APPLICATIONS OF FOURIER TRANSFORM ION CYCLOTRON RESONANCE SPECTROMETRY TO GAS PHASE IONIC PROCESSES

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Abstract:

The applications of a recently built Fourier Transform ion cyclotron resonance spectrometer are illustrated in this article. Present studies at the Institute of Chemistry in São Paulo include: (a) the use of the high resolution capability to distinguish ions of different chemical composition but of the same nominal m/q; (b) the use of the ion trapping properties to study the kinetics of ion/molecule reactions; (c) the study of negative ion/molecule reactions of fundamental interest to organic chemistry; and (d) the ability to undertake photodissociation spectroscopy as a means to probe the electronic spectra of ions.

1. INTRODUCTION

Fourier Transform ion cyclotron resonance spectrometry (FT-ICR), also known as Fourier Transform Mass Spectrometry (FT-MS), has found many applications in static and dynamic gas phase ionic processes since 1974 [1]. Ions are identified in this technique by their m/q relationship through the measurement of their cyclotron frequency in an homogeneous magnetic field.

$$\omega = (q/m)B$$

This is experimentally accomplished in FT-ICR by exciting the cyclotron motion of the ions with a burst of radiofrequency which is rapidly scanned through the frequencies of the ions of interest (typically between 10 kHz and 5 MHz). It is thus possible to excite coherently all ions independent of their m/q relationship. The orbiting of the ions close to the plates of a typical cubic cell induces an image current which decays in time due to ion-neutral collisions and to dephasing of the coherent motion. The transformation of the image current from the time domain to the frequency domain results in a mass spectrum with the Fellgett advantage [2].

An important feature of FT-ICR is the ability to trap ions for as long as seconds when the pressure is low (typically 10^{-8} Torr) and Coulumb repulsions are minimized. Time resolved experiments on the dynamics of ions can then be routinely carried out if the formation of ions is pulsed rather than continuous. Under these conditons, it is also possible to carry out elaborate sequences where specific ions are isolated, allowed to react and the product ions further re-isolated and investigated by their reactivity [3].

2. FT-ICR SPECTROMETER

The basic design of the FT-ICR spectrometer built at the Institute of Chemistry of the University of São Paulo has been recently described in detail[4]. A 9" field stabilized electromagnet is set typically at either 1.0, or 1.25 T depending on the experiment. The system is pumped by a Balzers 240 l s^{-1} turbo molecular pump and after repeated baking the background pressure reaches 3×10^{-9} Torr as measured with an ion gauge. The dimensions of the magnet pole caps and vacuum chamber have restricted our initial work to cells of cubic geometry of 2.54 cm by side. Ions are formed in this cell by electron bombardment from a heated rhenium filament held in position by a machinable insulating ceramic block (Figure 1).

The spectrometer has been interfaced to an IonSpec (Irvine, California) Data System which controls the time sequence of events, the acquisition of the transient currents and performs the Fourier transformation. In this system, ions can be excited by either a rapid digital scan of a frequency synthesizer (chirp) or by a narrow (less than 1 us) high voltage pulse (impulse excitation).

