Optimization of the Electrodynamic Ion Funnel for Enhanced Low Mass Transmission: Influence of Funnel Operational Pressure on Ion Transmission

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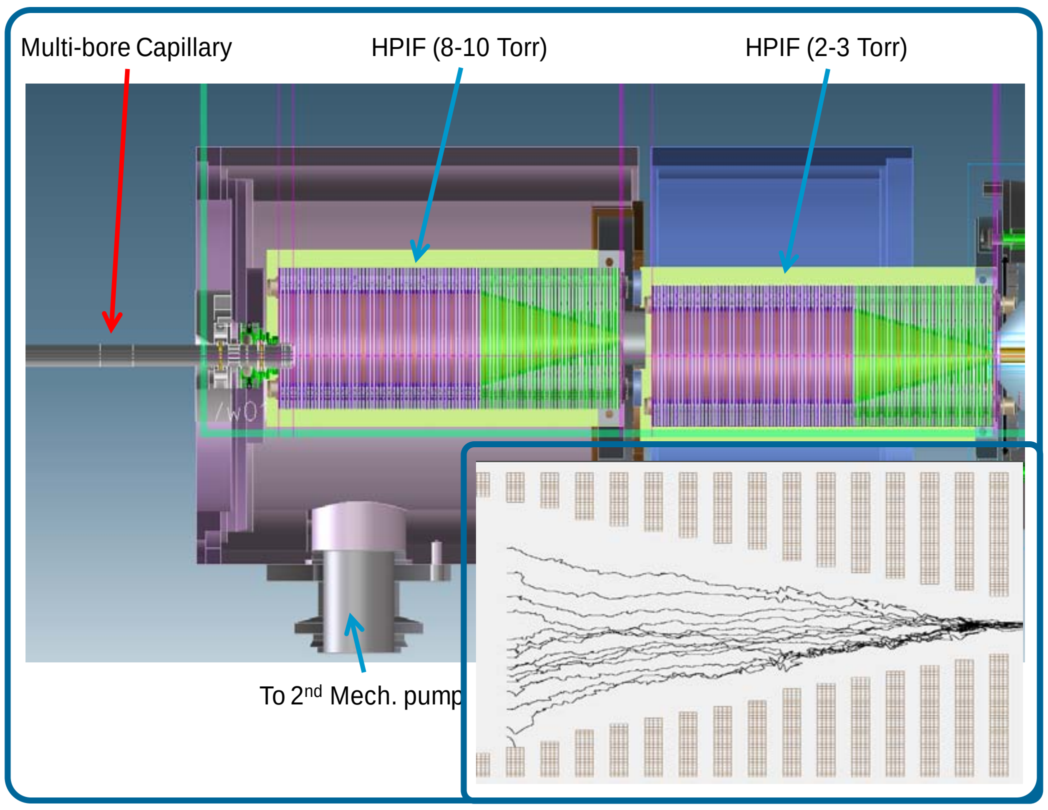
Introduction

The use of the electrodynamic ion funnel as a replacement of the skimmer has profoundly improved the transmission of ions from atmospheric pressure conditions to the sub-vacuum interiors of the mass spectrometer. In addition, the implementation of a dual ion funnel configuration permits the use of transmission interfaces with high gas-throughputs. Much has been done by R. D. Smith et al. to improve the overall transmission of ions through the ion funnel, for example, reducing the distance between plates (d), installation of the jet-disruptor, increasing the exit orifice radius (p) and more. We report optimization to the dual ion funnel resulting in a 3X increase in low mass ion transmission over the standard (p/d= 1.0) ion funnel configuration.



