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Cooling of direct current beams of low mass ions

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Abstract

Collisional focusing of low mass ions of 1–40 eV is investigated in a rf-only quadrupole. The final ion intensities and energies are monitored by an orthogonal-extracting time-of-flight mass spectrometer. It was found that in this energy range Na^+ and K^+ ions can be cooled and focused as well as Cs^+ ions if the residual gas pressure in this “quadrupole beam cooler” is high enough that each ion undergoes several collisions. (Int J Mass Spectrom 181 (1998) 27–30) © 1998 Elsevier Science B.V.

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1. Introduction

The energy of an ion beam can be reduced by collisions of the ions with residual gas atoms and molecules. Such coolings have been achieved for a pulse of light ions in ion traps [1, 2] as well as in rf-only quadrupole arrangements [3, 4] for a dc beam of large molecular ions. In such a “quadrupole beam cooler” the ions are dragged through residual gas while oscillating between quadrupolar rods to which a radio frequency signal of several 100 V amplitude is applied. Large ions are cooled in such an arrangement. However, for small ions it is not obvious that such a cooling is achievable at all since the energy exchanges per collision and the changes in flight direction are large for ions whose masses are similar to the buffer gas molecules/atoms [5]. This effect can be diminished by using He as a buffer gas. However, our experiments were performed with air.

The system used for the experiments was an existing electrospray-ionization time-of-flight mass spectrometer with an orthogonal ion acceleration [6]. In this system electrosprayed ions pass from a region of ≈ 1 mbar into the quadrupole beam cooler at $\approx 10^{-3}$ mbar. From here they exit into a region of $\approx 10^{-5}$ mbar. In this low pressure region the ions are accelerated orthogonally to their initial flight direction by 6000 V pulses (see Fig. 1.). Their flight times and intensities are recorded after a flight path $L_y \approx 3$ m. Due to the orthogonal extraction our detection sensitivity is strongly dependent on K_{2x}, the initial ion energy in x direction in the extraction region (see Sec. 2.2). Thus the energy distribution of the ions exiting the “cooler quadrupole” can be investigated.

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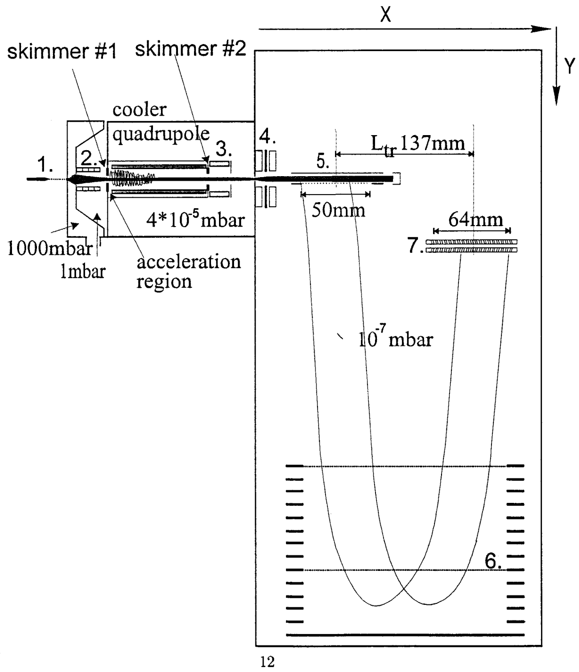

Fig. 1. The electrospray ionisation orthogonal extraction time-of-flight mass spectrometer (ESI-TOF) used for the experiments. (1) Spray capillary, (2) interface chamber, (3) dc quadrupole, (4) einzellens, (5) extraction region, (6) reflector, (7) detector.

Table 1
Free path lengths λ at a pressure of 0.015 mbar for Na^+, K^+, and Cs^+ ions at energies of 1/40 and 1 eV according to the Langevin ion–molecule interaction [7] and for hard spheres

m (amu)	λ (mm) for 1/40 eV ions	λ (mm) for 1 eV ions	λ (mm) for hard spheres
23	1.3	8	20
39	1.0	7	16
133	0.7	5	13

2. Performed experiments

In the described setup the ions enter the quadrupole beam cooler through a small skimmer #1 and exit the quadrupole beam cooler through a somewhat larger skimmer #2. The size of skimmer #2 has been varied in the experiments so that the pressure along the quadrupole beam cooler dropped to 4×10^{-5} mbar from 0.015 mbar (the “high pressure” case) or 0.005 mbar (the “low pressure” case), respectively.

