Desorption Ionization of Cesium Iodide by Fourier Transform Mass Spectrometry

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Results of studies on the secondary ion mass spectrometry (SIMS) of CsI by Cs$^+$ ion desorption ionization Fourier transform mass spectrometry (DI-FTMS) are reported. Owing to the relatively long time scale of the FTMS experiment, the "anomalous cluster ion intensity" for the Cs(CsI)$_n$$^+$ cluster ions observed by Campana is very distinct. A second objective of this study was to evaluate the utility of ion ejection methods for enhancing the dynamic range of FTMS. While ion ejection does improve the dynamic range of FTMS, care must be exercised to avoid translationally exciting other ions which are present in the ion cell. Translational excitation of these ions can lead to collision-induced dissociation (CID). Finally, estimates of the secondary ion yield for the Cs(CsI)$_{13}$$^+$ ion are given and used to estimate the sensitivity of DI-FTMS.

In the last several years there has been much discussion concerning the potential use of Fourier transform mass spectrometry (1–4) for the analysis of large biomolecules (5–8). The first demonstration of desorption ionization (DI) FTMS capabilities was laser DI-FTMS reported by Gross (9). Subsequently, our laboratory demonstrated the use of kiloelectronvolt energy Cs$^+$ ion DI-FTMS (10). Although the laser DI-FTMS experiments reported by Gross (9) were limited to relatively small molecules (m/z ~200), the results of the Cs$^+$ ion DI-FTMS demonstrated mass measurement capabilities to m/z 2792 (a dimer ion of vitamin B$_{12}$) (10). More recent work from our laboratory has concentrated on studies of organo alkali halide ions and the optimization of experimental conditions for ionizing large molecular species (500–5000 amu) by solid-state DI (11).

In this paper we wish to discuss the Cs$^+$ ion DI-FTMS of CsI crystals, and in particular the use of ion ejection methods for enhancing the dynamic range of FTMS. Although ion ejection methods are routinely used in a variety of FTMS experiments (12), a critical evaluation of the consequences of such a drastic pertubation of the ion population has not been performed. As will be demonstrated in this paper, care must be taken when using ion ejection methods in order to avoid collision-induced dissociation (CID) reactions.

Secondary ion mass spectrometry (SIMS) studies of alkali metal halide salts have been reported by several workers (13–15). However, early efforts to generate the ion sequence [Cs(CsI)$_n$]$^+$ by Cs$^+$ ion DI-FTMS on the FTMS 1000 at Texas A&M University were unsuccessful. Owing to the difficulty in successfully performing this experiment, additional studies were performed on a prototype FTMS-2000 which has lower background electronic noise (see Experimental Section). The major differences between the FTMS-1000 instrument used in the previous studies and the FTMS-2000 used for these studies are the detection electronics and better shielding of the detection electronics from external noise sources (16).

EXPERIMENTAL SECTION

The instrumentation used for these studies was a Nicolet FTMS-2000 equipped with a 3-T magnet. For the experiments described herein the instrument was operated in the single section cell mode. Therefore, the only differences in the present experiments and our previous studies where cluster ions of the type Cs(CsI)$_n$$^+$ were not detected are the detector electronics and the improved signal shielding. The samples were introduced into the system by using a standard direct insertion probe. The Cs$^+$ ion gun is mounted such that the incident Cs$^+$ ion beam travels parallel to the magnetic field. The Cs$^+$ ion gun is positioned approximately 17.8 cm away from the ion cell. The arrangement of the ion gun and ion cell is shown in Figure 1. For the experiments described herein the gun was operated at a potential of 5 kV and a Cs$^+$ ion beam current of approximately 10 × 10^{-9} A cm^{-2}. The DI was initiated by pulsing the Cs$^+$ ion gun on for ca. 5 ms, and the mass spectrum was acquired over the mass range 100–4000 amu. A typical experimental pulse sequence is shown graphically in Figure 2. In the broad-band signal acquisition mode (64K data points) the mass resolution (defined as $M/\Delta M$) was limited to approximately 1000 at m/z 1433. All other experimental conditions are similar to that described in our earlier report (10).

