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Cooling beams of negative ions

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Abstract

Negatively charged atomic ions have been cooled in gas-filled rf-quadrupoles from injection energies between 10 and 150 eV to final energies below 0.5 eV. By choosing the atoms or molecules of the buffer gas to have low masses as compared to the masses of the ions to be cooled, the energy transfer in ion–atom or ion–molecule collisions is minimized. For small enough initial ion energies thus only a small percentage of the ions is neutralized in the collision processes. For Cl^- and I^- ions cooled in a He buffer gas we have achieved absolute transmission efficiencies of more than 50%. (Int J Mass Spectrom 218 (2002) 199–205)
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1. Introduction

Collisional cooling effects have been used to reduce the energy spread and thus after acceleration the phase-space volumes of ion beams [1]. In such “beam coolers,” the ions are passed through gas-filled electric rf-quadrupoles to which a longitudinal dc-field is superimposed so that the ions keep their forward motion under all circumstances. This was achieved by segmenting the quadrupole electrodes (see Fig. 1) and applying to these segments through a resistor and capacitor network proper ac- and dc-potentials. In such quadrupoles the ions are cooled from energies of many 10 eV to energies of a few 0.1 eV. This cooling also reduces the transverse beam size and confines the ion beam to a region close to the optic axis of the quadrupole (see Fig. 1). After acceleration these ions can thus form a narrow beam of low divergence.

Collisional beam cooling has been achieved for positive ions [1]. In this article, we describe experiments in which beam cooling has been achieved also for negative atomic ions (see Fig. 2). Such ions are of importance for mass spectrometric investigations of ions but also for ions that later are to be accelerated in a tandem accelerator. This is done for instance in the Holifield Radioactive Ion Beam Facility (HRIBF) of the Oak Ridge National Laboratory to study astrophysical problems [2] or nuclear properties of neutron-rich or neutron-deficient nuclei [3].

Ions of already accelerated nuclei can also be cooled directly when they move in storage rings. In one such method the diameter of the beam of ions

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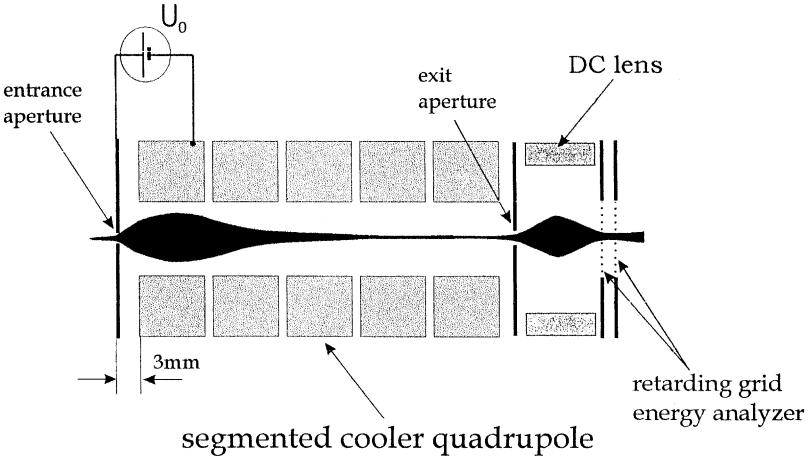

Fig. 1. Schematic diagram of the cooling experiment. The device used consists of a gas-filled rf-quadrupole whose electrodes are segmented and connected to a resistor and capacitor network that provides a longitudinal dc-field of ≈10 V/m that is superimposed to a much higher lateral rf-quadrupole field. Since the ions pass through the "entrance aperture" under large angles, the beam diameter is wide in the first part of the cooler quadrupole. It is narrow in the second part, however, at which position the ions have already lost most of their initial kinetic energy in ion–atom or ion–molecule collisions.

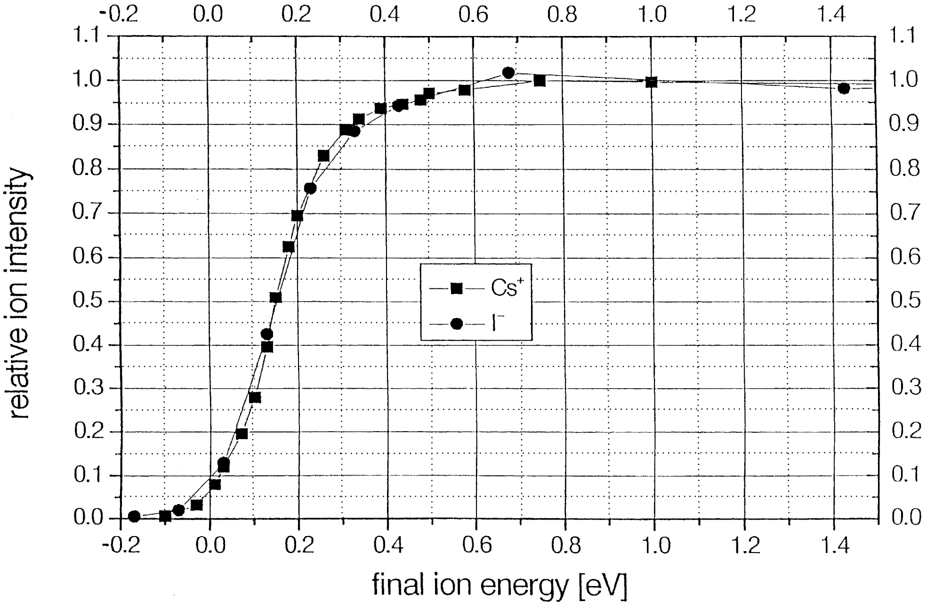

Fig. 2. Retardation curves for I^-- and Cs^+-ions, that have been cooled in a 170 mm long gas-filled cooler quadrupole, accelerated to 6.8 eV and energy analyzed by a retarding grid analyzer. Note that independent of the initial ion energy K_0 or the buffer gas used about 80% of the ions have final energies within a spread of $\Delta K \leq 0.3$ eV.

in the ring is monitored continuously and those ions that start to leave the beam are quickly deflected back toward the beam axis [4]. In another such method a beam of very monoenergetic electrons is forced to overlap a beam of positive ions in the ring, in which case the Coulomb forces between ions and electrons cause the ions to move with the velocity of the electrons [5]. Both methods require, however, at least a few seconds to become effective. The described cooling method on the other hand is effective in ≈1 ms, so that it can be used to cool ions of short-lived nuclei, like the ions of neutron-rich nuclei that all have life times of a few milliseconds at least.