3. PRESENT APPLICATIONS IN OUR LABORATORY

3.1 High resolution mass spectrometry

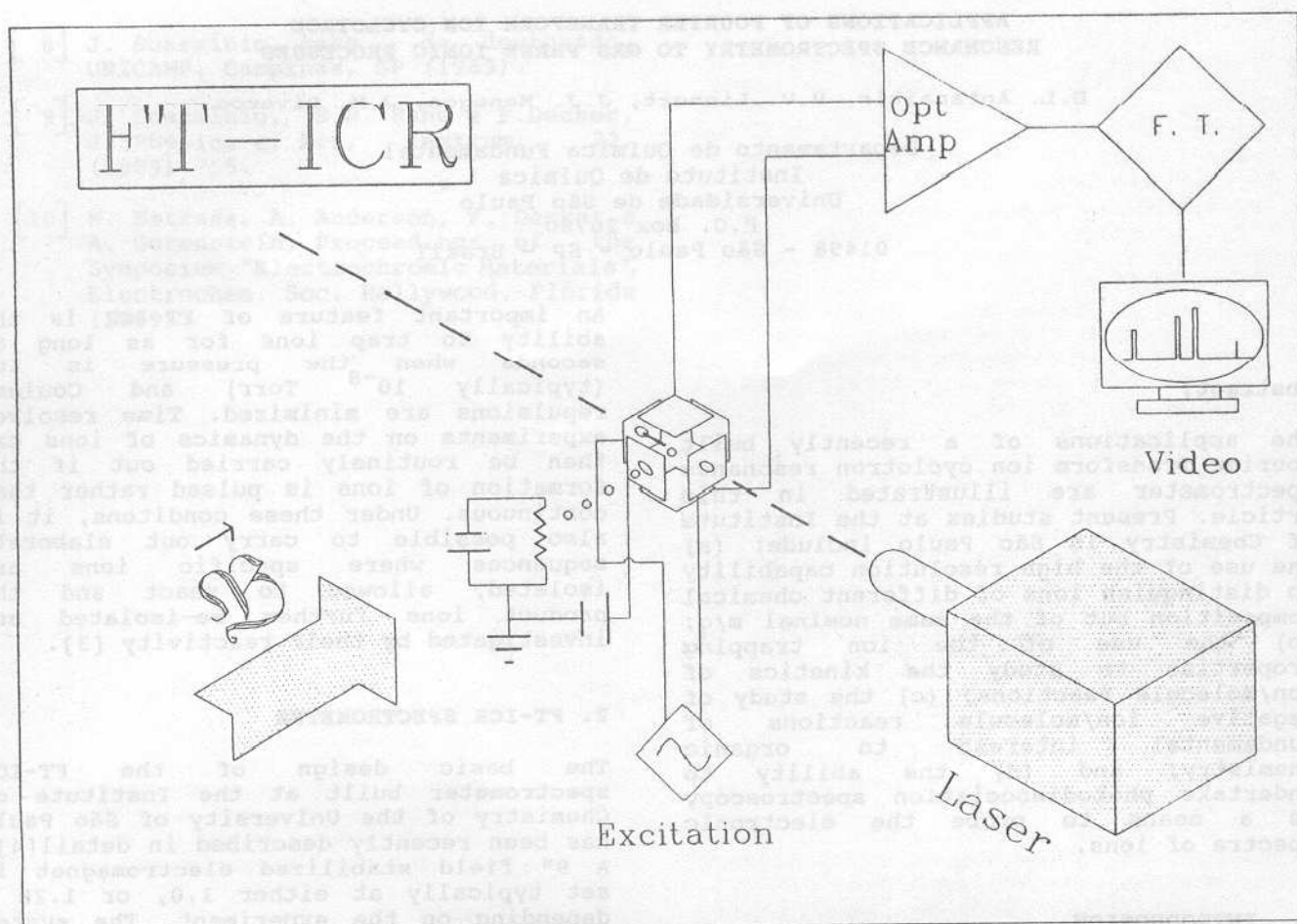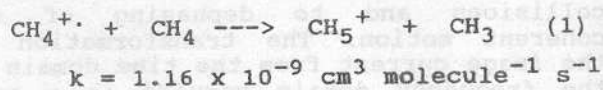The high mass resolution inherent to FT-ICR has been well documented in the

Figure 1. Schematic representation of the FT-ICR spectrometer. A sinusoidally oscillating radiofrequency electric field is applied to two plates perpendicular to the magnetic field direction. The coherent motion of ions in the cell induces an image current on the receiver plates. This signal is subjected to the data acquisition system. Photodissociation of desired ions are performed with a tunable source of light from a Nd:YAG laser.

literature [5] unsurpassed by any sector mass spectrometer. Experiments carried out in our spectrometer with a mixture of CO_2 and N_2O (where both molecular ions have a nominal m/q = 44) reveal a routine resolving power of approximately 15,000 at pressures of 5×10^{-8} Torr and B = 1.25 T. This feature has been extremely useful in measuring the branching ratio for the ion/molecule reactions of $CH_3O^-/HCOOC_2H_5$ previously studied in these laboratories [6]. Two of the main products, $HCOO^-$ and $C_2H_5O^-$, have a nominal mass of m/q = 45. The high resolution capability is particularly relevant in the study of the gas phase ion chemistry of substances like trimethyl borate (TMB) and tetraethyl silicate (TEOS) which can be used for etching and deposition. The detection solely of the nominal m/q of the ionic products may give rise to ambiguities about the exact chemical nature of the ions.

