Instrumentation and Methodology for Simultaneous Excitation/Detection of Ions in an FTICR Mass Spectrometer

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A method for direct and continuous detection of ion motion during different perturbation events of the Fourier transform ion cyclotron resonance (FTICR) experiment is demonstrated. The modifications necessary to convert an ordinary FTICR cell into one capable of performing simultaneous excitation/detection (SED) using a capacitive network are outlined. With these modifications, a 200-fold reduction in the detection of the coupled excitation event is only possible if the coupled signal from the applied rf potential is reduced below that for the ion signal. Asymmetries in cell construction and differences in the impedance of the electrical connections to the excitation and detection electrodes cause a capacitive imbalance to occur within the trapped ion cell. The condition for amplitude matching is that the voltage drop across each resistor within the differential amplifier is equal (eq 1).

\[ V_{R1} = V_{R2} \]  

\[ V_{R1} = I_{D1}R_1 = \frac{V_{E1}}{\sqrt{X_{(E1D1)}^2 + R_1^2}} + \frac{V_{E2}}{\sqrt{X_{(E2D1)}^2 + R_1^2}} R_1 \]  

\[ R_2 = \frac{V_{E1}}{\sqrt{X_{(E1D2)}^2 + R_2^2}} + \frac{V_{E2}}{\sqrt{X_{(E2D2)}^2 + R_2^2}} R_2 \]  

Equation 2 relates the potential across the resistor of the amplifier to the image current on detector electrode no. 1 (Figure 1a) from the excitation voltage applied to the first and second excite electrodes, \( V_{E1} \) and \( V_{E2} \), respectively. If \( V_{E1} = V_{E2} \) and \( R_1 = R_2 \), then eq 3 can be satisfied when all four capacitive reactances are equal, and since the frequency is the same, all four capacitances must be equal. Figure 1b illustrates the addition of variable capacitors to the circuit in an effort to correct for any capacitive mismatches in the circuit.

The concept of simultaneous excitation and detection (SED) is not new. In fact, it was the original technique used for both

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ICR and quadrupole ion traps, where a marginal oscillator was used to measure power absorption between the excitation circuitry and the ions. A design that somewhat resembles the SED technique is that proposed by McIver et al., where ion excitation is performed on one electrode of the trapped-ion cell and detection is performed on the opposing electrode while a balance capacitor is used to null the excitation signal during detection. The advent of the FTICR in 1974 brought about the use of a discrete pulsed waveform for ion excitation offering broad-band detection, while separating the ion excitation and detection events in time, provided for an increased signal-to-noise ratio. In this scheme, the ion excitation event is so brief relative to the detection event that it was considered to be essentially instantaneous. As a result, direct observation of ion motion during excitation has received little attention.

Recently Beu presented a method in which a capacitive network is used to match the amplitude of the coupled signal from out-of-phase, dipolar waveforms; the result was a substantial reduction in the detected excitation signal, which permitted observation of the ion image current. Presented here are efforts to utilize this technique of SED for the detection of ions during excitation. The specific cell geometry and experimental strategies for reducing the capacitive coupling are described. Several applications utilizing the optimized hardware configuration are presented. The effects of different dipolar excitation events are observed directly by applying single or multiple excitation events while simultaneously detecting the image current. For example, resonant single-frequency dipolar excitation of benzene ions is observed. In addition, several remeasurement events are accomplished in which a single population of benzene ions is continuously monitored using SED. Finally, ion motion during a resonant excitation/detection event is monitored by SED.

**EXPERIMENTAL SECTION**

SED was performed on the FTICR system illustrated in Figure 2, which includes a 1.0 T electromagnet and a 1 in. cylindrical closed trapped-ion cell of unit aspect ratio. Ions were formed by electron ionization (EI) with a 20 ms beam time and 180 nA of current as measured at the cell. Benzene and argon were introduced through a precision leak valve (Granville-Phillips Co., Boulder, CO) to a pressure in the $10^{-6}$–$10^{-7}$ Torr range. Benzene ions were excited at 194 kHz. Trapping potentials of 2 V were used initially but were reduced to 800 mV for excitation and detection. The length of the detection event varied depending on the requirements of a particular experiment. Spectra were collected on a MIDAS data system that incorporated a stand-alone EI controller capable of independent manipulation of emission current, beam time, and ionization energy during the experimental sequence. Of particular value was the capability of the MIDAS to control excitation duration and amplitude independent of the detection parameters. This enabled detection to occur simultaneously as one or more excitation waveforms were applied.

