

lations in the other channel. The slight shift of the optimum ion transmission conditions to lower jet disturber voltages for higher  $m/z$  ions, as shown in FIG. 6, may be related to the higher inertia of the ions in the gas flow.

A square waveform voltage signal of different frequencies and duty cycles with adjustable DC offset is applied to the jet disturber. The reserpine sample solution was used for the jet disturber channel electrospray. Selected ion monitoring mode with an 0.8-amu scan window centered at reserpine ions and a 250-ms scan time were used for the MS operation. FIG. 7 shows the ion peak intensity variation for 1 min of data acquisition. The frequency of the square waveform is 0.2 Hz with 95% duty cycle, which results in a 250-ms open and 4.75-s closed time. The amplitude of the square wave is 56 Vp-p with a DC offset of 128 V, which results in a 156 V high and 100 V low potential variation on the jet disturber. The regularly spaced peaks, as shown in FIG. 7, clearly indicate that dynamic ion transmission modulation can be effectively achieved at very short time. Experimentally, it was observed that effective dynamic ion transmission modulation can be obtained even at a square waveform frequency of 0.8 Hz with 99% duty cycle, which results in a 12.5-ms open time. The data acquisition may become a problem at such high modulation speeds because of the limitations of the mass spectrometer scanning speed. Even at the scan speed of 250 ms, as shown in FIG. 7, the number of data points across each peak is significantly reduced. This may have resulted in the apparent broadening of the peak width. However, the present results confirm that the effective ion modulation is feasible at high speed.

The experimental investigation of the dual-channel ion funnel interface was further accompanied by theoretical studies. Ion trajectories in the jet disrupter channel of the ion funnel were simulated with a DC-only jet disturber positioned on the axis. The computer model was based upon theoretical approaches and algorithms developed previously for the simulation-based optimization of the ion funnel as described in Shaffer, S. A.; Tolmachev, A.; Prior, D. C.; Anderson, G. A.; Udseth, H. R.; Smith, R. D. *Anal. Chem.* 1999, 71, 2957–2964, Tolmachev, A. V.; Kim, T.; Udseth, H. R.; Smith, R. D.; Bailey, T. H.; Futrell, J. H. *Int. J. Mass Spec.* 2000, 203, 31–47 and Tolmachev, A. V.; Kim, T.; Masselon, C. D.; Rakov, S. V.; Pasa-Tolic, L.; Harkewicz, R.; Tang, K.; Udseth, H. R.; Smith, R. D. Proceedings of the 49th ASMS Conference, Chicago, Ill., May 2001. The model allowed us to review various configurations of the device and obtain appreciation of its operation at different conditions, as given by RF frequency and amplitude, DC potentials, gas pressure, ion  $m/z$ , and gas flow configuration. The ion trajectory calculations take into account RF and DC electric fields and the bath gas influence. The original model described in Tolmachev, A. V.; Kim, T.; Udseth, H. R.; Smith, R. D.; Bailey, T. H.; Futrell, J. H. *Int. J. Mass Spec.* 2000 was modified to account for the ion funnel geometry changes as described below.

A 9-mm channel diameter was used for the jet disturber ion funnel channel. At the jet disturber position, two RF rings were replaced by a DC-only ring with the DC potential being equal to the jet disrupter potential. The jet disturber was simplified as a 2-mm-o.d. conductive disk positioned at the center of the channel. The gas flow was simplified as a superposition of the constant flow in the axial direction and a circular flow field satisfying the condition of the zero velocity at the jet disturber surface to account for the turbulence around the jet disturber. Divergent gas flows can also be predefined at the exit of the channel as shown in Tolmachev, A. V.; Kim, T.; Masselon, C. D.; Rakov, S. V.;

Pasa-Tolic, L.; Harkewicz, R.; Tang, K.; Udseth, H. R.; Smith, R. D. Proceedings of the 49th ASMS Conference, Chicago, Ill., May 2001.

As in previous ion funnel studies, it was found that the gas flows can be of significance for relatively high pressure and for ions with large cross section. Ion motion in the 1 Torr pressure range occurs in a transition region between vacuum type motion for distances  $\ll 1$  mm and drift motion, where ions follow the direction of the field in the reference frame of the gas flow, which typically provides the dominant component. The model used was capable of realistically describing this behavior, including the random (i.e., diffusion) component of the ion motion, collision damping of the ion kinetic energy, effective focusing of ions in the RF fields, and ion motion in the DC fields.

The simulated ion transmission curve, as shown in FIG. 8 for 10 nA total ion current, is qualitatively consistent with the experimental results, as shown in FIG. 6. Ion transmission in the ion funnel was suppressed when a sufficient DC offset, defined as the potential difference between the jet disturber and the neighboring ion funnel plate, was applied to the jet disturber (either positive or negative). At zero, or slightly positive DC offsets, the ion transmission reached a maximum. The ion trajectories (FIG. 8) also show the different operation modes for negative, optimal, and positive DC offsets. FIG. 8a shows ion trajectories for an offset  $V_{jd} = -30$  V. All ions were attracted to the jet disturber plate and recombined on its surface. For zero or small positive DC offset, ions avoided the jet disturber, drifting at larger radii (FIG. 8b). Finally, for significantly large positive DC offsets, ions encountered a DC potential barrier and were forced to recombine on the neighboring RF ring electrodes (FIG. 8c). The DC potential profile corresponding to the latter case is further shown in the FIG. 9. The simulation in FIG. 9 clearly indicates that a DC potential barrier exists at any radial position at the jet disturber location, which explains the effective ion transmission modulation in the channel. It is also expected that a potential well will be developed near the jet disturber for the negative DC offset on the jet disturber, which is equally efficient for ion transmission modulation. These results show the experimentally observed behavior of the device is consistent with the physical concept outlined above and can be described reasonably well with the theoretical model. Both experimental evaluation and theoretical simulations show that the ion transmission efficiency for different  $m/z$  ions in the small diameter channel of the ion funnel can be effectively modulated by varying the bias voltage on the jet disturber. The optimum ion transmission voltage on the jet disturber is approximately equal to the DC potential on the neighboring regular ion funnel plate. Efficient ion transmission, similar to the standard single channel ion funnel, is maintained in the main channel of the ion funnel for a broad range of  $m/z$  ions (100–2500), whereas ion transmission in the jet disturber channel is effectively modulated. This indicates negligible “cross talk” of ion transmission between the two ion funnel channels. The approach ensures that both the spatial and the kinetic energy distributions for calibrant and analyte ions are identical, which is important for accurate mass measurements in Fourier transform ion cyclotron mass spectrometry. Both static and dynamic modulations of the ion transmission have been experimentally demonstrated by applying a constant voltage, either DC or AC, to the jet disturber. Consistent ion transmission behavior in the jet disturber channel of the ion funnel is obtained from both experiment and theoretical simulations. The dual channel interface developed through this study, when combined with FTICR, provides the basis