

- 3 F.M. Devienne, *Entropie*, 24 (1968) 35.
- 4 G.I. Gellene and R.F. Porter, *Acc. Chem. Res.*, 16 (1983) 200.
- 5 G.I. Gellene, D.A. Cleary and R.F. Porter, *J. Chem. Phys.*, 77 (1982) 3471.
- 6 G.I. Gellene and R.F. Porter, *Bull. Am. Phys. Soc.*, 29 (1984) 154; *High Temp. Sci.*, 17 (1984) 171.
- 7 K.P. Huber and C. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. IV, Van Nostrand Reinhold Company, New York, 1979.
- 8 J. Gray and R.H. Tomlinson, *Chem. Phys. Lett.*, 7 (1969) 523.
- 9 G.I. Gellene and R.F. Porter, *J. Chem. Phys.*, 79 (1983) 5975.
- 10 J.F. Garvey and A. Kuppermann, *Chem. Phys. Lett.*, 107 (1984) 491.
- 11 G. Herzberg, *Faraday Discuss. Chem. Soc.*, 71 (1981) 165.
- 12 J.D. Payzant, A.J. Cunningham and P. Kebarle, *Can. J. Chem.*, 51 (1973) 3242.
- 13 H.Z. Cao, E.M. Evleth and E. Kassab, *J. Chem. Phys.*, 81 (1984) 1512.
- 14 G.I. Gellene and R.F. Porter, *J. Phys. Chem.*, (Dec.) (1984).
- 15 B.W. Williams and R.F. Porter, *J. Chem. Phys.*, 73 (1980) 5598.
- 16 J. Ast, C.J. Porter, C.J. Proctor and J.H. Beynon, *Bull. Soc. Beograd*, 46 (1981) 135.
- 17 M. Durup, G. Parlant, J. Appell, J. Durup and J. Ozenne, *Chem. Phys.*, 25 (1977) 245.
- 18 K. Hirao, T. Fujikawa, H. Konishi and S. Yamabe, *Chem. Phys. Lett.*, 104 (1984) 184.

## COUPLING A QUADRUPOLE MASS SPECTROMETER AND A FOURIER TRANSFORM MASS SPECTROMETER

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### ABSTRACT

Experiments performed by the authors during the last year have demonstrated the feasibility of a new analytical instrument called a tandem quadrupole-Fourier transform mass spectrometer (QFT-MS). Ions made in the source of a quadrupole mass spectrometer are extracted and focused into a beam. The ion beam is then injected axially into a superconducting electromagnet where the ions are stored in an analyzer cell and detected by Fourier transform mass spectrometry (FT-MS).

The goal of this project is to combine the highly developed chromatographic and sample ionization features of a quadrupole mass spectrometer with the versatility and high mass resolution that is available with Fourier transform detection. High mass resolution is possible because differential pumping separates the ion source of the quadrupole mass spectrometer from the analyzer cell of the FT-MS instrument. A novel method is described for efficiently injecting ions axially into the solenoidal magnetic field.

The QFT-MS instrument has many features in common with triple quadrupole mass spectrometers but with QFT-MS, much higher mass resolution is possible. For example, a mass resolution of 140 000 is demonstrated for  $m/z$  78 ions produced by collision-induced dissociation of bromobenzene molecular ions.

### INTRODUCTION

Fourier transform mass spectrometry (FT-MS) utilizes advanced electronic techniques to achieve unmatched stability and mass resolution [1-4]. The operating principles of FT-MS are quite different from conventional quadrupole and sector mass spectrometers. There are no slits, flight tubes, high voltage power supplies, or electron multipliers needed. Instead, ions are trapped in an analyzer cell by a strong magnetic field and are detected by the image current induced by their cyclotron motion [5,6]. Two important features of FT-MS are that weak ion currents can be integrated for several seconds in the analyzer cell, and all ions can be detected simultaneously. In addition, a series of experiments, such as collision-induced dissociation and

laser photodissociation, can be performed on the *same* set of ions while they are stored in the analyzer cell [7–10]. Mass spectrometry experiments involving pulsed lasers can be readily performed by FT-MS because all ions formed by the laser are trapped in the analyzer cell and a complete mass spectrum can be obtained for each laser pulse [11–13].

