High Pressure Trapping in Fourier Transform Mass Spectrometry: A Radiofrequency-Only-Mode Event

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A new event for the Fourier transform mass spectrometry (FTMS) sequence is developed and demonstrated. During this event, called a radiofrequency (RF)-only mode event, the typical passive cubic trap of a Fourier transform mass spectrometer is made to operate as an active quadrupole ion trap. The transition between active and passive modes is developed so that ion loss as a consequence of the transition can be held to 15% or less. The adduct of the ion-molecule reaction of the 1,3-butadiene radical cation and methyl vinyl ether was detected during the RF-only-mode event at a helium pressure of $\sim 1 \times 10^{-3}$ torr even though this adduct is not detectable under standard FTMS operating conditions. (*J Am Soc Mass Spectrom* 1992, 3, 590-594)

Metastable is a problem word for Fourier transform mass spectrometry (FTMS) in at least two ways. First, the magnetron mode is metastable as described in Brown and Gabrielse [1]. This is seen by considering that the electric potential energy of the ion decreases faster than the magnetron kinetic energy increases when the magnetron radius increases. Thus any mechanism that removes energy from the ion's magnetron motion results in an increase of the magnetron radius. As an inevitable consequence, outward radial diffusion occurs because of ion-neutral collisions, with the ultimate result of ion loss [2] at long sequence times or high neutral pressures. McIver and co-workers [3] modeled radial diffusion with a detailed random walk for the magnetron-mode-amplitude distributions, whereas Dunbar et al. [4] described the outward movement of ions by making use of the solutions of Beauchamp's phenomenological equation [5].

The second way that *metastable* is a problem word for FTMS is that metastable adducts are not always observable in one of the main uses of FTMS; the study of ion-molecule reactions [6]. This is because buffer gas pressures cannot be made high enough to stabilize collisionally the reaction product before it fragments. The reaction of the 1,3-butadiene neutral and the vinyl methyl ether cation radical illustrates this point [7]. The adduct at m/z 112 is formed as a product and can be stabilized in a conventional chem-

ical ionization source, but the only evidence for its existence in FTMS is the fragments at m/z 80 and 97.

In this communication, we report the incorporation of a temporary dynamic trapping-mode event (RF-only-mode event) into the FTMS sequence [8, 9] to deal with metastability. During the event, outward radial diffusion is thwarted as demonstrated by the retention of benzene molecular ions when the trap is pressurized with He. Collisional stabilization of reaction products is achieved as demonstrated by the appearance of the m/z 112 adduct in the 1,3-butadiene-vinyl methyl ether system. Although the adduct ion can be seen in high pressure sector mass spectrometry, preselection of the reacting ion for more unambiguous interpretation is not possible in the sector mass spectrometer without the concatenation of another mass-selecting instrument. Concatenated double-focusing sector mass spectrometers have been used for the study of gas-phase ion-molecule reactions as originally described by Futrell et al. [10]. This is achieved with ease in FTMS by ejecting all but the desired reactant ion. The adduct at m/z 112 would also be observable in a three-dimensional radiofrequency quadrupole ion trap (QUISTOR) [11] that is pressurized with He.

The possibility for the RF-only-mode event in FTMS builds on a number of facts about dynamic traps such as the QUISTOR. The QUISTOR has stable behavior in a magnetic field as shown by Fischer [12]. Trap electrode shapes other than hyperboloids of revolution that are used in FTMS are expected to cause little difficulty because they work for the QUISTOR as was demonstrated by Wuerker et al. [13] for a cubic shape and Langmuir et al. [14] for a cylindrical shape. The

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QUISTOR stores ions at higher pressures with no difficulty, and collisions between ions and lower mass neutrals focus the ions in a QUISTOR toward the center of the trap as shown by Bonner et al. [15]. What are needed are efficient transitions to and from the RF-only-mode event in the FTMS sequence, and these were designed by taking advantage of the results of numerical calculation [8]. Numerical demonstration of pressure focusing during the FTMS sequence was also shown.

