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# Quadrature Detection for the Separation of the Signals of Positive and Negative Ions in Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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**Abstract.** Positive and negative ions may be confined simultaneously in a nested open cylindrical Malmberg-Penning trap. However, ion charge sign cannot be distinguished by conventional dipolar (linearly-polarized) detection with a single pair of opposed electrodes. Here, the signals from each of two orthogonal pairs of opposed detection electrodes are acquired simultaneously and stored as real and imaginary parts of mathemetically complex data. Complex Fourier transformation yields separate spectra for positive and negative ions. For a fullerene sample, experimental quadrature detection yields $C_{60}^+$ and $C_{60}^-$ signals separated by ~1440 u rather than by the mass of two electrons, ~0.001 u in conventional dipolar detection.

## INTRODUCTION

Both anionic and cationic particles may be trapped simultaneously in Penning-like ion traps by either nested trapping geometries [1] or dynamic trapping, i.e. the combination with an rf trapping field [2]. These investigations have also been extended to Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry (see ref. e.g. [3,4] and [5], resp.). Under such trapping conditions the conventional FT-ICR detection scheme does not distinguish between positive ion signals and negative ion signals.

To overcome this shortcoming we have implemented quadrature detection to distinguish the ion polarity. Quadrature detection not only determines the ion cyclotron frequency but also the sense of cyclotron rotation for each ion signal. Positive and negative ions may then be easily identified based on the opposite senses of their cyclotron rotation. As an example, positively and negatively charged fullerenes, $C_{60}^+$ and $C_{60}^-$, produce signals at m/z = +720 and -720 for a total separation of 1440 u compared to a difference of just about 1/1000 u in the absolute values due to the mass of the two electrons. Thus, in this particular case, the signal separation is increased by six orders of magnitude.

# EXPERIMENTAL SETUP AND PROCEDURE

All experiments were performed with a 6 tesla FT-ICR mass spectrometer described elsewhere [6]. A heated solids probe was inserted into the source region of the vacuum system. After the $C_{60}$ sample was heated to ~475 °C, the volatilized fullerene gas was pulsed into the analyzer region by opening a mechanical shutter.

In the present work ions were formed by application of a 100 eV electron beam through the trap volume. The FT-ICR analyzer region was equipped with a modified 2 1/4" diameter open cylindrical cell. To create the nested trapping potential each trapping electrode was axially segmented into two pieces.
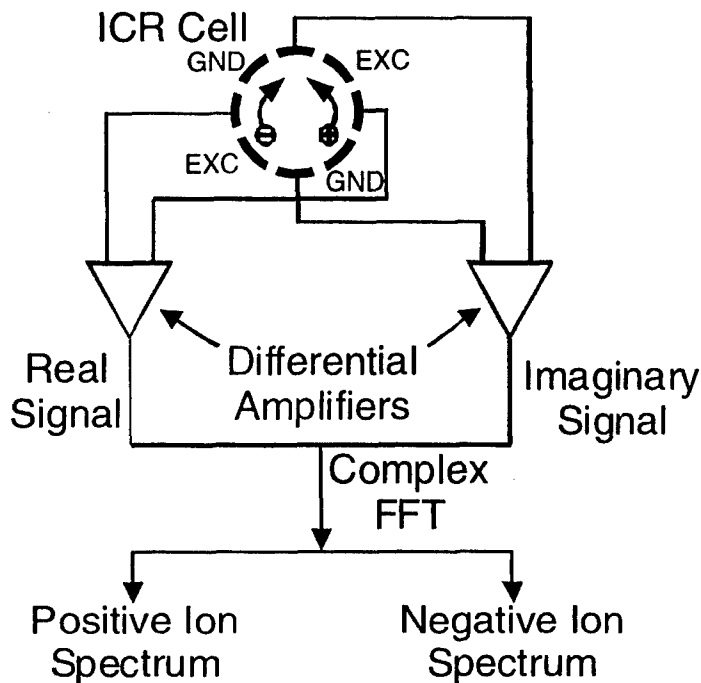