In spite of the many advantageous features of FT-MS, it has not been widely accepted for analytical applications. One difficulty is that the mass resolution and detection sensitivity of the spectrometer decrease severely at pressures exceeding about  $10^{-6}$  Torr. Thus, a mass resolution of  $M/\Delta M$  500 000 at a pressure of  $1 \times 10^{-8}$  Torr decreases to just  $M/\Delta M$  1000 at  $5 \times 10^{-6}$  Torr. This makes it difficult to interface an FT-MS instrument to previously developed separation and ionization techniques, such as fast atom bombardment (FAB), gas chromatography (GC) and liquid chromatography (LC), because all of these present a large gas load to the mass spectrometer. Another problem is that the analyzer cell does not work properly if the ion density exceeds about  $10^6$  ions  $\text{cm}^{-3}$ . An excessive number of ions in the analyzer cell causes the cyclotron resonance signals to become distorted and makes it difficult to detect minor components in the presence of abundant ions at another mass [14–16].

In 1982, we began working on a new approach to overcome these limitations of conventional FT-MS instruments. It involves coupling a quadrupole mass spectrometer and a Fourier transform mass spectrometer so that the ion production region is separated from the ion detection region. Ions are formed in the source region of a quadrupole mass spectrometer and are injected into a Fourier transform mass spectrometer where they are trapped and detected. This idea arose from the realization that FT-MS is a versatile and sensitive means for detecting ions, but an alternative means was needed for producing the ions and handling the high gas loads associated with coupling a GC or LC to the mass spectrometer.

In this paper, we describe a "tandem quadrupole-Fourier transform mass spectrometer" (QFT-MS) that was built during the last year and has been operational for about six months. A novel means for guiding the ion beam from the quadrupole mass spectrometer to the FT-MS analyzer cell is described and recent results showing high mass resolution and injection efficiency are presented.

## EXPERIMENTAL

Figure 1 illustrates the concept of QFT-MS. Ions extracted from an ion source are injected into a first set of quadrupole rods (Q1) which can be operated in the rf-only or the rf/d.c. mode to transmit ions in a selected region of the mass spectrum. It functions as a bandpass filter having a

variable high mass and low mass cutoff. Unwanted ions are rejected by Q1 while the ions of interest are transmitted.

Next, the ion beam enters a second quadrupole mass filter (Q2) which is normally operated in the rf-only mode. The purpose of Q2 is to guide the ion beam through the intense fringing fields of the superconducting magnet. As the ions enter the homogeneous region of the magnetic field, they are decelerated and trapped in the FT-MS analyzer cell. Several methods have been used to decelerate the ions. A description and comparison of these will be presented in a separate paper when more definitive data have been obtained. Once the ions are trapped in the analyzer cell, FT-MS detection can be performed in the conventional manner.

In January 1983, construction of a prototype QFT-MS instrument began with the assistance of engineers from the Finnigan Corporation [17]. The instrument has been modified extensively since then. Presently, it consists of a model 4500 ion source and vacuum manifold made by Finnigan MAT (355 River Oaks Parkway, San Jose, CA). The source is evacuated by a turbomolecular pump and liquid nitrogen trap. The guiding quadrupole Q2, which was designed specially for this project, is constructed of stainless steel rods held in place by ceramic spacers. An elongated trapped ion analyzer cell having dimensions  $8.9 \times 3.8 \times 3.8$  cm is used to store the ions and detect them by FT-MS [18]. The cryomagnet was made by Oxford Instruments (Osney Mead, Oxford, Gt. Britain). It has a room temperature bore diameter of 15 cm and can be energized to a peak field strength of 7 T. The manifold containing the analyzer cell is pumped by a closed-loop liquid helium cryopump to a base pressure in the mid- $10^{-9}$  Torr range. A pressure gradient of 120 was measured between the source housing and the analyzer cell. The electronics and computer data system developed for FT-MS