3.2 Ion/molecule kinetics and pressure measurements

The time evolution of ions stored in the FT-ICR cell as a function of trapping time can easily yield the kinetics of ion/molecule reactions. Rate constants can be obtained in principle in a straightforward way from these plots (Figure 2). Nevertheless, accurate measurements of the operating pressures for this system is a formidable problem arising from two main factors: a) substrate sensitivity of the ion gauge, and b) position of the ion gauge with respect to the cell and turbomolecular pump. We have used the well known reaction
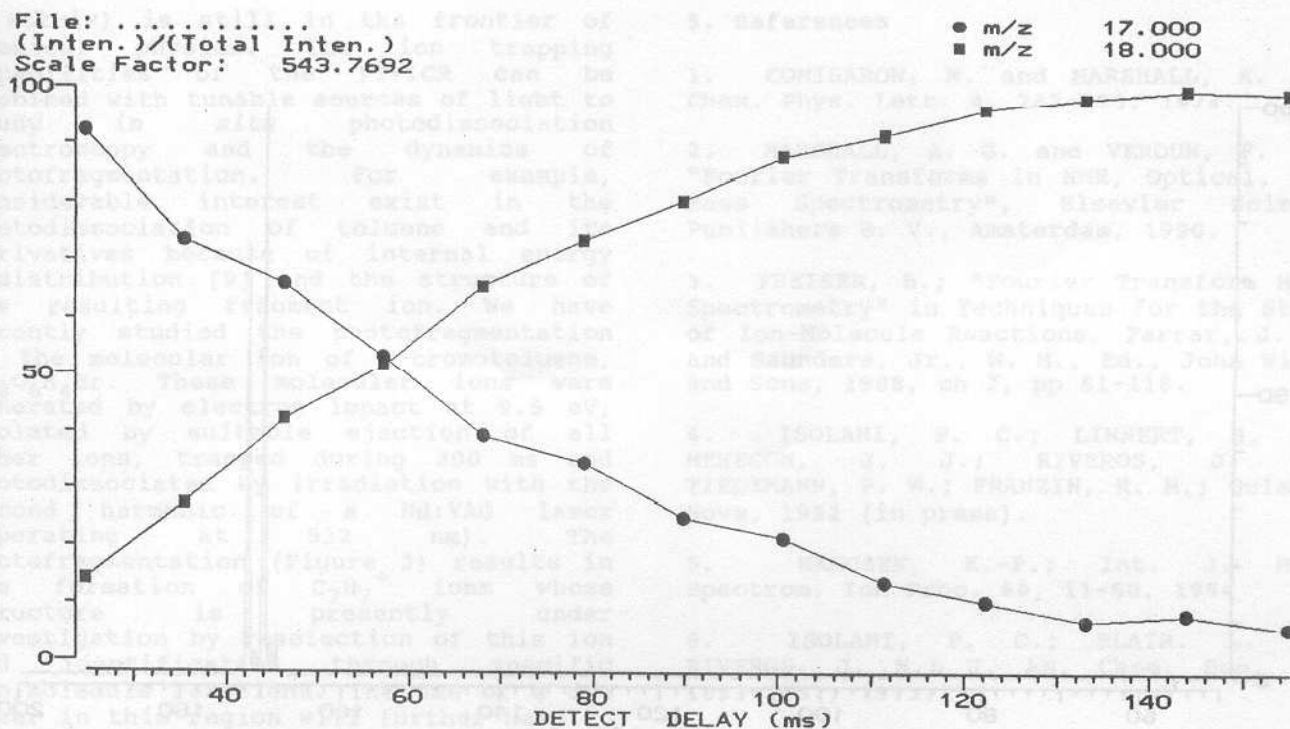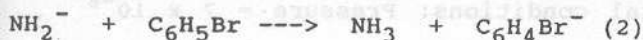
$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^+ + CH_3 \quad (1)$$

$$k = 1.16 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Figure 2. Kinetic reaction of $NH_3^+\cdot + NH_3 \longrightarrow NH_4^+ + \cdot NH_2$, showing the disappearance of the $NH_3^+\cdot$ (m/q = 17) ion and the generation of the NH_4^+ (m/q = 18) ion. Pressure = 1 x 10^{-8} Torr, 15 eV, 1 T.
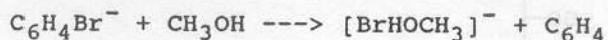
to establish gauge and position sensitivity. For example, the actual pressure of methane in the cell has been found to be almost two times higher than that registered in the ion gauge. Pressure calibration for other substances can then be accomplished by comparing the ion gauge vs. Baratron calibration in the 10^{-4} Torr for methane and for other substances. This procedure assumes a linear extrapolation over 4 orders of magnitude but is similar to that proposed by other authors [7].