**FIGURE 1.** Wiring of ICR cell and data processing for quadrature detection FT-ICR MS.

For quadrature detection the excitation and detection electrodes were segmented into a total of eight electrodes. Two pairs of opposed electrodes were used for the two channels of quadrature detection (Fig. 1). Dipolar excitation was performed on two electrodes while the remaining two electrodes were grounded. As in conventional FT-ICR MS, the signal from each pair of detection electrodes was differentially amplified. A MIDAS data station [7] was modified to incorporate two HP E1437A modules (Hewlett Packard, Palo Alto, CA) to digitize the two ICR transient signals simultaneously for storage as real and imaginary components of mathematically complex data. The MIDAS analysis software was modified to process this data and display both positive and negative ion spectra.

# RESULTS AND DISCUSSION

Quadrature detection distinguishes the sense of ion rotation for a given ion polarity. The sense of rotation is manifested as a signal at positive or negative frequency in the complex Fourier transform spectrum of the quadrature time-domain data. An example of quadrature detection for simultaneous storage and detection of cationic and anionic fullerenes is given in Figures 2 and 3. Figure 2 shows the transients from each of the two pairs of electrodes and the resulting frequency spectrum after a complex Fast Fourier Transform (FFT) of this data, as well as the corresponding mass-to-charge ratio spectra.
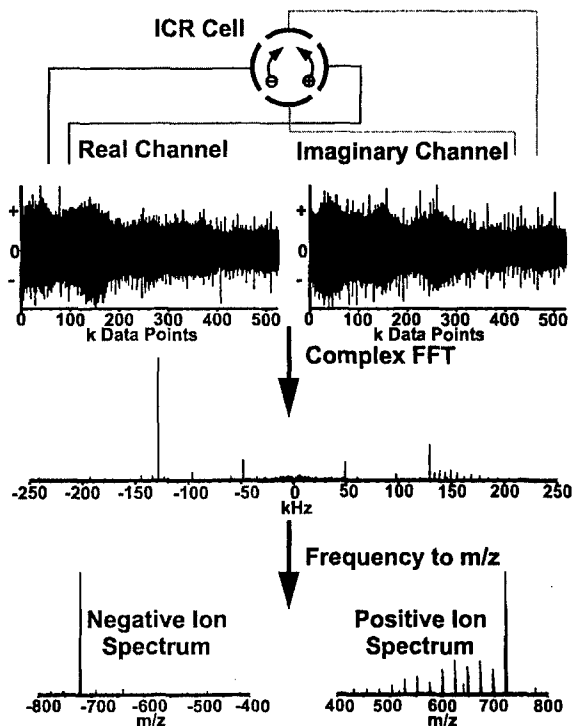


**FIGURE 2.** From top to bottom: Schematic wiring, transients, frequency spectrum and mass spectra from quadrature detection FT-ICR MS of fullerenes. (For details see text.)

In Fig. 3 these mass spectra (middle and bottom) are compared to the corresponding spectrum (top) acquired as before, but with complex FT of only the real time-domain data. A strong $C_{60}$ signal at m/z = 720 and several species corresponding to n $C_2$ (n = 1 - 12) losses are present. Quadrature detection reveals that most of the fullerene signal at m/z = 720 is due to anionic and only a small fraction to cationic fullerenes. Because $C_{60}^{+}$ and $C_{60}^{-}$ differ in mass by only two electrons, a resolving power of 720,000 is necessary to distinguish the two species with dipolar detection. In the quadrature detection mode, however, there is no problem in distinguishing the same species.