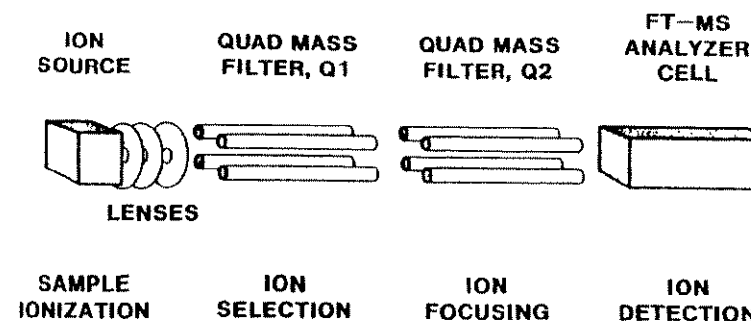


Fig. 1. Concept of QFT-MS. Ions produced by a quadrupole mass spectrometer are guided by a second quadrupole mass filter to an FT-MS analyzer cell where they are detected.

detection are now available as a commercial product from the IonSpec company (1 Longstreet, Irvine, CA).

The guiding quadrupole mass filter, Q2, is a key feature of this design because, without it, few ions would be able to pass to the FT-MS analyzer cell. The magnetic mirror principle, which is utilized in plasma physics for the containment of ionized gases, predicts that ions leaving the source of the quadrupole mass spectrometer (at a magnetic field strength of about 0.02 T) will be decelerated and reflected backwards as they approach the strong magnetic field (7 T) around the analyzer cell [19]. However, Q2 operated in the rf-only mode overcomes this problem because it focuses the ion beam and directs it precisely down the axis of the solenoidal magnet. The ions are not significantly decelerated by the magnetic mirror effect because they do not encounter the off-axis magnetic lines of force. We have modeled and studied the trajectories of ions in quadrupolar electric fields and inhomogeneous magnetic fields. The results of these calculations will be presented in a separate publication [20].

#### RESULTS AND DISCUSSION

An important goal for the QFT-MS instrument is to combine the best features of FT-MS and quadrupole mass spectrometry. Thus, the existing sample separation and ionization methods developed for quadrupole mass spectrometers could be utilized along with the high mass resolution available with FT-MS. With a properly designed vacuum manifold, the same GC and LC interfaces and FAB guns that are currently available on quadrupole mass spectrometers could be used with the QFT-MS. As improved interfaces are developed, they too could be readily adapted to the QFT-MS instrument because ample space is available in the region around the ion source. This is a cost effective approach because it eliminates the need to develop new types of interfaces suitable for the low pressure requirements of FT-MS.

All of these goals have not been realized with the prototype instrument, but the feasibility of injecting ions into the analyzer cell and detecting them at high mass resolution has been proven. The next six figures illustrate the level of performance achieved thus far with the prototype instrument.

Figure 2 is a plot of the ion current that reaches the FT-MS analyzer cell as the potential on a collector plate is varied. Both Q1 and Q2 were operated in the rf-only mode. The lower trace shows a maximum ion current of 280 pA when the FT-MS analyzer cell is withdrawn from the magnet by 2 m, while the upper trace shows that a much larger ion current, 1020 pA, is recorded, when the spectrometer is returned to its normal position where the FT-MS analyzer cell is in a field strength of 4.1 T. These results are opposite from what was expected. Apparently, Q2 is very effective in focusing the ion