The ion ejection experiments were performed by applying a fixed-frequency radio frequency excitation or by sweeping the rf oscillator over a small frequency range above and below the cyclotron frequency of the ion to be ejected. For example, ion ejection of Cs$^+$ was performed by applying a fixed-frequency (346.924 kHz) excitation signal; to eject the m/z 393 ion, the rf oscillator was swept from 116 to 119 kHz (m/z 400–390) at a rate of 1 MHz s^{-1}. As shown in Figure 2, the ejection rf signal was applied following the ionization step but prior to the initiation of the ion detection sequence (17, 18). In these experiments the amplitude of the ejection rf was approximately 32 V (peak to peak) or 720 V m^{-1}.

The modifications made to improve the noise level of the FTMS-2000 are all related to improved instrument grounding and shielding of signal components and removal of noisy electronic components. For example, the computer visual display unit is a major source of 46-kHz noise, and this unit is now shielded and remote from the CPU console. By far the major improvement made to reduce noise involves shielding of the electrical leads connecting the high-vacuum feed-throughs on the source flange to the ion cell excite/receive plates.

In the DI-FTMS spectra reported herein ions are observed at m/z 301 and 821 which are assigned to Cs(CsCl)$^+$ and Cs(CsCl)(CsI)$_2$$^+$, respectively. In addition, an ion of unknown origin is observed at m/z 495. In each case these ions arise from impurities in the sample or contaminants from the vacuum system.

The CsI sample was dissolved in methanol (ca. 0.5 µg/mL) and a small fraction (ca. 2 µL) of the solution was placed on the solids probe and the solvent was removed by air-drying. The CsI sample was obtained from MCB Chemicals Co.

RESULTS AND DISCUSSION

Owing to the large ionic clusters formed on DI of alkali metal halids, these systems are interesting candidates for evaluating the general capabilities of high mass DI-FTMS. In addition, these ionic clusters provide an opportunity to examine the effects of ion lifetime on the DI-FTMS data. That is, the typical secondary ion mass spectrometer samples ions with lifetimes of several microseconds. Conversely, the time scale of the FTMS experiment, i.e., the total length of time between ion production and ion detection, is variable over the range milliseconds to seconds. Therefore, any changes in the secondary ion abundance arising from slow dissociation reactions of the ionic clusters would be more easily detected
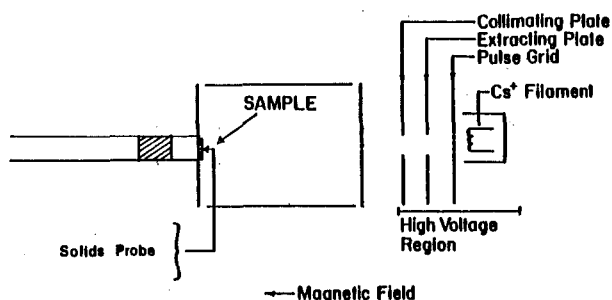
Figure 1. Schematic of the ion cell and ion gun configuration used for the Cs^+ ion DI-FTMS studies.
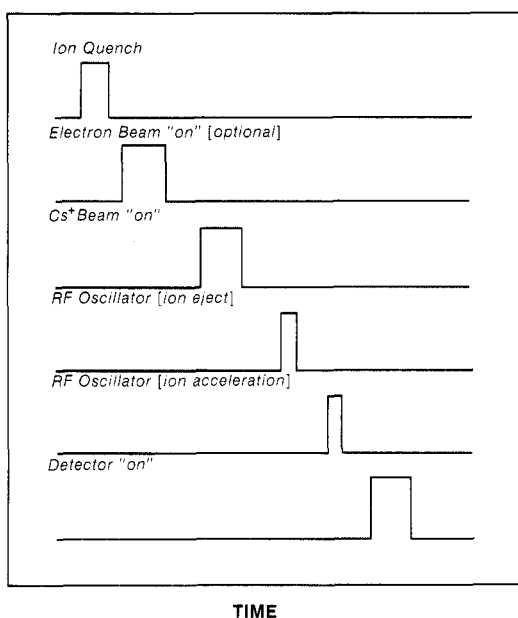

Figure 2. Experimental pulse sequence. The step involving the electron beam (optional) was not used in these studies.

on the FTMS instrument time scale.

