low mass cutoff of *m/z* 100). A higher resonance excitation voltage amplitude was needed for the $\Omega\text{-}\omega_z$ resonance in order to dissociate the *m/z* 264 ion to the same extent as that obtained using the fundamental secular frequency. This is illustrated in Fig. 4, which compares the product ion spectra obtained using the ω_z resonance (137 kHz) at an auxiliary ac voltage of 380 mV [Fig. 4(a)] with that obtained using the $\Omega\text{-}\omega_z$ resonance (963 kHz) at an auxiliary voltage of 5760 mV [Fig. 4(b)]. In the latter case, an auxiliary voltage amplitude fifteen times higher is required for the $\Omega\text{-}\omega_z$ resonance in order to impart the same internal energy to the precursor ion. The effect is much less marked at a q_z of 0.688 (corresponding to a low mass cutoff of *m/z* 200), where auxiliary ac voltages of 400 mV (at 302 kHz) and 1250 mV (at 798 kHz) resulted in similar internal energy deposition. These observations are consistent with ion frequency measurements, where the strength of the $\Omega\text{-}\omega_z$ resonance as a proportion of ω_z has been shown to increase with increasing q_z [16].

The mass range extension experiments were repeated using the Teledyne spectrometer in order to confirm the resonant ejection observations under the normal operating conditions of an alternative instrumental configuration. The results of these experiments are shown in Fig. 5. Mass range extension was again

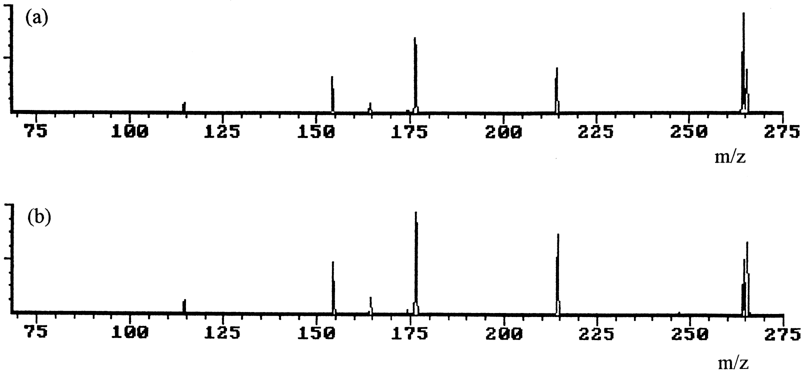

Fig. 4. Product ion tandem mass spectra obtained following resonance excitation of the *m/z* 264 ion of perfluorotri-*n*-butylamine at $q_z = 0.344$ using (a) the ω_z resonance at a tickle voltage of 380 mV and (b) the $\Omega\text{-}\omega_z$ resonance at a tickle voltage of 5760 mV.

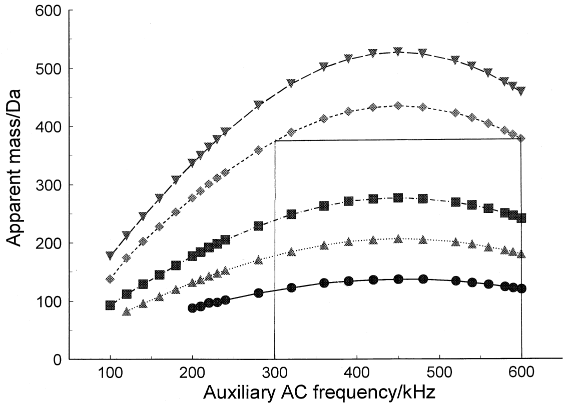

Fig. 5. Variation of apparent mass with applied auxiliary ac frequency (1.2 V_{p-p} + 200 μV_{p-p}/DAC) for the perfluorotri-*n*-butylamine ions at *m/z* 502 (upside down triangles), 414 (diamonds), 264 (squares), 219 (triangles), and 131 (circles) recorded using the Teledyne Discovery spectrometer ($\Omega = 900$ kHz).

observed both at low and high frequencies, but in this case the maxima for the apparent masses of the perfluorotri-*n*-butylamine ions are centered around 450 kHz, compared to 550 kHz in the ITMS experiment (Figs. 1 and 3). This shift is explained by the difference in rf drive frequency for the two instruments, since the normal operating frequency is at 900 kHz for the Teledyne and at 1.1 MHz for the ITMS, giving fundamental secular frequencies at the $\beta_z = 1$ boundary of the stability region of 450 kHz and 550 kHz, respectively. The frequencies at which the apparent masses are the same are therefore expected to be ω_z and 900-ω_z kHz for the Teledyne trap compared to ω_z and 1100-ω_z kHz for the ITMS spectrometer. This is observed for the data presented in Fig. 5. For example, similar apparent masses are detected at 300 kHz and 600 kHz for the perfluorotri-*n*-butylamine ions, and this coincidence is illustrated for the *m/z* 414 ion in Fig. 5. The assignment of the Ω-ω_z component of the frequency spectrum associated with resonant ejection of ions at higher frequencies is therefore confirmed by the frequencies at which the mass range extension is identical for the two spectrometers. As with the Finnigan spectrometer, a lower mass range enhancement was observed for the Ω-ω_z resonance than the fundamental secular frequency at the same resonance frequency voltage amplitude using the Teledyne instrument. Increasing the voltage sufficiently would be expected to result in a similar mass range extension to that observed in Fig. 3 for the Finnigan ITMS.