Four nonmagnetic variable capacitors (Voltronics Corp., Denver, NJ) with a range of 0.45–3.0 pF were attached to the excitation and detection electrodes. A rotatable mechanical feedthrough was used to allow for external adjustment of one of

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**Figure 1.** Capacitor representation of trapped-ion cell (a) before the addition of variable capacitors and (b) with variable capacitors in place.

**Figure 2.** Instrumentation diagram of the 1T FTICR system used for simultaneous excitation/detection (SED). The inset details the capacitor tuning assembly utilized for reducing the coupled excitation.
the four capacitors when the matching network was mounted internal to the vacuum chamber. All data were processed on a personal computer with ICR-2LS data analysis software.17

A typical cell constructed for the 1T system has a capacitive mismatch as large as 3 pF. This can result in the excitation event delivering up to 500 pA of current to each detection electrode when using a 40 Vp-p excitation voltage. This signal will mask a typical ion signal of approximately 10–50 pA. To correct for the capacitive mismatch and reduce the coupled excitation, variable capacitors were installed between the excitation and detection electrodes as shown in the inset of Figure 2. In initial impedance matching experiments, each of the four capacitors was optimized with the cell assembly located outside the vacuum chamber. A signal generator was used to apply a test waveform on the excitation electrodes while an oscilloscope was connected to the detection electrodes. After optimization with the oscilloscope, each of the leads from the excitation electrodes was connected to a differential amplifier and the capacitors were once again optimized. When the cell assembly was placed in the vacuum chamber, an increase in excitation coupling occurred due to the additional capacitance between the cell and the vacuum chamber. Even with this increase in capacitance, only a small adjustment of one capacitor using the external feedthrough, shown in the inset of Figure 2, was required to reduce the differentially amplified coupled excitation voltage to less than 50 mV. After the system was pumped down to a base pressure in the low 10–8 Torr range, dipolar excitation at 40 Vp-p and 194 kHz was applied to each excitation electrode. Once adjusted and under vacuum the capacitor matching network was stable over a period of several weeks.

RESULTS AND DISCUSSION

As a first experiment, the trapped ion cell was tuned to a minimum coupled excitation amplitude to evaluate the cell for SED in a typical FTICR pulse sequence. As a control, presented in Figure 3a is a waveform detected during an 8 ms excitation event of 40 Vp-p, with the ionization source deactivated, prior to installing the capacitive matching network. The detected signal exceeds the dynamic range of the preamplifier, and the resulting signal is clipped. An FT of the first 8 ms of the transient indicates that the coupled excitation signal is 3000 times the background noise. In Figure 3b the system was configured with variable capacitors mounted directly to the trapped-ion cell between the excitation and detection electrodes. In this case the coupled signal cannot be distinguished from the background noise in the transient. Fourier transformation of the first 8 ms transient during which excitation occurs yielded a detected signal that was only 14 times the background noise. The coupled signal of the tuned capacitive network results in a 200-fold decrease in the detected excitation signal. This ability to suppress the excitation interference was an essential first step in permitting direct examination of ion motion during excitation.

Having assembled a suitable tuned circuit, the next step was to examine ion motion during excitation. The benzene transient shown in Figure 4 utilizes SED throughout the entire FTICR experiment including the 500 µs excitation event. Expansion of the first 0.8 ms of the transient includes the dipolar excitation on the benzene ions. As the excitation is applied for the first 0.5 ms, the ions assume a coherent signal at the cyclotron frequency that can be observed in the transient. This portion of the FTICR pulse sequence is typically not observable because the ion signal is masked by the high-amplitude excitation signal that is applied at the resonant frequency of the ions. Presented in Figure 5a–c are transients of benzene ions using varying amplitudes of excitation.

Figure 3. Coupled excitation from the FTICR cell. The transient was detected during an 8 ms excitation waveform of 40 Vp-p at 194 kHz in which (a) no efforts have been made to reduce capacitive coupling of the excitation and (b) with optimized variable capacitors mounted to the trapped ion cell.