Using the prototype FTMS-2000 system, which has a much better dynamic range (see Experimental Section) than the system at Texas A&M University, we have successfully obtained DI mass spectra of CsI clusters up to m/z 3513, e.g., $Cs(CsI)_n^+$, where $n = 13$. This particular instrument is presently limited to approximately m/z 4000. The upper mass limit is imposed by the detection system electronics, and this mass range can be extended by relatively simple modifications to the detector preamplifier. When these studies were performed, an RC filter network, which has a frequency cutoff of ca. 10 kHz, was used to reduce the low-frequency noise. By removal of this filter the mass range of the FTMS-2000 has been extended and ions have been detected beyond m/z 11 833, i.e., $Cs(CsI)_n^+$, where n equals 45 (19).

The DI mass spectrum of CsI contained in Figure 3 was obtained by irradiating the sample with Cs^+ ion beam energy of 5 keV and beam current of 10×10^{-9} A cm^{-2}. The beam was turned "on" for a period of 5 ms at a repetition rate of 1 Hz. The low duty cycle is used to minimize thermal effects associated with the DI process (11). The major ions in this spectrum correspond to $[Cs(CsI)_n]^+$, where $n = 0$ (m/z 133), 1 (m/z 393), 3 (m/z 913), 4 (m/z 1173), and 6 (m/z 1692), with weaker signals at $n = 2$ (m/z 653) and 9 (m/z 2471). The spectrum in Figure 4 was obtained by using the same conditions as those for Figure 3; however, in this spectrum the Cs^+ ions (m/z 133) (formed by DI) were ejected by applying a fixed-frequency (346.924 kHz) radio frequency (rf) signal (17, 18). The applied rf frequency signal corresponds to the cyclotron frequency for Cs^+ and causes the Cs^+ ions to be
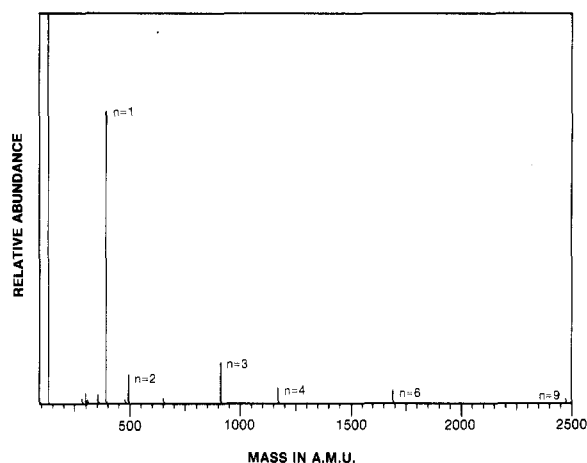

Figure 3. Cs^+ ion DI-FTMS spectrum of CsI obtained with an incident beam energy of 5 keV and beam current of 10×10^{-9} A cm^{-2}. The figure shows the mass range of 100–2500; no ions were detected at higher m/z values.
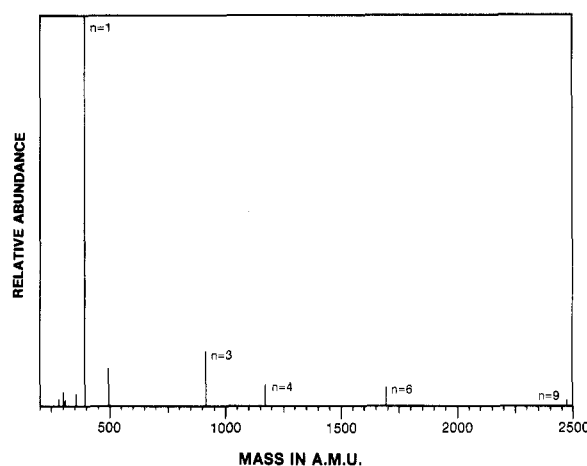