The QUISTOR had been used previously in overtly applied magnetic fields. Fischer [12] made use of a magnet field to increase the path length of the ionizing electrons. Dehmelt and co-workers [16] used a magnet field to make possible the observation of spin dependence in collision processes. In both works, the magnet induction (≤ 0.01 T) was weak relative to that used in the present research (1.2 T) and was rationalized as having only a small effect on ion motion.

There is a Mathieu stability diagram for each ion's motion in the trap center approximation for the cubic trap in FTMS. This is readily apparent in the zero pressure limit from the work of Fischer [12] in which the radial equations of motion are transformed into the Mathieu equation by using a coordinate transformation that rotates at the Larmor frequency of $qB/2m$. The transformation introduces the magnetic induction B into the stability constant a_r for the radial motion of an ion as shown in eq 1. The stability constant q_r for the radial motion is shown in eq 2.

$$a_r = \left(\frac{qB}{m\Omega} \right)^2 - \frac{8q\alpha V_T}{ma^2\Omega^2} \quad (1)$$

$$q_r = \frac{4q\alpha V_{\text{mod}}}{ma^2\Omega^2} \quad (2)$$

No change from what has been done for the QUISTOR is required for the treatment of the z component of the ion motion in FTMS. The z -mode stability constants a_z and q_z are shown in eqs 3 and 4.

$$a_z = \frac{16q\alpha V_T}{ma^2\Omega^2} \quad (3)$$

$$q_z = -\frac{8q\alpha V_{\text{mod}}}{ma^2\Omega^2} \quad (4)$$

The above equations have been adapted to the notation of Jeffries et al. [17] for the quadrupolar electric potential at the center of the cubic trap. Here, α is a geometric constant and has a value of 1.3869; q is the charge of the ion; B is the magnetic induction; m is the ion's mass; V_T is the constant portion of the voltage impressed on the two trapping plates; V_{mod} is the zero-to-peak amplitude of the sinusoidal modulation component impressed on the trapping plates; a is the length of the inside edge of the cubic trap; and Ω is the angular frequency of the modulation.

Unlike the superimposed diagrams always displayed for QUISTORS and quadrupole mass filters [11], the Mathieu stability diagrams for the z -mode

and radial motion in FTMS must be considered separately. This is because a_r has two zeros, whereas a_z has only one zero. In the radial stability diagram, the stability constant a_r is a quadratic function of $1/m$, whereas the stability constant q_r is a linear function of $1/m$. With only m changing, the operating point on the stability diagram traces out a parabola as shown in Figure 1a. The zeros of a_r occur when the mass is

Figure 1. Mathieu stability diagrams for (a) the radial motion and (b) the z motion during the RF-only-mode event. An expanded region of the origin is shown as an inset in each diagram. The loci of operating points for when only m/z varies are shown as thick lines for $V_{\text{mod}} = 1000$ V. The locus folds into the a axis in each diagram as the RF is turned off. The movement of an operating point for an arbitrarily chosen m/z during an adiabatic transition to and from the RF-only-mode event is represented by the dashed lines. The dotted line, whose slope matches that of the parabola at the origin in (a), shows the locus that would occur if B were taken to zero.

Figure 2. Mass spectra for the 1,3-butadiene neutral and the vinyl methyl ether radical cation reaction obtained by using (a) a sequence with a He pulse and RF modulation and (b) a sequence with no He or RF. The overall reaction delay was 3.6 s in both cases. An expanded view of the area around m/z 112 is shown in the insets.

infinite and when the mass is the critical mass. The critical mass m_c for the cubic trap [18] is shown in eq 5.

$$m_c = \frac{qB^2a^2}{8V_T\alpha} \quad (5)$$

In contrast to the radial stability diagram, the operating point in the z-mode stability diagram traces out a line through the origin (see Figure 1b) with only one zero for the stability constant a_z . The slope is 0.002 for the experiments described below. The slope is small, and "RF-only mode" is used as a name for the new event for this reason. Because of the difference between the number of zeros of the parabola and line locus of operating points, there seems to be no reasonable way to continuously deform one diagram to superimpose it on the other while matching the loci of operating points. For comparison, the operating point traces out a line in both the radial and z-mode stability diagrams for a QUISTOR.