In detail the ions exit skimmer #1 in a supersonic beam with a narrow energy distribution below 1 eV [7]. In the 2 mm acceleration region between skimmer #1 and the cooler quadrupole (see Fig. 1.) ions will be accelerated to an initial energy K_{x1} (up to 40 eV) by varying the potential of skimmer #1. The free path length in the acceleration region depends on the ion energy. For low energy ions (up to ≈2 eV) polarization will lower the free path length [8], whereas for high energy ions the hard sphere cross section determines the free path length. Table 1 shows that all free path lengths are sufficiently large so that ions can be accelerated for both pressure cases by the potential difference set in the acceleration region.

Singly charged ions of Na^+ (M = 23 u), K^+ (M = 39 u) and Cs^+ (M = 133 u) were selected by their flight times through the full mass spectrometer with beam cooling achieved by rf voltages on the quadrupole electrodes of 200 and 440 V over the quadrupole aperture of 7 mm. The 200 V case was optimal for K^+ ions and still allowed Na^+ ions to be recorded while the 440 V case lead to higher intensities of the Cs^+ ions but cut off the Na^+ ions. The data acquisition software we used [9] allowed us to collect series of mass peak intensities as a function of various parameters.

2.1. Intensity as a function of the initial ion energy

Ion intensities were recorded on the detector (see Fig. 1) for different initial energies K_{x1} ranging from 1 to 40 eV as is shown in Fig. 2 for Cs^+ and K^+ ions for both the “high pressure” and the “low pressure” case. It was found that: (1) low mass ions must have an initial energy K_{x1} of a few electron volts to be transported efficiently into the quadrupole beam cooler (≈2, ≈5, and ≈10 eV for Cs^+, K^+, and Na^+ ions, respectively); (2) for K^+ and Na^+ ions the recorded intensities are almost independent of the initial energy K_{x1} up to 40 eV for both pressure cases; (3) for Cs^+ ions the intensity is reduced by a factor of ≈10 if the initial ion energy K_{x1} is raised from 2 to 40 eV in the low pressure case while this drop off is considerably reduced for the high pressure case.

The small-ion transmission through the quadrupole

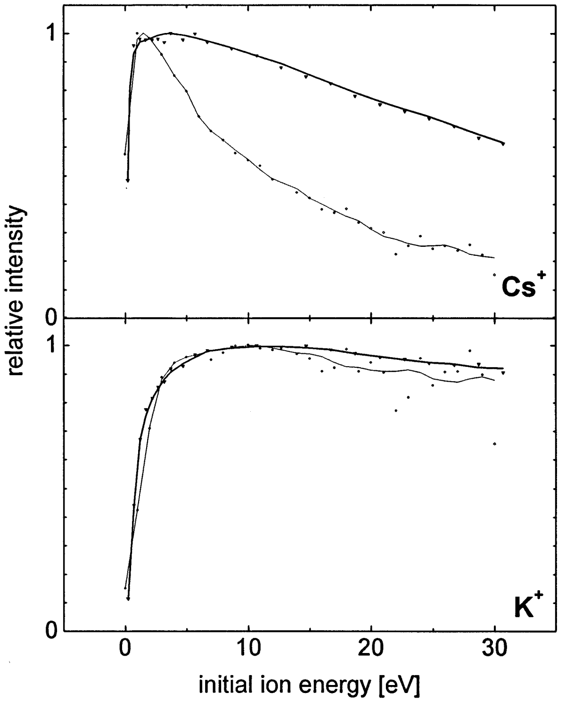

Fig. 2. Recorded ion intensities as function of the ion input energy into the rf-only quadrupole for Cs^+ and K^+: for the high pressure case (thick line) and for the low pressure case (thin line). The large scatter for the low pressure case is due to unstable spraying conditions during the experiment. The rf voltage was 440 and 200 V for the low and the high pressure cases, respectively.

beam cooler thus does not depend on the initial ion energy as long as K_{x1} is larger than a few electron volts. For the heavier Cs^+ ions, however, we conclude that in the low pressure case the transmission is poor at higher energies since the ions do not undergo sufficiently many collisions to be cooled. The signal intensity for the two pressure cases seems to be very similar for cooled ions, however, our experiment is not really set up for this comparison.

These results suggest that there is beam cooling for light ions despite their large energy transfers per collision. They suggest also, however, that the cooling for heavier ions requires increased gas pressures since the fractional energy loss per collision corresponds to $2mM/(m + M)^2$ for hard sphere collisions, with m being the mass of the residual gas molecule or atom and M being the ion mass (according to this formula it requires about 10 collisions for 20 eV Na ions and about 25 collisions for 20 eV Cs ions to equilibrate with the surrounding gas). To confirm this conclusion we have investigated the energy distribution of the "cooled ions."