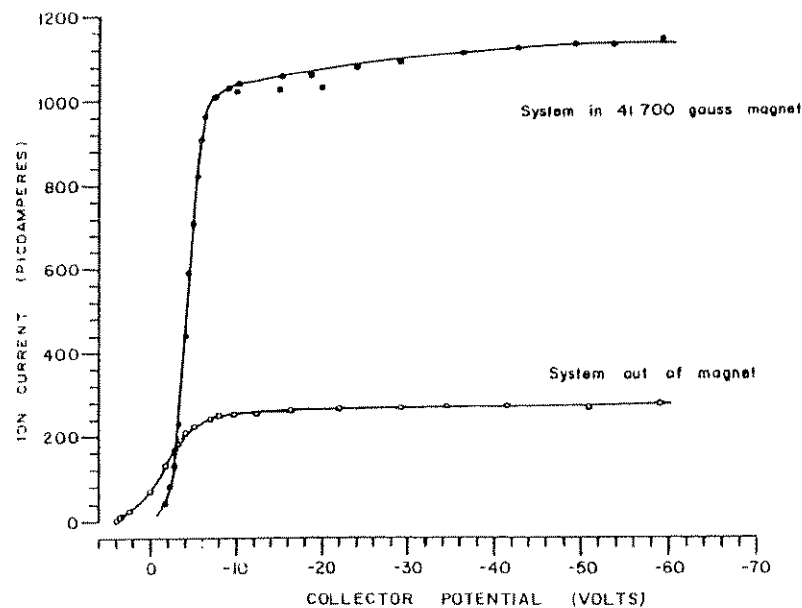


Fig. 2. Ion current transmitted to the analyzer cell as a function of the voltage applied to a collector plate of the cell.

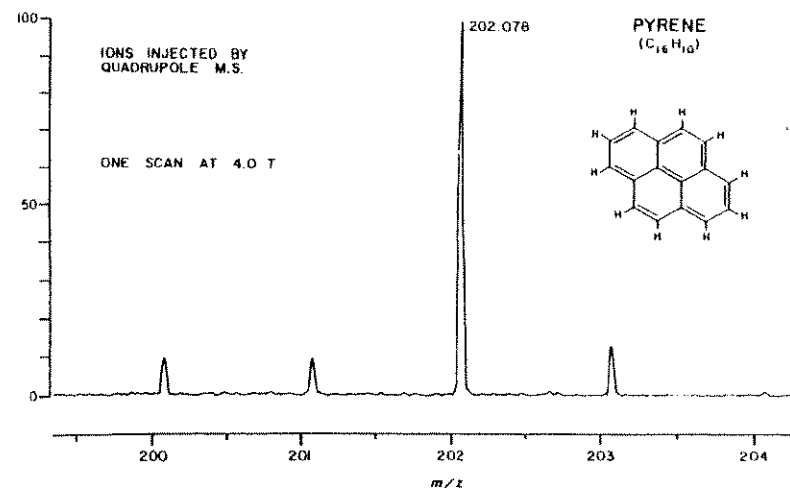


Fig. 3. FT-MS signals for pyrene ions injected by the quadrupole mass spectrometer into the analyzer cell.

beam so that it is not decelerated significantly by the magnetic mirror effect. In addition, the increases in ion current observed when the vacuum manifold is brought close to the magnet seems to be caused by collimation of the ion and electron beams in the ion source by the fringe fields of the magnet. Another important feature of Fig. 2 is the sharp drop in ion current at a retarding voltage of about  $-4$  V. This indicates that the energy distribution of the ion beam is not broadened appreciably by the rf fields and the magnetic mirror effect.

Mass spectra showing the molecular ion region of pyrene are shown in Figs. 3 and 4. Figure 3 is an expanded portion of a single acquisition from  $m/z$  185 to  $m/z$  215 for ions injected from the source of the quadrupole mass spectrometer into the analyzer cell. Notice that the peak at  $m/z$  203, the carbon-13 component of the pyrene molecular ion, has a relative abundance very close to the theoretical value of 17.8%. Even the peak at  $m/z$  204, the molecular ion with two carbon-13 atoms, is very close to its theoretical relative abundance of 3.0%.