3.3 Kinetics and structure of negative ions

The reactivity of gas phase negative ions has been an area of intense work by this group for almost 20 years [8]. Some recent work has been carried out in our FT-ICR in order to understand the unusual reactivity of halobenzenes. For example, NH_2^- produced by dissociative electron attachment in NH_3 at 6 eV reacts readily with bromobenzene according to reaction (2)

$$NH_2^- + C_6H_5Br \longrightarrow NH_3 + C_6H_4Br^- \quad (2)$$

An amazing observation about this process is the fact that when the $C_6H_4Br^-$ ion is isolated in the FT-ICR instrument by selective ejection of all other ions and allowed to react with neutral substrates it does so exclusively by transfer of a Br^- ion

$$C_6H_4Br^- + CH_3OH \longrightarrow [BrHOCH_3]^- + C_6H_4$$

This is an extremely interesting and novel procedure to promote Br^- (and also I^- in the case of $C_6H_4I^-$) attachment to neutral substrates in the gas phase. It also reveals that the structure of the $C_6H_4Br^-$ corresponds to that of a Br^- weakly bound to a benzyne molecule, i.e. $Br^-(C_6H_4)$. The stability of such a species is indeed remarkable and has prompted us to look into a theoretical explanation for the interaction responsible for the preferred structure of this ion.