The same holds for the smaller fullerenes (dissociation fragments). The positive ion mass spectrum indicates the well-known pattern due to sequential $C_2$ losses (For a recent review on the mass spectrometry of fullerenes see e.g. [8]). No fragments, however, do appear in the anions' mass spectrum, since $C_{60}^-$ more readily loses its excess electron than a carbon dimer [9] and the neutral product, $C_{60}$, is no longer stored nor detected by FT-ICR MS.

Furthermore, electronic noise peaks are more easily identified than by conventional detection because they tend to appear in the spectra of ions of both polarities.
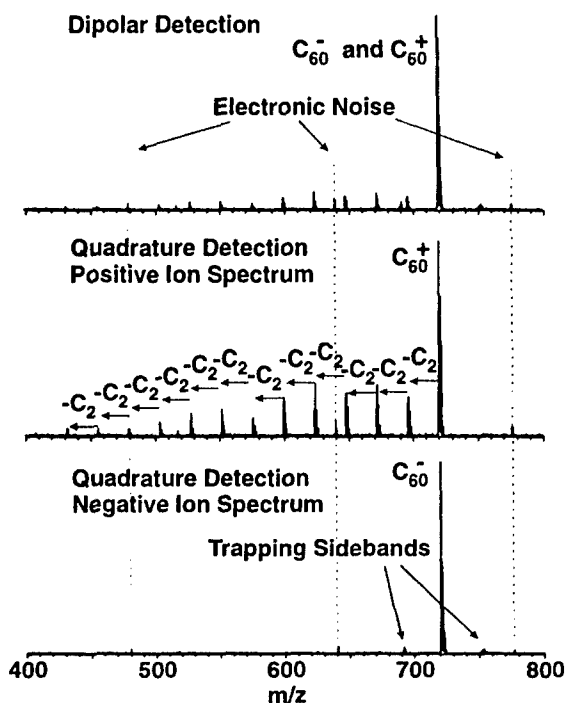


**FIGURE 3.** Fullerene FT-ICR mass spectra. Top: Spectrum in dipolar detection mode, i.e. the transient from only one pair of opposed detection electrodes, generated by Fourier transform processing of real time-domain data. Middle and bottom: Evaluation of the full "complex" transient yields separate mass spectra for positive and negative ions.

It may be noted, that there is a second, closely related method to distinguish the polarity of simultaneously stored ions, namely by the application of quadrature (i.e., circularly-polarized) excitation [10, 11]. In this case only ions of one polarity, either the cations or the anions, are excited and thus only their FT-ICR signal appears in conventional dipolar detection. However, in order to extract all of the information, the mass measurement has to be performed twice (once for each polarity) whereas dipolar excitation/quadrature detection results in the full information after one measurement. (In principle, the dipolar and quadrupolar excitation and detection schemes can be used in any combination – depending on the experimental results of interest.)  A

further advantage of the use of two simultaneous transients instead of one is an increased signal-to-noise ratio of the FT-ICR MS spectra.

Finally, the present "physical" quadrature detection may be conducted in either "direct" or "heterodyne" mode. In heterodyne mode, a similar factor of $2^{1/2}$ enhancement in signal-to-noise ratio may be realized (versus single-phase heterodyne) by so-called "digital" quadrature heterodyne-mode detection [12]., in which the signal from a given pair of opposed detection electrodes is multiplied by digital sine or cosine waveforms and stored as real and imaginary data. "Digital" quadrature heterodyne detection distinguishes signals whose cyclotron frequencies are above or below the reference frequency. However, "physical" quadrature detection is required to distinguish the sense of ion cyclotron rotation (and thus ion polarity).

## CONCLUSIONS

We have demonstrated the experimental implementation of quadrature detection to distinguish positive ions from negative ions in a nested FT-ICR ion trap. The use of quadrature detection circumvents the problem of identifying ions with the same mass but opposite charge. In particular, cationic and anionic fullerenes, $C_{60}^+$ and $C_{60}^-$, at m/z = 720 may be differentiated without the need to resolve their mass difference of just two electrons.

## ACKNOWLEDGMENTS

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