Experimental

Funnel Description

A standard ion funnel design is composed:

- *100 electrodes 0.5 mm thick*
- *Adjacent electrodes are insulated by Teflon sheets*
- *The inner diameter (ID) of the entrance and first 54 electrodes is 25.4 mm. The remaining electrodes then taper at an angle (α = 27.0) to an ID of 2 mm forming a "funnel"*
- *RF voltages, 180 out of phase, is applied to adjacent electrodes. The RF field confines highly dispersed ions*
- *Superimposed on the RF voltage is a DC voltage gradient which directs the ions axially through the funnel.*

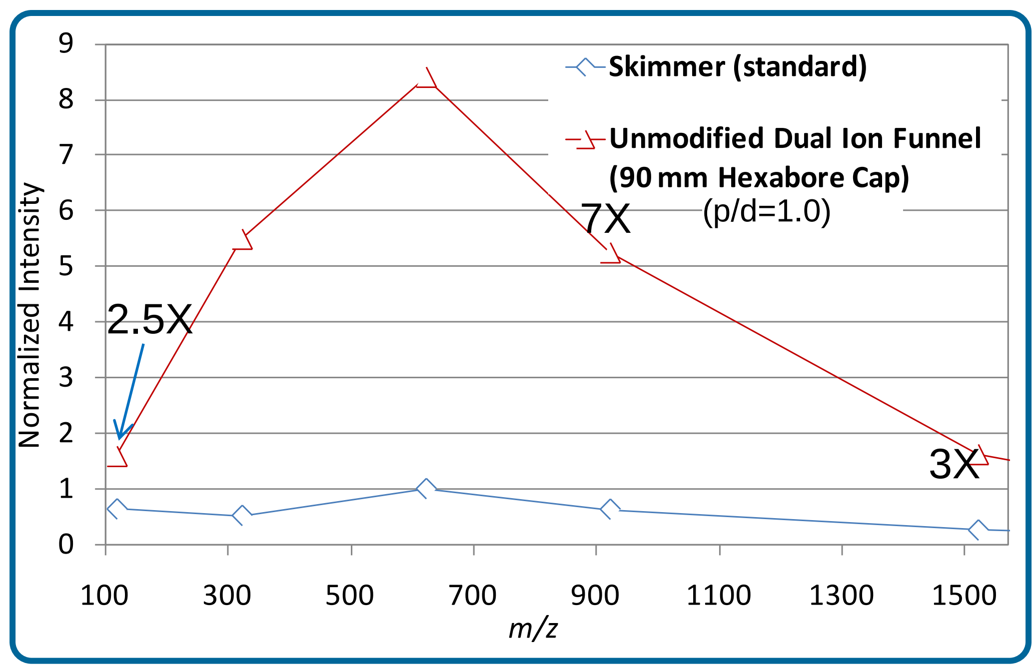
Experimental Cont'd

Due to higher gas throughput from the multi-bore capillary, a tandem ion funnel configuration (dual ion funnel, DIF) is employed [J. Am. Soc. Mass Spectrom. 17, 2006, 1299]. The first of the two ion funnels was optimized for high pressure conditions (7 – 30 Torr) and second ion funnel was optimized for pressures between 0.5 and 4.0 Torr. With the DIF, the pressure downstream of the capillary exit is differentially reduced. The Agilent 6460 QQQ equipped with the AJS source was employed for this investigation.

Results and Discussion

Observed Gains using the Un-Modified Dual Ion Funnel

With the unmodified IF, a 7X gain was realized for 922 m/z. The observed gain for the 118 m/z ion was 2.5X. The low gain observed for the 118 m/z ion indicate most of the low mass-high mobility ion population are lost within the ion funnel. Previous experiments and calculations (not shown) indicated relatively high transmission through the capillary.



Stalling Fields, RF Traps, and Ion Scattering

The lackluster gain observed for the 118 m/z ion has to do with poor transmission efficiency through the ion funnel for low masses as a result of "RF traps," RF stalling fields, and gas-induced ion scattering losses. Two different trapping mechanisms can be envisioned as occurring in the funnel. The first is the result of a mass dependent RF confining "wall" removed from the electrode edges by a finite distance, d_{rf}. The confining potential, V^*_{RF}, "felt" by each ion varies inversely by mass as shown in Eq. 1

$$V_{RF}^{*}=(q^2 V_{rf}^2)/(4m\omega^2) \qquad (1)$$

where q is the ion charge, V_{rf} is the 0 – p RF voltage, m is the mass of the ion and ω is angular frequency equivalent to 2πf, and f is the RF frequency. In other words, the effective confining diameter, d_{eff}, "felt" by each ion is smaller than the electrode diameter, d, (d_{eff} < d).