3.4 Photodissociation of ions

Unlike neutral substances, the spectroscopy of ions in the gas phase (in the absence of the stabilizing effect of
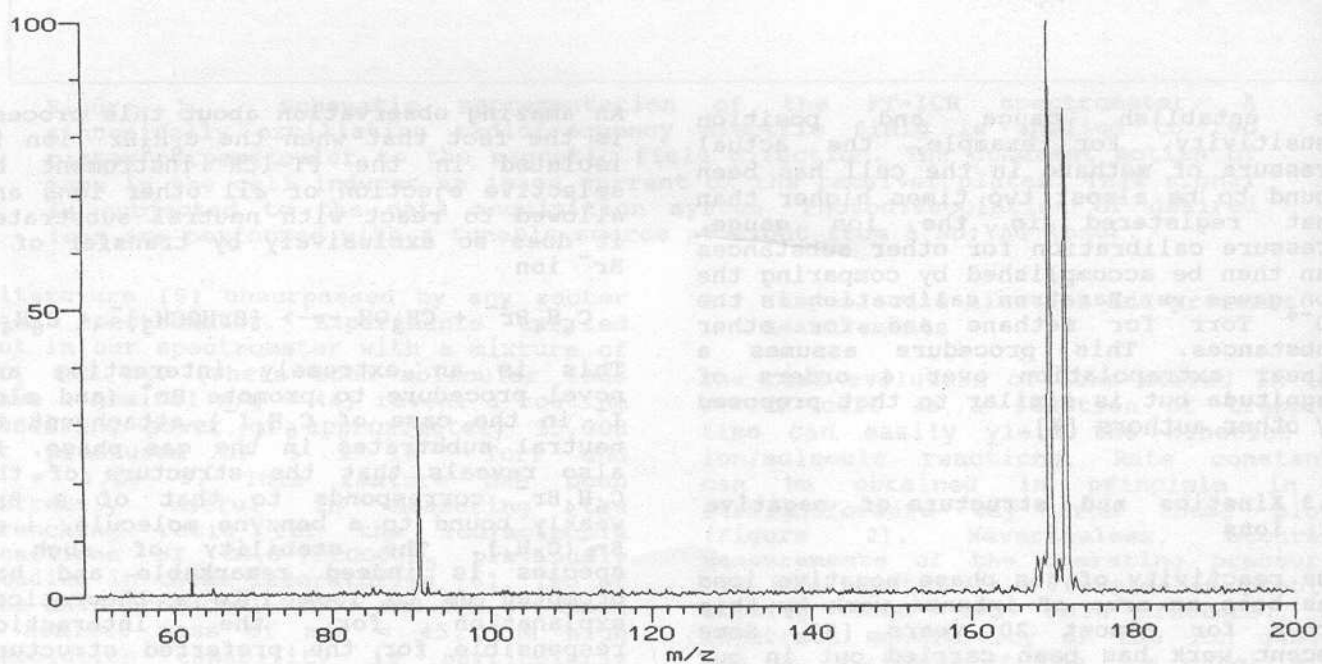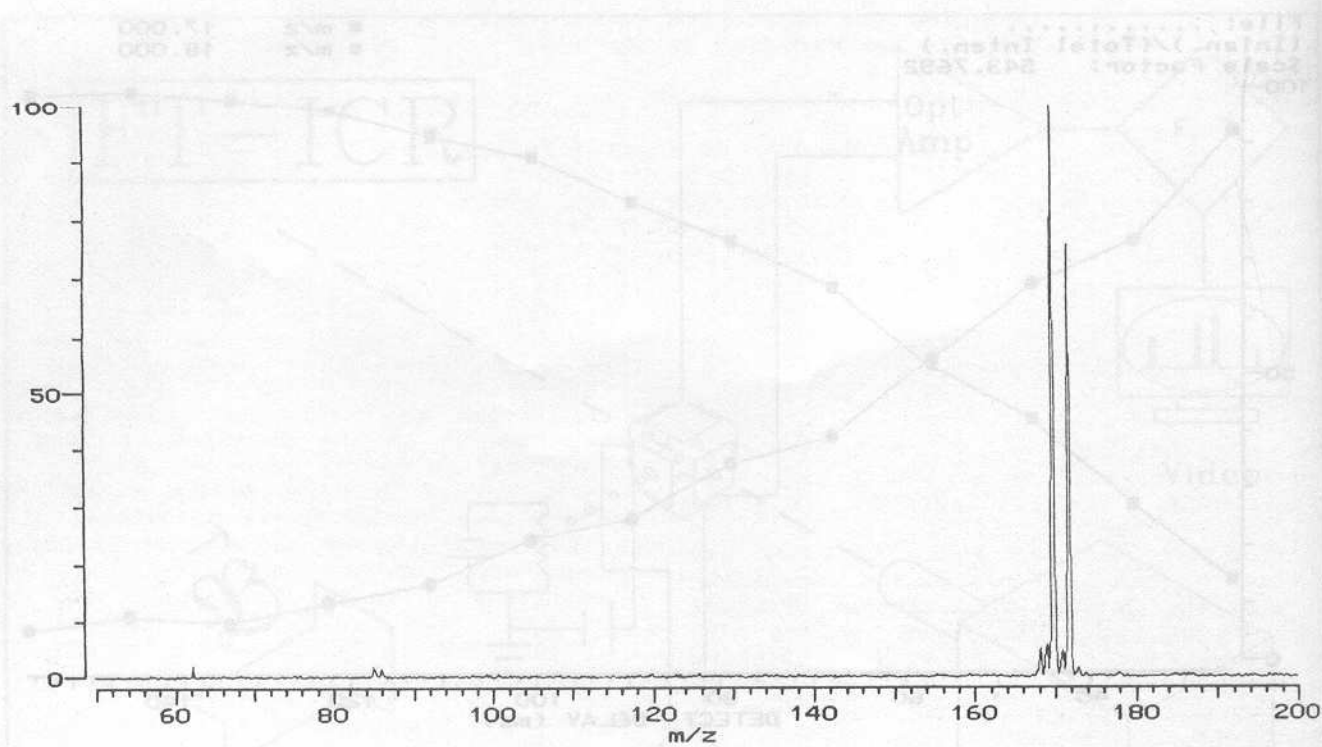
Figure 3. Top. Molecular ion of p-bromotoluene generated by electron bombardment at 9.7 eV. Bottom. Dissociation of the molecular ion upon irradiation with the second harmonic (532 nm) of a pulsed Nd:YAG laser generating the m/q = 91 ion. Experimental conditions: Pressure = 7 x 10^{-8} Torr, 1 T.

a matrix) is still in the frontier of chemical physics. The ion trapping capabilities of the FT-ICR can be combined with tunable sources of light to study *in situ* photodissociation spectroscopy and the dynamics of photofragmentation. For example, considerable interest exist in the photodissociation of toluene and its derivatives because of internal energy redistribution [9] and the structure of the resulting fragment ion. We have recently studied the photofragmentation of the molecular ion of p-bromotoluene, $CH_3C_6H_4Br$. These molecular ions were generated by electron impact at 9.5 eV, isolated by suitable ejection of all other ions, trapped during 200 ms and photodissociated by irradiation with the second harmonic of a Nd:YAG laser (operating at 532 nm). The photofragmentation (Figure 3) results in the formation of $C_7H_7^+$ ions whose structure is presently under investigation by reselection of this ion and identification through specific ion/molecule reactions. The use of a dye laser in this region will further help to establish the actual electronic spectrum of these molecular ions.

4. Acknowledgments

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