Figure 4. Same spectrum as shown in Figure 3 except the Cs^+ ions formed by desorption ionization are ejected (see text).
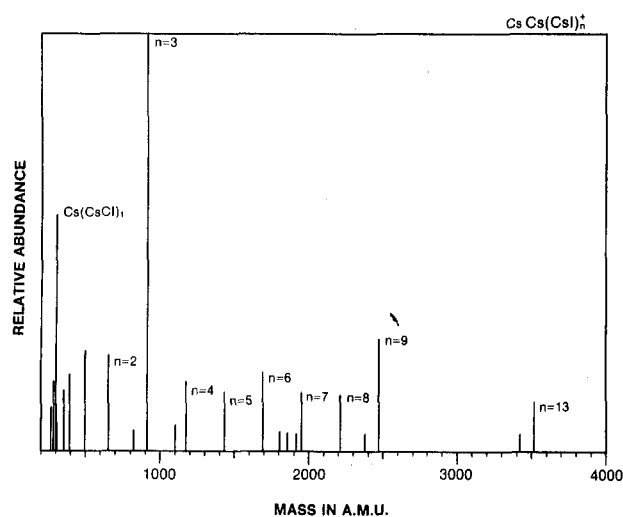

Figure 5. Same spectrum as shown in Figure 3 except both Cs^+ and $Cs(CsI)^+$ are ejected (see text).

ejected from the ion cell. Similarly, the spectrum in Figure 5 was obtained by ejecting both Cs^+ (m/z 133) and $Cs(CsI)^+$ (m/z 393) (see Experimental Section). The purpose of the ejection experiments was to increase the dynamic range of ion detection by removing the most abundant ions from the ion cell. The dynamic range of FTMS is limited by the total number of ions which can be trapped without causing

space-charge effects (ca. 10^6–10^7) and the smallest number of ions which produces a measurable image current (20). At present, a practical estimate of the dynamic range is ca. 10^3–10^4. That is, the minimum number of ions that can be detected is 10^3–10^4. Owing to the similar abundances for the Cs^+ and $Cs(CsI)^+$, there is very little difference between the spectra of Figures 3 and 4; e.g., this corresponds to a scale expansion factor of 1.3. However, the larger scale expansion (factor of 5.5) between Figures 4 and 5 reveals the presence of cluster ions at m/z 1433, 1952, 2212, and 3513 (n = 5, 7, 8, and 13, respectively) which were not observed in Figures 3 and 4 due to the low yields for these secondary ions. Owing to thier low relative abundance (<5%) the cluster ions corresponding to n = 5, 7, and 8 are not plotted in Figure 4; i.e., the threshold in the plot routine was set for 5% relative abundance, and ions of lower relative abundance are not plotted.

An anomaly concerning the spectrum of Figure 5 should be noted. In the scale expansion using the ion ejection method the abundances of the m/z 1173 and 1692 ions are attenuated (relative to m/z 913) by approximately a factor of 2; e.g., note the ratio 912/1173 ((n = 3)/(n = 4)) and 912/1692 ((n = 3)/(n = 6)) in Figure 4 in comparison to Figure 5. Typically, the signal intensities in the Cs^+ DI-FTMS spectrum are reproducible to 10–15%. However, when ion ejection is used, the signal intensities for some ions vary by as much as ±100%. This effect is most obvious at higher mass (see below). Similar results have been observed when performing ion ejection studies on ion–molecule reaction product ions at relatively high mass, e.g., transition metal carbonyl ions (21). We attribute this effect to the occurrence of CID reactions of some of the cluster ions. For example, CID of the ions m/z 1173 and 1692 lead to formation of m/z 913 by loss of CsI and 3 CsI, respectively (22). Likewise, the ion m/z 1433 (n = 5) is most probably arising by loss of CsI from m/z 1692. Note also that the signal at m/z 301 (Figure 4) is enhanced relative to the signal at m/z 913 in Figure 5. The details, percent conversion to product ions (CID efficiency) and the most dominant reaction channels, of low-energy CID of ionic alklai metal halide clusters by FTMS are presently under investigation (22).