Figure 4 shows excellent signal-to-noise and mass resolution from a single 20 kHz narrow-band scan for the pyrene molecular ion at  $m/z$  202. About 1  $\mu$ g of pyrene placed on the direct insertion probe of the quadrupole mass spectrometer gave a very stable ion signal for several minutes.

Figure 5 shows QFT-MS signals for coronene. Very strong signals were obtained, even with one FT detection cycle, when the probe in the quadru-

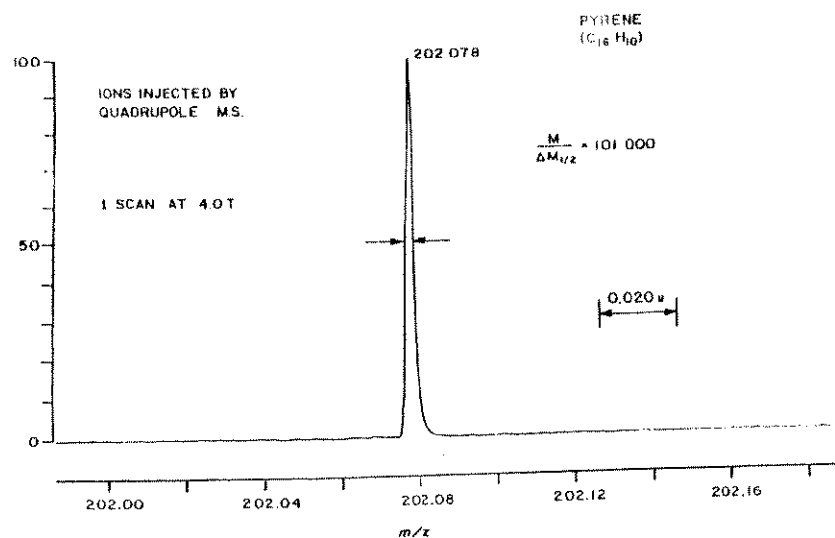


Fig. 4. High resolution QFT-MS signals for the molecular ion of pyrene.

pole was at  $140^{\circ}\text{C}$ . Notice that the relative abundance of the carbon-13 peak height at  $m/z$  301 is very close to its theoretical value of 26.6%. The elongated analyzer cell used in these studies seems to give better isotope ratios than a cubic cell used previously [18]. But with both cell designs, it is important to limit the number of ions in the analyzer cell to less than about  $10^6$ – $10^7$ . In our experience, ion space charge effects are the primary cause of incorrect isotope ratios.

Earlier, it was stated that the quadrupole rods could be used to select which ions are transmitted to the FT-MS analyzer cell. This is demonstrated in Fig. 6. The upper trace shows the intensity of the QFT-MS signal for  $m/z$  202 from pyrene at various mass settings for the quadrupole rf unit. The lower trace shows similar data for  $m/z$  300 from coronene. In these experiments, Q1 and Q2 were connected together and were operated in the rf-only mode. Both plots in Fig. 6 show that the quadrupole rods function as a bandpass filter for the ions. The transmission efficiency for  $m/z$  300 maximizes at a mass setting of about 300, but decreases at lower and higher settings. Similar behavior is seen for  $m/z$  202, but the maximum in the transmission curve is shifted to a mass setting of about 200.

Adding a differential d.c. voltage to the quadrupole rods narrows the bandpass and decreases the transmission efficiency, just as is expected for conventional quadrupole mass filters. When these experiments were first contemplated, it was feared that the intense magnetic field needed for FT-MS would interfere with the operation of the quadrupole mass filters.