2.2. Energy distribution of ions exiting the quadrupole beam cooler

The ion motion from the orthogonal extraction region (see Fig. 1) to the detector can be split into velocity components $v_x \propto \sqrt{K_{x2}/m}$ and $v_y \propto \sqrt{K_{y2}/m}$ in x and in y direction. K_{y2} is the energy the ions have acquired by the 6000 V pulse extraction and K_{x2} is the energy the ions have when they enter the extraction region. K_{x2} is determined by the energy the ions have acquired by the potential difference between the extraction region and skimmer #2 as well as by the energy distribution at the exit of the "cooler quadrupole."

The overall flight time of a selected ion from the extraction region to the detector (see Fig. 1) is $T = L_y/v_y$, where L_y is the so-called effective flight path length. During this time the ion moves in the x direction over the path length $L_x = Tv_x$. The ion will be detected if L_x is in the range determined by the dimensions and relative positions of the extraction region and the detector. Thus, the sensitivity curve as a function of the ion energy in the x direction is broad as is shown in Fig. 3. The relative intensity is calculated for a monoenergetic ion beam at different energies K_{x2}. (The shown curve is corrected for an energy dependent loss of ions in the acceleration region.). The average energy of 12.5 eV for K_{x2} is obtained from the relations $v_x/v_y = L_x/L_y$, and hence $K_x/K_y = L_x^2/L_y^2$, using $L_y \approx 3$ m and $L_x = 0.137$ m (the distance between the centers of extraction and detector windows) for our mass analyzer.

In the experiment K_{x2} is varied by the skimmer #2 potential, which is the same as the cooler quadrupole potential. For initial energies $K_{x1} = 1.5$ eV and $K_{x1} = 20$ eV the energy distribution K_{x2} of the ions was investigated. Fig. 3 shows the recorded intensities in dependence of the skimmer #2 potential. The measured, normalized intensity dependencies follow

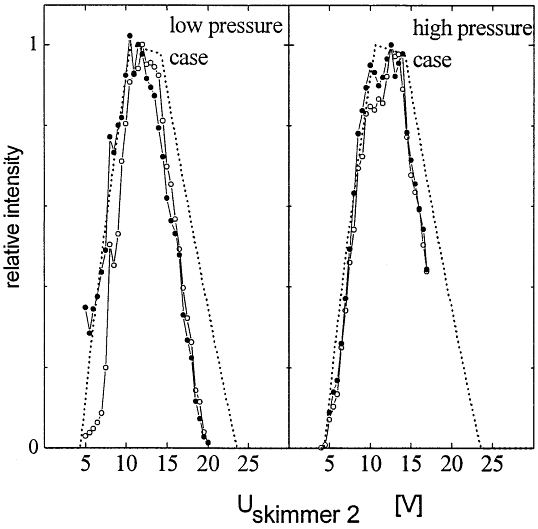

Fig. 3. Normalized Cs^+ intensities as function of the skimmer #2 potential for two different input energies. The upper graph corresponds to the high pressure case and the lower graph to the low pressure case; for 1.5 eV ions (○); for 20 eV ions (●); theoretical intensity for cooled ions (· · ·). Similar results were obtained for K^+ and Na^+.

closely the theoretical ones for Cs^+ ions (see Fig. 3) as well as for K^+ and Na^+, which are not shown. These curves imply that the energy distribution of the ions at the exit of the cooler quadrupole is rather small since a broad energy distribution would lead to a measured intensity dependence that is broader than the theoretical one. The fact that the measured and the theoretical maximum intensities are very similar, also supports the assumption that the energy of the ions is determined precisely by the skimmer #2 potential. Therefore, we conclude that all detected ions are thermalized within 1 eV at the exit of the cooler quadrupole. Actually the measured curves are narrower than the theoretical ones, which may be due to the dc focusing optics between skimmer #2 and the ion acceleration region, which is optimized for 12.5 eV ions.

It is surprising that even 20 eV Cs^+ ions follow closely the theoretical sensitivity curve, in spite of the fact that a large percentage of the ions is not detected (see Fig. 2). Probably either the more energetic ions are preferentially located far away from the initial beam axis and are not well focused into the extraction region or they are lost preferentially within the cooler quadrupole. Bad transmission at the quadrupole exit is rather unlikely considering that the aperture of skimmer #2 is larger than the quadrupole aperture at least for the low pressure case.

3. Conclusion

It is shown that collisional focusing can be achieved in a rf-only quadrupole for ions that have the same masses as the buffer gas molecules/atoms. For higher mass ions ($m = 133$) a higher pressure is required to cool the ions sufficiently within the rf-only quadrupole. The transmission efficiencies themselves could not be investigated with the our experimental setup. From comparison with a similar electrospray time-of-flight mass analyzer without a cooler quadrupole the transmission is estimated to be rather high.

Acknowledgements

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