There is a low mass limit, also, just as there is one for the operation of the QUISTOR. As the mass decreases, a_r and q , increase beyond the region of stability. In the limit of low amplitude modulation, the low mass limit is the mass for which the stability constant a_r is 1. At this point, Ω coincides with the frequency required to excite parametrically the radial motion of ion. This frequency is the trap-shifted cyclotron frequency minus the magnetron frequency. Parametric excitation was done previously in a hyperbolic trap [19]. For increasing modulation amplitudes, the operating point for a given mass moves horizontally across the diagram, possibly into a region of instability. Thus for higher modulation amplitudes, the low mass limit is increased. The low mass limit is m/z 39 for 1000 V modulation and the conditions used in the experiment below.

The RF-only-mode event was implemented by modulating the trap plates of a 1-V, 0.0254-m cubic trap at 1.2 T with a 1000-V, 1.1-MHz sinewave during the reaction delay interval of the sequence. The waveform was exponentially turned on and off with a time constant that was changeable from 30 μ s to 3 ms. During this interval, the cell could be pressurized with He to approximately 10^{-3} – 10^{-2} torr by opening for 1.3 s a Varian variable leak valve model 951-5100 with a solenoid (Varian Associates, Walnut Creek, CA). Pressure values are the uncorrected measurements from a Bayard-Alpert gauge.

The transition to and from the dynamic trapping mode was done without He present and was observed to be efficient for the benzene molecular ion as indicated by at most a 20% drop in peak amplitude when compared with the same experiment without the modulation. The RF was on for 50 ms, and the benzene pressure was 1×10^{-7} torr. Minimal ion loss pertains for transitions between the RF-only-mode and normal operation that occurred with time constants of 500 μ s or less with modulation amplitudes

ranging from 300 to 1000 V. The best result at 1000 V is a peak amplitude drop of only 6%, which occurred when transition time constants were near 500 μ s. For the longest mode transition time constant of 4 ms, the biggest drop of 30% occurred. For longer RF on times, the peak amplitude dropped until it was 40% at 11 s.

When He was pulsed to 1.4×10^{-3} torr, peak amplitudes first appeared when the RF was turned off 0.3 s after the leak valve was closed. The signal increased and maximized at 85% when the RF was turned off 2.3 s after the valve closing. In the same experiment, but without the RF modulation on the trapping plates, no ions were detected at any time after the leak valve was closed.

Formation of the adduct $C_7H_{12}O^+$ at m/z 112 was observed in the reaction of the 1,3-butadiene neutral and the vinyl methyl ether cation radical as shown in Figure 2a. 1,3-Butadiene and vinyl methyl ether were introduced at pressures of 1.6×10^{-7} and 3.7×10^{-7} Torr, respectively. The He was pulsed to 3.3×10^{-3} torr. The adduct peak amplitude is about 5% of the adduct fragment peak amplitude at m/z 80. In this experiment, the m/z 58 ion was selected by double resonance before the RF-only-mode event from ions generated with 15-eV electrons.

Normally, this adduct is not observed in FTMS and, as stated earlier, requires collisional stabilization in a conventional chemical ionization source for observation. In an identical experiment but without the RF modulation and the He pulse, there was no detected signal at m/z 112, as shown in Figure 2b. The m/z 80 peak height in Figure 2b is 1.31 times that of the corresponding peak in Figure 2a.

In addition to ion-molecular chemistry, we propose applications of the RF-only-mode event for ionization events, exact mass and high mass studies, and high pressure interfaces. For ionization, the RF-only-mode event might be used with a low frequency modulation to suspend microparticles in the FTMS trap for laser excitation. Muezelaar and co-workers [20] suspended 1- μ m particles in an electrodynamic balance for rapid heating by a laser. This approach may be appropriate for direct laser desorption of biological cells [21]. The RF-only mode may also be used to shape the ion cloud in the radial direction by pressure focusing as a preparatory step before subsequent operations in the FTMS sequence. This may prove to be important for exact mass measurement, which is affected by the magnetron mode amplitude distribution [22], and for high mass detection, which is degraded if the ion cloud is excessively large in the radial direction [23]. Finally, the RF-only-mode event may serve as an interface "across time" between the normal low operating pressure and other ion-producing methods that temporarily generate high pressures.

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