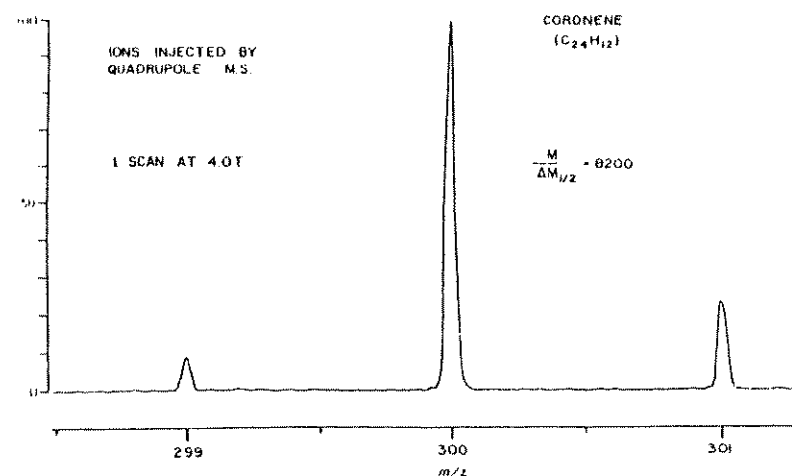


Fig. 5. QFT-MS signals for the molecular ion region of coronene.

Fortunately, this turns out not to be the case. The operating parameters for the quadrupole ion source are typical and it seems that the fringe fields of the cryomagnet have little effect on the ions. Thus, a desirable situation has been realized in that the operating parameters for the tandem instrument are very similar to those of the separate instruments. The guiding quadrupole not only passes ions efficiently from Q1 to the FT-MS analyzer, but it also separates the two analyzers sufficiently for them to be adjusted and optimized independently.

Figure 1 shows that the QFT-MS instrument is conceptually similar to a triple quadrupole mass spectrometer [21,22]. The main difference is that, in QFT-MS, mass analysis and ion detection are performed by a Fourier transform analyzer cell instead of a third quadrupole and an electron multiplier. Collision-induced dissociation of ions, a powerful means for obtaining structural information, is readily performed with a triple quadrupole mass spectrometer and similar experiments can also be done with the

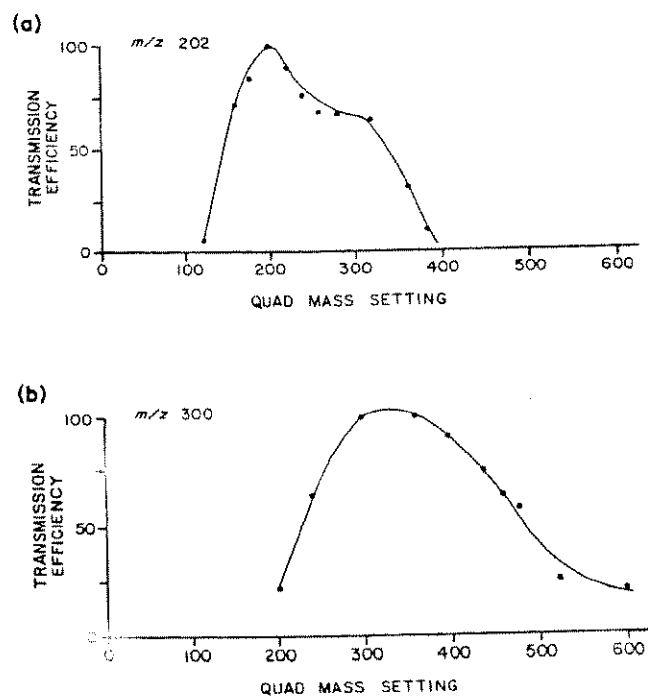


Fig. 6. Transmission efficiency for ions injected by the quadrupole mass spectrometer into the FT-MS analyzer cell. Both Q1 and Q2 were operated in the rf-only mode. (a) Injection of  $m/z$  202; (b) injection of  $m/z$  300.

QFT-MS instrument. Figure 7 is a mass spectrum of  $m/z$  77 daughter ions formed by collision-induced dissociation of bromobenzene molecular ions. Nitrogen collision gas was pulsed into the manifold for 100 ms using an automobile fuel injector valve. The mass resolution shown in Fig. 7 is 140 000, over a thousand times better than can be achieved in daughter ion mass spectra recorded with triple quadrupole or sector MS/MS instruments [21-23].