The occurrence of CID upon ion ejection is due to two factors: (1) the ion ejection experiments were performed by sweeping the rf oscillator over a small mass range near m/z 393, e.g., m/z 390 (119 kHz) to m/z 400 (116 kHz). The rf oscillator which is used to eject the ions has a relatively broad band-pass; thus, the actual frequency output from the oscillator shows considerable tailing out to approximately 50 kHz. The translational energy imparted to a particular ion by the applied rf field can be calculated by using eq 1 (17, 18).

$$E_{tr} = \frac{e^2 E_1^2}{2m(w_1 - w_c)^2} \sin^2 [(w_1 - w_c)t/2] \qquad (1)$$

The terms in this equation are e, the electronic charge (e^2 equals 1.6×10^{-19} C), E_1, the applied rf electric field (V/m), m, the mass of the ion (in kilograms), and t, the duration of the applied rf field (in seconds). Thus, according to eq 1 a relatively broad range of ions receives some translational excitation during the time required to eject m/z 393. The actual energy imparted to the ion will depend upon the time duration (t) and amplitude (E_{rf}) of the applied rf excitation signal. If any of the ions receive appreciable translational excitation and undergo a collision with the residual gas molecules, it is possible that CID will occur (2). Previous studies have shown that some of the $Cs(CsI)_n^+$ cluster ions readily undergo CID. For example, McLafferty has shown that the CID efficiency (conversion of the incident ion to product ions upon collision) of $Cs(CsI)_n^+$ cluster ions ap-

proaches unity (ca. 80%) (23). This reported CID efficiency for $Cs(CsI)_n^+$ cluster ions is orders of magnitude larger than that observed for organic ions (24, 25). The reported high efficiency for CID of $Cs(CsI)_n^+$ cluster ions is also consistent with Standing's interpretation (14) of the "anomalous cluster ion intensities" in the SIMS spectrum reported by Campana (12, 13).

It may appear rather unlikely that an ion of m/z 1600 will receive sufficient translational excitation during the ejection of m/z 393 to undergo CID. However, it must be realized that the term ($w_1 - w_c$) (from eq 1) is relatively small in the high mass range. For example, the cyclotron frequencies (in hertz) for m/z 393 and m/z 1692 are 118.135 kHz and 27.430 kHz, respectively, which gives a frequency difference, ($w_1 - w_c$), of approximately 90 kHz. We routinely perform FTMS-CID studies at kiloelectronvolt energies on small molecules by applying rf excitation where the difference between the cyclotron frequency of the ion and the applied rf signal is as large as 5–15 kHz (26). Low-energy CID, which is much more efficient than kiloelectronvolt energy CID (27–29), can be performed by using excitation frequencies which differ by as much as 15–50 kHz from the ion's cyclotron frequency (30). At m/z 78, e.g., $C_6H_6^+$, a frequency difference of 50 kHz only corresponds to a mass difference of 5 amu, whereas at m/z 1600 a frequency difference of 50 kHz corresponds to a mass difference of approximately 1000 amu. On the basis of this reasoning it is quite apparent that ion ejection methods must be used with extreme caution if translational excitation of the ions is to be advoided. On the other hand, this caution should be tempered with the understanding that the results for CID of $Cs(CsI)_n^+$ during ion ejection represent a special case. However, while most organic ions do not undergo CID as readily as $Cs(CsI)_n^+$ ions, it may be possible to induce isomerization/rearrangement reactions of organic ions at energies below the dissociation threshold. If these ions are then probed further, i.e., by CID or photodissociation, the structural information obtained may be erroneous.

Having pointed out the negative aspects of using ion ejection methods, one must ask the question can ion ejection be used successfully to enhance the dynamic range of FTMS and how would such an experiment be performed? In order to enhance the mass resolution of the ion ejection step it is necessary to minimize excitation of all ions except those to be ejected. That is, one must consider what factors lead to excitation of m_x^+ ions during the ejection of m_i^+ ions, e.g., minimizing the ratio $E(m_x^+)/E(m_i^+)$. The uncertainty in the frequency of the applied rf used to eject m_i^+ is proportional to t^{-1} (31). Thus, if an rf signal is applied for 10 μs, the uncertainty in the applied frequency will be 100 kHz. On the other hand, this uncertainty in the applied frequency can be diminished by applying the excitation signal for a longer period of time. For example, the uncertainty in the applied excitation frequency can be diminished to 1 kHz if the signal is applied for 1 ms. Therefore, to enhance the resolution of the ion ejection step, it is best to use longer irradiation times. An additional advantage of longer irradiation times is that low rf amplitudes (E_1 in eq 1) can be used to eject ion m_i^+ and this will also reduce the amount of translational energy received by ions m_x^+. It must be understood, however, that there may also be adverse effects associated with longer experiment times, i.e., the occurrence of ion–molecule reactions. The concept of stocastic excitation developed by Marshall is yet another approach to enhancing the mass resolution of ion excitation/ion ejection (32). In Marshall's experiment the excitation pulse is tailored and shaped by digital (Fourier transform/ inverse transforms) filtering procedures. Although Marshall's stocastic excitation scheme is potentially useful for a variety of experiments, it is certainly of great importance for ion

ejection and tandem MS experiments.