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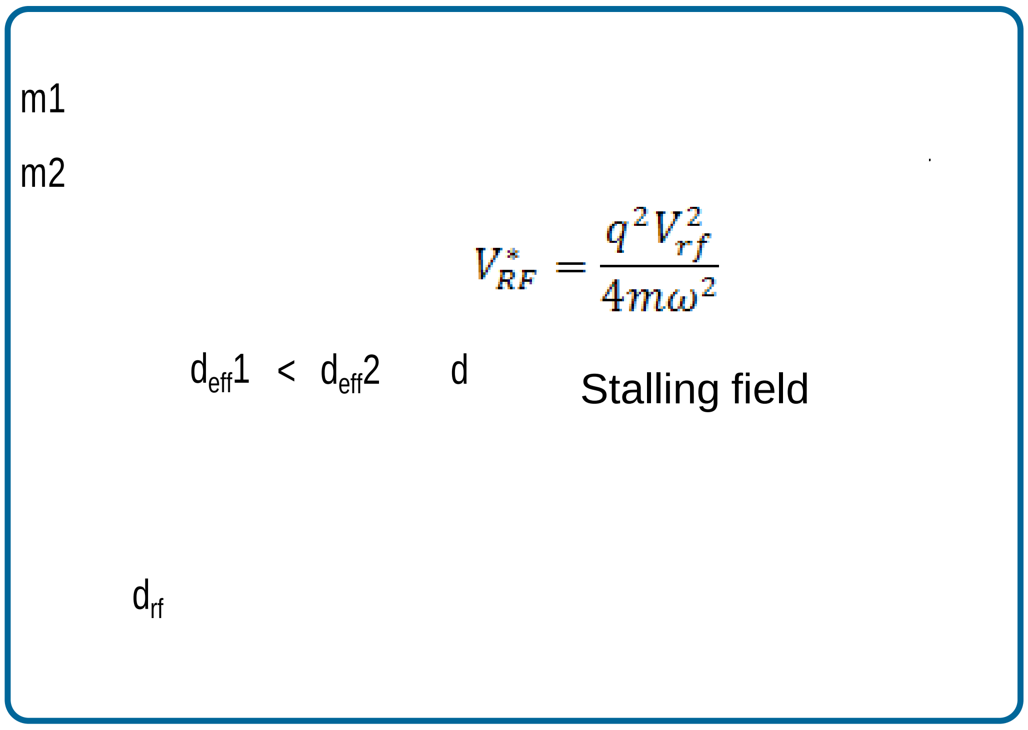
Results and Discussion Cont'd