In 1974, Smith and Futrell built a tandem mass spectrometer by coupling a Dempster mass analyzer with an ion cyclotron resonance (ICR) cell [24]. Subsequently, a similar instrument was constructed by Kemper and Bowers [25,26]. Both of these had high pressure ion sources and the ions were mass analyzed by magnetic deflection prior to being injected into the ICR analyzer cell. Fourier transform detection has not been performed with these instruments but, in principle, it is possible. Comparing the QFT-MS and tandem Dempster-ICR instruments, it appears that the QFT-MS concept will be more useful for analytical applications because it uses a high-field cryomagnet instead of a conventional electromagnet with pole caps. This not only provides higher mass resolution and ion trapping efficiency, but also allows greater access around the ion source of the quadrupole for coupling various interfaces.

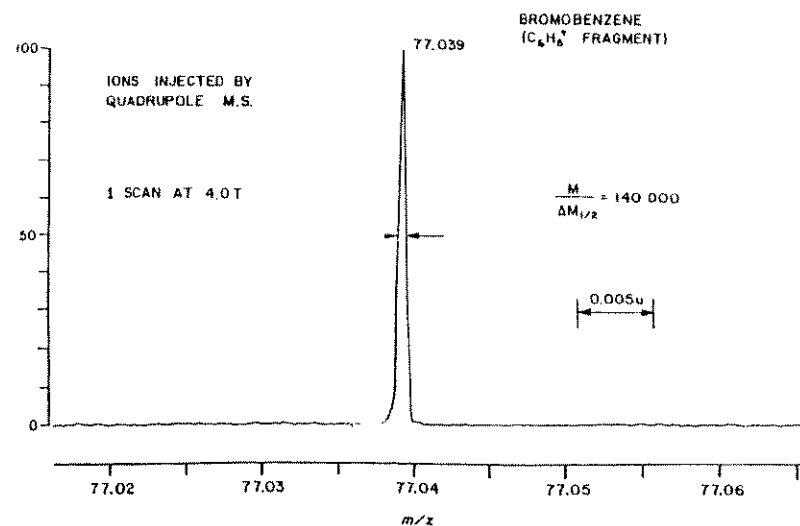


Fig. 7. Demonstration of MS/MS capabilities of the QFT-MS instrument. Daughter ions  $m/z$  77 were produced by collision-induced dissociation of bromobenzene molecular ions by a pulse of  $N_2$  collision gas.

An important use of the quadrupole rods in QFT-MS is to control the number of ions which are delivered to the FT-MS analyzer cell. In particular, ions such as the abundant glycerol peaks in FAB and the solvent cluster ions in LC would greatly overload the analyzer cell and causes space charge distortion of the FT signals. By pre-selecting which ions are passed to the analyzer cell, space charge effects can be minimized and the full dynamic range of the image current detector can be used for the ions of interest. Also, differential pumping in QFT-MS provides a low pressure in the FT-MS analyzer cell so that weak ion currents can be integrated for several seconds until a sufficient number of ions are accumulated for performing structure elucidation experiments utilizing laser photodissociation and collision-induced dissociation.

#### CONCLUSIONS

Preliminary results with QFT-MS are encouraging. The feasibility of injecting and detecting ions at high resolution has been demonstrated and it is clear that the quadrupole is capable of passing large ion currents to the FT-MS analyzer cell.

All our experiments with the prototype instrument have been conducted with a needle valve for adding liquid samples and a direct insertion probe for solids. The prototype instrument does not have a sufficient pumping capacity to handle a FAB gun or LC inlet, but appropriate modifications to the manifold will be made during the coming months so that these experiments can be attempted.