4. Conclusions

Resonant ejection of ions in a quadrupole ion trap has been investigated using resonance excitation with the fundamental secular frequency and with the Ω-ω_z overtone component of the frequency spectrum. Mass range extension is demonstrated using two commercial ion trap mass spectrometers operating at different drive rf frequencies, that establish the assignment of the overtone resonance. These experimental observations confirm that the Ω-ω_z component of the frequency spectrum may be used for mass range extension with performance characteristics that are similar to those obtained using the fundamental component of the secular frequency along the *z* axis, provided that the applied axial frequency amplitude is increased sufficiently. Other higher order components such as ω_z/n, $n\omega_z$, and $\Omega + \omega_z$ may also be suitable for resonance excitation experiments in ion traps with both linear and nonlinear fields.

Acknowledgements

We acknowledge financial support from Nottingham Trent University. The authors also wish to acknowledge the support and inspiration provided by Professors John Todd and Ray March over many years.

References

[1] J.N. Louris, R.G. Cooks, J.E.P. Syka, P.E. Kelly, G.C. Stafford, J.F.J. Todd, Anal. Chem. 59 (1987) 1677.
[2] R.E. March, J.F.J. Todd (Eds.), Practical Aspects of Ion Trap Mass Spectrometry, CRC, Boca Raton, 1995, Vol. 1.
[3] R.E. March, R.J. Hughes, Quadrupole Storage Mass Spectrometry, Wiley, New York, 1989.
[4] M. Splendore, F.A. Londry, R.E. March, R.J.S. Morrison, P.

Perrier, J. Andre, Int. J. Mass Spectrom. Ion Processes, 156 (1996) 11.

[5] J.E.P. Syka, J.N. Louris, P.E. Kelly, G.C. Stafford, W.E. Reynolds, U.S. Patent No. 4 736 101, April 1988.

[6] R.E. Kaiser, J.N. Louris, J.W. Amy, R.G. Cooks, Rapid Commun. Mass Spectrom. 3 (1989) 225.

[7] R.E. Kaiser, R.G. Cooks, G.C. Stafford, J.E.P. Syka, P.H. Hemberger, Int. J. Mass Spectrom. Ion Processes 106 (1991) 79.

[8] X. Wang, D.K. Bohme, R.E. March, Can. J. Appl. Spectrom. 38 (1993) 55.

[9] R.J. Strife, J.R. Simms, Int. J. Mass Spectrom. Ion Processes 124 (1993) 1.

[10] R.J. Strife, P.E. Kelly, M. Weber-Grabau, Rapid Commun. Mass Spectrom. 2 (1988) 105.

[11] R.L. Alfred, F.A. Londry, R.E. March, Int. J. Mass Spectrom. Ion Processes 125 (1993) 171.

[12] S.A. McLuckey, D.E. Goeringer, G.L. Glish, J. Am. Soc. Mass Spectrom. 2 (1991) 11.

[13] F. Vedel, M. Vedel, R.E. March, Int. J. Mass Spectrom. Ion Processes 99 (1990) 125.

[14] R.E. March, A.W. McMahon, F.A. Londry, R.L. Alfred, J.F.J. Todd, F. Vedel, Int. J. Mass Spectrom. Ion Processes 95 (1989) 119.

[15] J. Franzen, Int. J. Mass Spectrom. Ion Processes 130 (1994) 15.

[16] D.M. Eades, J.V. Johnson, R.A. Yost, Proceedings of the 41st ASMS Conference on Mass Spectrometry and Allied Topics, San Francisco, CA, May 1993, p. 693.

[17] S.A. Lammert, C.D. Cleven, R.G. Cooks, J. Am. Soc. Mass Spectrom. 5 (1994) 29.

[18] W. Mo, M.L. Langford, J.F.J. Todd, Rapid Commun. Mass Spectrom. 9 (1995) 107.

[19] R. Alheit, Th. Gudjons, S. Kleineidam, G. Werth, Rapid Commun. Mass Spectrom. 10 (1996) 583.

[20] G.C. Stafford, P.E. Kelly, J.E.P. Syka, W.E. Reynolds, J.F.J. Todd, Int. J. Mass Spectrom. Ion Processes 60 (1984) 85.