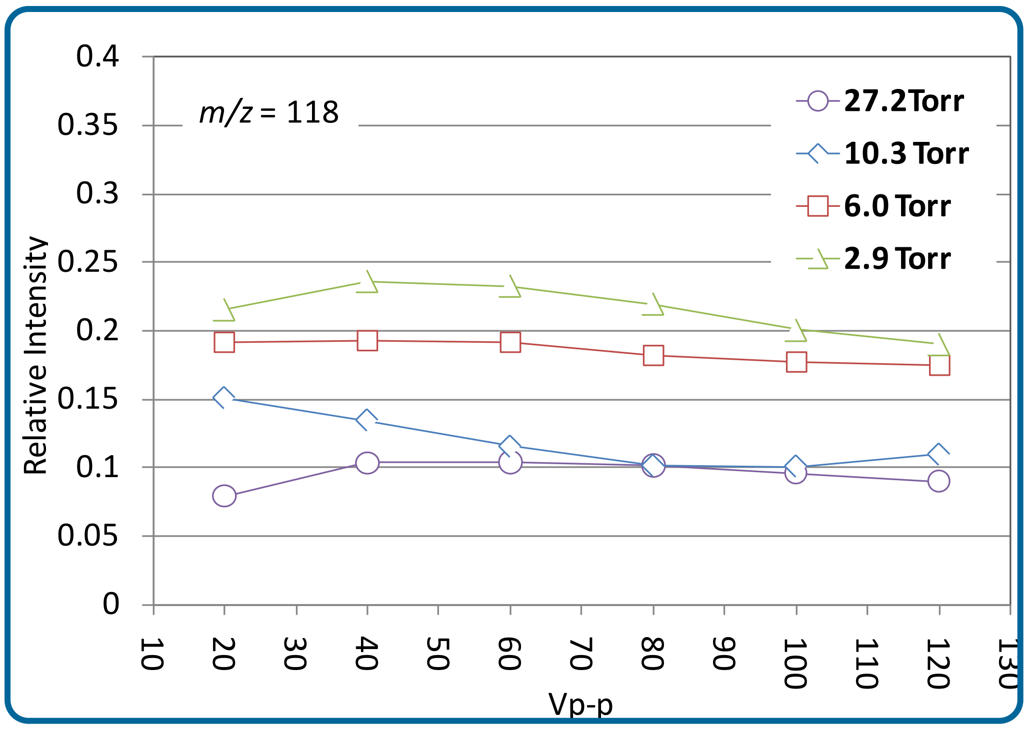
Stalling Fields, RF Traps, and Ion Scattering cont'd

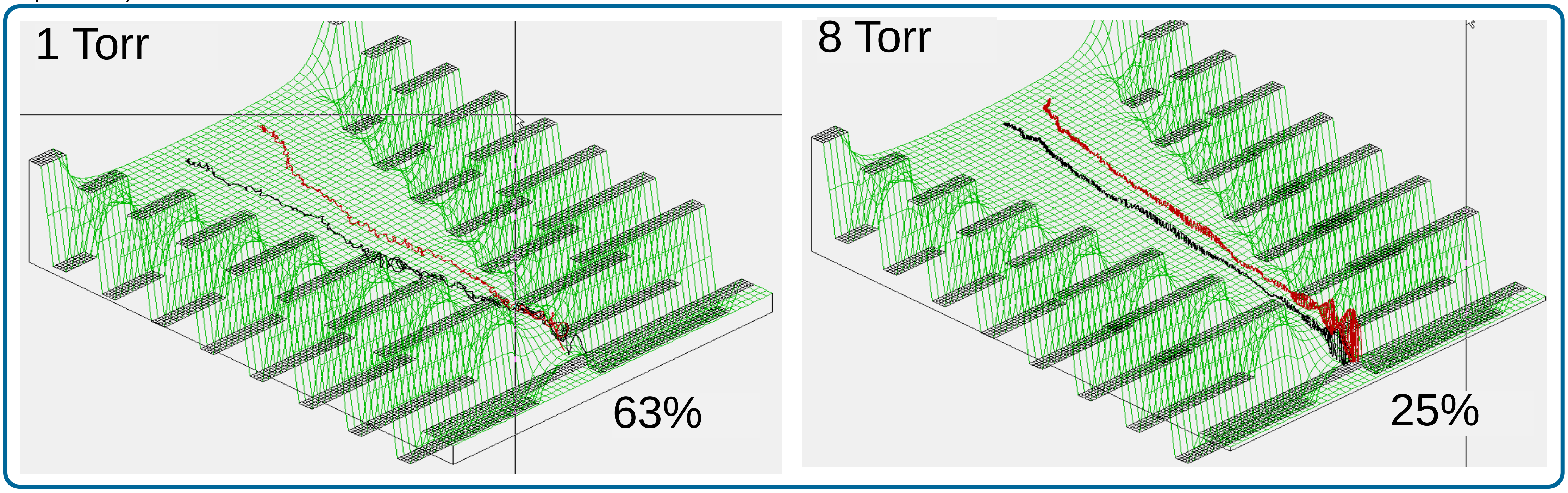
Eq. 1 shows that the d_{rf} for low mass ions (m2) is larger than the d_{rf} of the larger mass ions (m1). Now as the ion funnel electrodes orifice, d, decreases, d_{rf} remains unchanged. A critical d is reached where d_{rf} collapses on itself thus forming a stalling field for the low mass ions. Smaller ions stalled by the RF field eventually become unstable and are lost to the funnel electrodes.