It is rather difficult to make absolute measurements for the secondary ion yields by Cs^+ ion DI-FTMS. However, by using estimated secondary ion yields for 5-keV Cs^+ ions reported by Standing (33), we estimate that approximately 10^5 secondary ions are produced per Cs^+ ion beam pulse. Although the secondary ion yields reported by Standing (33) are for small amino acids, e.g., alanine, measurements made in our laboratory suggest that the secondary ion yields for small molecules and CsI are comparable (11). By far the dominant fraction of the secondary ions produced by DI-FTMS of CsI are Cs^+ and $Cs(CsI)_1^+$, e.g., these two ions account for about 90% of the total ion current. From the data contained in Figures 3–5, we estimate that the secondary ion yield for $Cs(CsI)_{13}^+$ is 0.001 that for Cs^+. This estimated secondary ion yield suggests that we are detecting ca. 500 ions as $Cs(CsI)_{13}^+$. Of course, the margin for error in this estimate is rather large, possibly as large as a factor of 10. However, a good signal-to-noise ratio (greater than 5/1) can be obtained for $Cs(CsI)_{13}^+$ by using a Cs^+ beam current of 1×10^{-9} A cm^{-1}; therefore, we feel confident in saying that as few as 500 secondary ions per Cs^+ pulse can be detected, and it is feasible that as few as 50 ions can be detected with a signal-to-noise ratio of 5:1 by using broad band signal detection. However, such low signal levels cannot be detected unless the much more abundant Cs^+ and $Cs(CsI)^+$ ions are removed by ion ejection.

It is interesting to compare the DI-FTMS of CsI with the data reported by Campana (12) and also Standing (14). The ratio of signal intensities for the $n = 1$ and $n = 3$ clusters agree reasonably well with the previously reported data. Similarily, the signal intensities for the $n = 4$, 6, and 9, cluster ions compare favorably with the SIMS data. The major differences in the present and previous data are in the region of $n = 2$, 5, 7, 8, 10, 11, and 12 cluster ions. The regions where the DI-FTMS signals are weak or absent correspond to the "anomalous cluster ion intensity" in the data reported by Campana (12). For example, Campana observed reduced signal intensities at $n = 5$, 7, and 8 in the SIMS spectra there are no measurable signals in the region $n = 10$, 11, and 12, which corresponds to the second "anomalous cluster ion intensity" region in the SIMS data (12, 13). Using a time-of-flight mass spectrometer and Cs^+ ion SIMS, Standing and co-workers did not observe the "anomalous cluster ion intensity" (14). Standing attributes the "anomolous cluster ion intensity" observed by Campana to the occurrence of slow decompositon reactions of the $Cs(CsI)_n^+$ cluster ions during the flight time from the ion source to the detector, which in the magnetic sector instrument is several hundred microseconds. During this long flight time a large fraction of the ions undergo unimolecular dissociation and/or CID. Beynon has recently reported on the unimolecular dissociation of alkali metal halid ionic clusters and reached similar conclusions (34).

The effect of slow decomposition reactions will be magnified for FTMS studies due to the longer time scale of this experiment. The time scale for our experimemts is roughly 20 ms. That is, the ions are detected approximately 20 ms following the ionization step. The length of time between ionization and ion detection is limited by the time required to sweep the rf excitation for detection and the signal observation time; thus, all FTMS experiments are performed on the millisecond to second time scale. Studies are presently underway to evlauate the effect of the FTMS instrument time scale on the DI spectra of large organics, viz., molecules such

as chlorophyll a which are thought to undergo slow decomposition reactions (35).

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