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#### REFERENCES

- 1 M.B. Comisarow and A.G. Marshall, *Chem. Phys. Lett.*, 25 (1974) 282.
- 2 C.L. Wilkins, *Anal. Chem.*, 50 (1978) 493A.
- 3 R.T. McIver, Jr., *Am. Lab.*, 12 (11) (1980) 18.
- 4 C.L. Wilkins and M.L. Gross, *Anal. Chem.*, 53 (1981) 1661A.
- 5 M.B. Comisarow, *Int. J. Mass Spectrom. Ion Phys.*, 26 (1978) 369.
- 6 R.T. McIver, Jr., R.L. Hunter, E.B. Ledford, Jr., M.J. Locke and R.J. Francl, *Int. J. Mass Spectrom. Ion Phys.*, 39 (1981) 65.
- 7 R.T. McIver, Jr. and W.D. Bowers, in F.W. McLafferty (Ed.), *Tandem Mass Spectrometry*, Wiley, New York, 1983.
- 8 R.B. Cody and B.S. Freiser, *Int. J. Mass Spectrom. Ion Phys.*, 41 (1982) 199.
- 9 R.L. White and C.L. Wilkins, *Anal. Chem.*, 54 (1982) 2211.
- 10 M.P. Irion, W.D. Bowers, R.L. Hunter, S. Delbert, F.S. Rowland and R.T. McIver, Jr., 31st Annu. Conf. Mass Spectrom. Allied Top., Boston, MA, 1983, Paper WOD 1.
- 11 R.B. Cody, R.C. Burnier, C.J. Cassidy and B.S. Freiser, *Anal. Chem.* 54 (1982) 2225.
- 12 M.P. Irion, W.D. Bowers, R.L. Hunter, F.S. Rowland and R.T. McIver, Jr., *Chem. Phys. Lett.*, 93 (1982) 375.
- 13 T.J. Carlin and B.S. Freiser, *Anal. Chem.*, 55 (1983) 955.
- 14 T.J. Francl, M.G. Sherman, R.L. Hunter, M.L. Locke, W.D. Bowers and R.T. McIver, Jr., *Int. J. Mass Spectrom. Ion Processes*, 54 (1983) 189.
- 15 E.B. Ledford, S. Ghaderi, R.L. White, R.B. Spencer, P.S. Kularni, C.L. Wilkins and M.L. Gross, *Anal. Chem.*, 52 (1980) 463.
- 16 R.L. White, E.C. Onyiriuka and C.L. Wilkins, *Anal. Chem.*, 55 (1983) 339.
- 17 R.T. McIver, Jr., R.L. Hunter, M.S. Story, J. Syka and M. Labunsky, paper presented at 31st Annu. Conf. Mass Spectrom. Allied Top., Boston, MA, 1983.
- 18 R.L. Hunter, M.G. Sherman, R.T. McIver, Jr., *Int. J. Mass Spectrom. Ion Phys.*, 50 (1983) 259.
- 19 F.F. Chen, *Introduction to Plasma Physics*, Plenum Press, New York, 1974, pp. 27-29.
- 20 R.T. McIver, Jr., unpublished work, 1982.
- 21 R.A. Yost and C.G. Enke, *Anal. Chem.*, 51 (1979) 1251A.
- 22 F.W. McLafferty (Ed.), *Tandem Mass Spectrometry*, Wiley, New York, 1983.
- 23 G.L. Glish, S.A. McLuckey, T.Y. Ridley and R.G. Cooks, *Int. J. Mass Spectrom. Ion Phys.*, 41 (1982) 157.
- 24 D.L. Smith and J.H. Futrell, *Int. J. Mass Spectrom. Ion Phys.*, 14 (1974) 171.
- 25 P.R. Kemper and M.T. Bowers, in H. Hartmann and K.-P. Wanczek (Eds.), *Ion Cyclotron Resonance Spectrometry, Lecture Notes in Chemistry*, Vol. 31, Springer, Berlin, 1982, p 308.
- 26 P.R. Kemper and M.T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, 52 (1983) 1.