The second trapping mechanism is the so-called "axial traps." [Tolmachev, A. V.; Kim, T.; Udseth, H. R.; Smith, R. D.; Bailey, T. H.; Futrell, J. H. Simulation-based Optimization of the Electrodynamic Ion Funnel for High Sensitivity Electrospray Ionization Mass Spectrometry. Int. J. Mass Spectrom 2000, 203, 31 – 47] These are wells formed by the pseudo potential field between funnel electrodes. The depth of these wells increase as the electrode orifice diameter decreases. As with RF stalling fields, axial traps become especially detrimental to low mass ion transmission at the ion funnel exit where the electrode orifice diameters tend closely to the distance between adjacent electrode plates (1.0 mm)

The combination of RF traps and stalling fields, gas scattering effects, space charge, and radial gas flows leave the low m/z ions vulnerable to loss at the funnel exit. Serendipitously, one modification - increasing the funnel exit orifice, mitigates most of the exit-field problems. Increasing the exit orifice also has the negative effect of increasing the gas load downstream of the MS.

Low mass-high mobility ions are susceptible to scattering upon collision with buffer gas especially in the decelerating pseudo-potential fields near the funnel exit. Experiments and simulations monitoring the dependence of the 118 m/z ion transmission efficiency on buffer gas pressures is shown below. In this figure, the relative intensities of 118 m/z, RI_{118}, where $RI_{118} = I_{118}/\Sigma(I_{118}, I_{322}, I_{622}, I_{922}, I_{2122})$, was plotted as a function of RF voltage (Vp-p) at different buffer gas pressures. The 118 m/z ion intensity showed an inverse relationship to gas pressure, the transmission efficiency dropped with increasing pressure indicating gas-dynamics induced ion-scattering of the low mass ions. SIMION simulations also showed the same trend