Figure 4. SED time domain transient of benzene ions. SED was used to view ion signal during the excitation and detection segments of the FTICR experiment.

with detection occurring concurrently over 3 ms. As expected, the greater the excitation amplitude, the larger the rate of increase of the ion signal, and the more quickly the ion signal is damped.

In this case, the signal is damped due to ion ejection as ions are accelerated beyond the cell radius. It is interesting to note that the time domain transients in Figure 5 are the real-time equivalent of an excitation profile which is often used to follow the evolution of an ion cloud during the FTICR experiment.\(^{(18)}\)

Having demonstrated SED for the standard dipolar excitation experiment, a more elaborate collection of FTICR experiments were performed in which excitation events were detected. The first example is ion remeasurement\(^{(19)}\)\(^{-21}\) in which a single ionization event is followed by multiple excitation and detection events. Figure 6 illustrates the continuous detection of the transient produced from a single population of benzene ions as it undergoes 5 cycles of excitation and relaxation. Careful steps were taken to deactivate the electron ionization source after the EI event to ensure that no additional ions were formed. Although strong benzene signal is observed even after several cycles, reduced remeasurement occurs due to collisions between excitation events. This method for implementing SED allows the continuous evaluation of remeasurement efficiency and ion loss due to excitation.

As discussed above, an entire remeasurement experiment can monitor ions from the time they are formed until they are lost from the cell. This allows for the rapid optimization of dipolar excitation amplitude, time, and cooling conditions required for


A second experiment to demonstrate SED performance was the execution of an excitation/forced relaxation experiment in which an excite—r—excite sequence was applied. Ions are excited with this pulse sequence to half the radius of the cell, and then a 180° phase delay is inserted in the excitation signal to return the ions to the center of the cell. Presented in Figure 7 are the pulse sequences and transients for an FTICR signal resulting from multiple excitation events for a single ion packet. Figure 7a presents a standard dipolar excitation and detection experiment performed as a control to illustrate that, with a single excitation event, the ion cloud grows, collides with the detect electrodes, and is lost from the cell. In Figure 7b a 2.6 μs delay is introduced following a 1 ms, 200 mVp-p excitation event. This delay corresponds to half the cycle of a benzene ion at 194 kHz and was chosen to control the phase angle of the ion packet relative to the first excitation event. This delay causes a phase shift of the excitation signal, leading to deceleration of the ion packet, and its return to the center of the cell. At or near the center of the cell the ion packet again comes in phase with the applied excitation signal and the ion radius expands again until it is quenched. This behavior is shown in Figure 7b, where the ions are excited for 1 ms, de-excited for approximately 1 ms, and then excited out of the cell over a period of 4 ms. Figure 7c is included as a control and is executed with the same experimental sequence as Figure 7b but with the EI source deactivated. The excitation signal was amplified 40-fold to better illustrate the discontinuity in the waveform due to the r-delay. The continuous monitoring of this more sophisticated excitation event is a good demonstration of the capability of SED.

CONCLUSIONS

The efficacy of SED for directly monitoring the effects of an applied excitation waveform on ion motion is demonstrated. SED allows the entire FTICR experiment to be continuously detected without interruption. With SED, ion trajectory during dipolar excitation events such as single frequency, chirp, stored waveform inverse Fourier transform (SWIFT), and SORI can be investigated. This is particularly important since little experimental evidence has been published on the nature of ion trajectories during excitation. Several applications for SED are being investigated. For example, SED can be used to determine the effect CID excitation has on fragment ions. The technique should also permit detection of fast ion chemistry, including the observing the formation of metastable species during the matrix assisted laser desorption (MALDI) ionization process. In this experiment, the use of SED allows for excitation/detection to begin prior to ionization allowing instantaneous observation of ion evolution. Another use is the observation of ion signal during the application of tailored waveforms. Although not previously studied, the possibility exists that such a waveform could affect ion motion and an apodized or tailored pulse could reduce ion loss and increase sensitivity. A final application of SED is to the generation of real-time excitation profiles that have been used extensively for investigating nonideal ion behavior in FTICR. Using SED for excitation profile generation could be performed in a small fraction of the time of a conventional experiment with greater reliability.

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