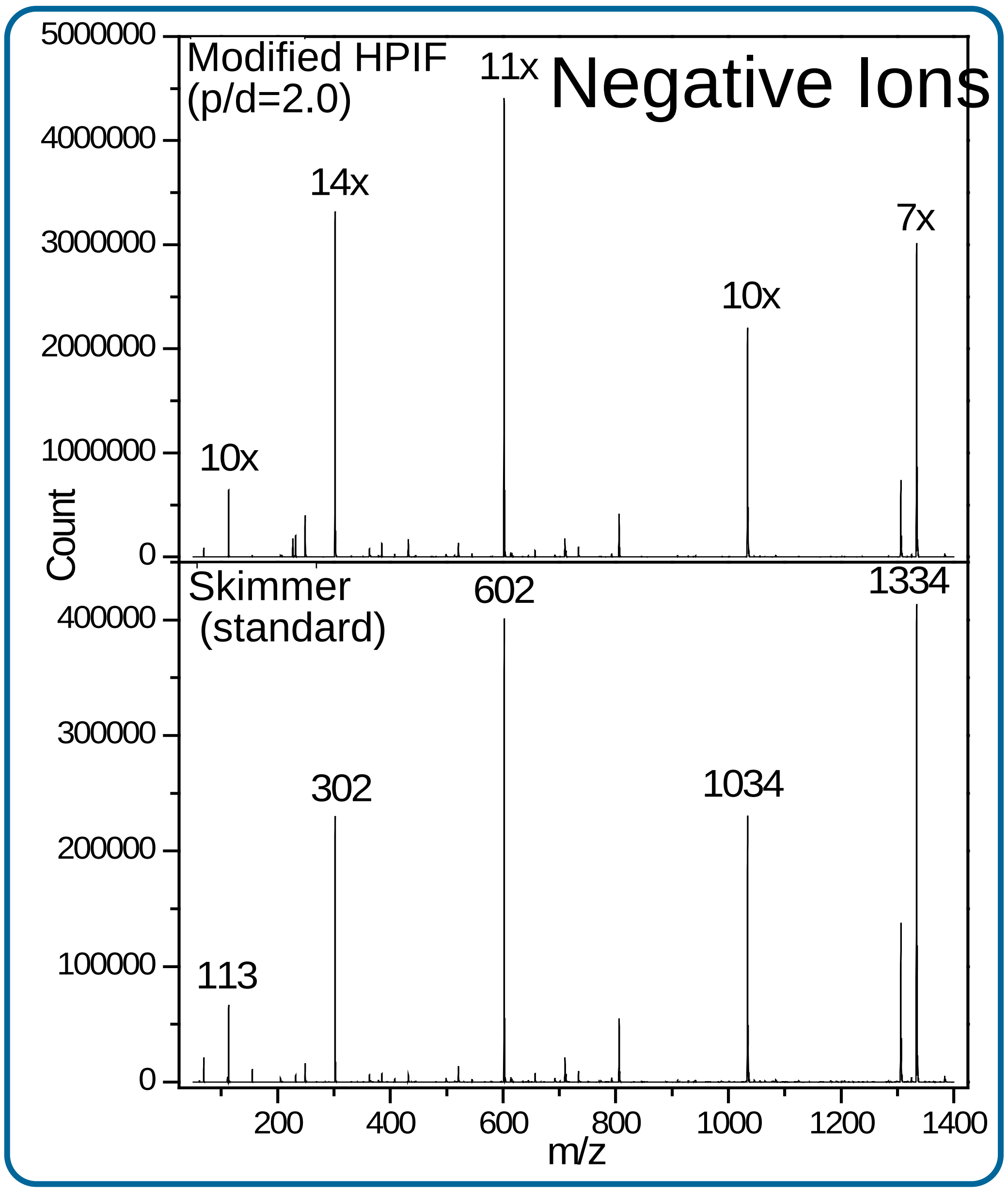
Results and Discussion Cont'd

The inverse relationship trend between ion intensity and funnel pressure was not observed for the high masses

This observation suggest several things:

(i) Ion loss due to gas scattering occurs predominately in the HPIF where the operational pressure is between 8 and 13 Torr. Therefore, measures to improve low mass ion transmission need not be applied monolithically to both funnels as they operate at distinctly different pressures

(ii) Gas dynamic induced ion losses are just as important as RF traps and stalling fields especially for funnels operating at high pressures. Any increase in the funnel exit orifice diameter above the critical diameter, should be informed by the operating pressure of the funnel



It should be added that the trend described above was not due to the pressure influence on the RF field confining strength as described by Eq. 2

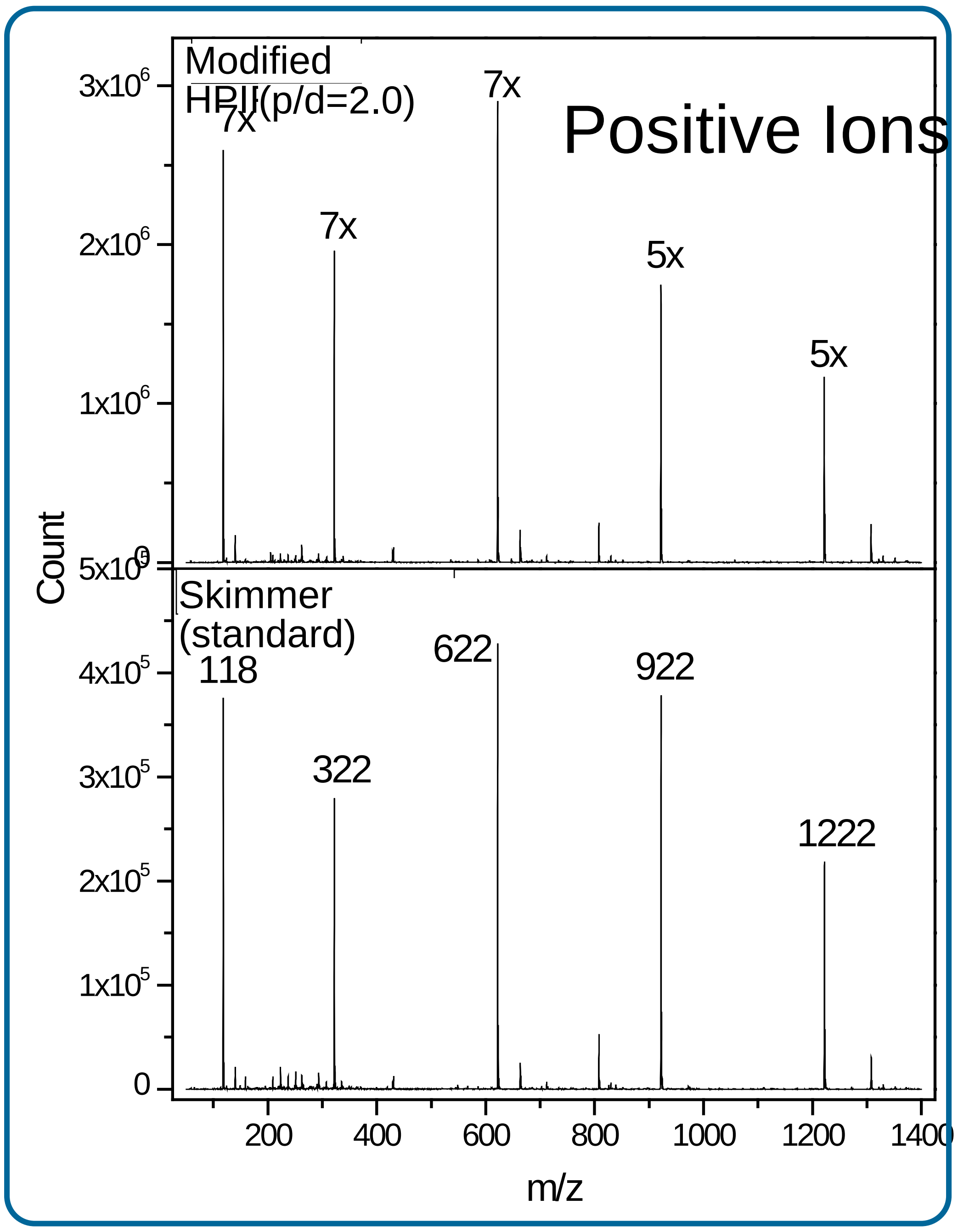
$$V_{eff}^{*(p)} = (\tau(p)^2 \omega^2)/(1+\tau(p)^2 \omega^2) \qquad (2)$$

where τ(p) is the relaxation time

Even though the confining field strength at 27 Torr is only 7% of the field strength at 3 Torr, the former adequately confined the higher mass ions which showed enhanced signal with pressure increase

Modification to the Dual Ion Funnel

When the exit orifice of the high pressure ion funnel (HPIF) was increased from a p/d ratio of 1.0 to ≈2.0, the transmission of the 118 m/z ion increased by 7X compared to the standard capillary configuration. This is approximately a 300% increase compared the HPIF with p/d ratio of 1.0. It should be added that the same change made to the low pressure ion funnel resulted in a mere 17% increase in low mass transmission



Conclusions

- *The absolute intensity of low mass ions through the dual ion funnel was increased 7X compared to the skimmer configuration without increasing the pressure downstream of the MS*
- *Measures to increase the ion funnel efficiency should be informed by the operating pressure of the funnel*
- *Gas-induced ion scattering is just as important as stalling fields and axial traps for low mass ion transmission especially for funnels operating at high pressures*