2. Basic considerations

2.1. Ion–atom and ion–molecule collisions in a buffer gas

The energy loss an ion experiences in elastic collisions with buffer gas atoms or molecules, when it moves through a gas-filled quadrupole, can be calculated by computer simulations by repeatedly determining the energy transfer ΔK in ion–atom or ion–molecule collisions [6]. For such calculations, ion–atom or ion–molecule collision cross-sections should be used that vary with the relative ion–atom or ion–molecule velocities v. For higher relative velocities v the "hard sphere collision model" should be used that predicts velocity-independent cross-sections, σ_{H} [7] that are largely determined by the sum of the geometrical cross-sections of the collision partners. For lower relative velocities v the Langevin collision model [7] should be used that predicts collision cross-sections $\sigma_{\mathrm{L}}(v)$ that increase with $1/v$. For one specific velocity $v = v_{\mathrm{H}}$ the two cross-sections should be equal, i.e., $\sigma_{\mathrm{L}}(v_{\mathrm{H}}) = \sigma_{\mathrm{H}}$.

Entering ions of initial velocity v_0 into a gas-filled "cooler quadrupole" the ions will loose energy by ion–atom or ion–molecule collisions continuously until they move with a rest velocity $v_{\mathrm{f}} \ll v_0$ that is limited by the thermal energy of the atoms or molecules of the buffer gas and by the lateral rf-fields that exist close to the quadrupole axis.

1. To reduce the initial ion velocity v_0 to the "critical velocity" v_{H} the ions must move in the cooler quadrupole for a distance [6]

$$l_{\mathrm{H}} = \frac{(m_{\mathrm{i}} + m_{\mathrm{g}})^2}{n \sigma_{\mathrm{H}} m_{\mathrm{i}} m_{\mathrm{g}}} \ln\left(\frac{v_0}{v_{\mathrm{H}}}\right), \qquad (1)$$

   where n is the gas density and σ_{H} the velocity independent hard sphere collision cross-section between the ions and the gas-atoms or gas-molecules while m_{i} and m_{g} are the masses of the collision partners.
2. To reduce the "critical velocity" v_{H} to a final rest velocity v_{f} the ions must move in the cooler quadrupole for an additional distance [6]

$$l_{\mathrm{L}} \approx v_{\mathrm{H}} \kappa \left(\frac{m_{\mathrm{i}}}{q}\right), \qquad (2)$$

   where κ is the ion mobility [7] and m_{i}/q is the mass-to-charge ratio of the ion under consideration. In this region, the ion–atom or ion–molecule collisions are dominated by cross-sections σ_{L} that are inversely proportional to the velocities v between ions and atoms or molecules, respectively.

When cooling Cs^+-ions in a N_2-gas at 0.013 mbar we found $l_{\mathrm{H}} \approx 110$ mm from Eq. (1) and $l_{\mathrm{L}} \approx 20$ mm from Eq. (2). For this reason, we used in most of our experiments a 170 mm long "cooler quadrupole" though in one experiment we used a 400 mm long one.

2.2. Electron detachment

Electron detachment cross-sections for negatively charged halogen ions colliding with noble gas atoms have been measured [8,9] showing that threshold energies, E_{th} for electron detachment are found to be approximately a factor 2 higher than the electron affinity for these ions. While for instance the electron affinity for I^--ions is 3.1 eV, the electron detachment threshold for I^--ions, that collide with He atoms, is about 8.6 eV in the center of mass frame of reference.

If the collisions between a negative ion of energy K_0 and mass m_{i} and a buffer gas atom or molecule of mass m_{g} are elastic, the energy transfer, ΔK, in the center of mass frame of reference is given by

$$\frac{\Delta K}{K_0} = \frac{2m_{\mathrm{i}}m_{\mathrm{g}}}{(m_{\mathrm{i}}+m_{\mathrm{g}})^2}(1-\cos\theta), \tag{3}$$

where θ is the center of mass scattering angle.

As long as this energy transfer ΔK in a single collision is only a small fraction of the threshold energy, E_{th}, of the colliding ion, the probability is high that this ion will not be neutralized. Such a situation is given if the m_{i} and m_{g} differ sufficiently and if the initial ion energy K_0 is not too large. Since the electron detachment cross-section σ is proportional to $(\Delta K - E_{\mathrm{th}})^2$ [9], however, a sizeable fraction of the negative ions of a beam can be cooled without electron detachment, even for $\Delta K \geq E_{\mathrm{th}}$.

In principle small values of $\Delta K/K_0$ can be achieved for $m_{\mathrm{i}} \gg m_{\mathrm{g}}$ as well as for $m_{\mathrm{i}} \ll m_{\mathrm{g}}$. However, only the case $m_{\mathrm{i}} \gg m_{\mathrm{g}}$ is useful for beam cooling purposes since only in this case the incoming ions are scattered under small angles.

3. Experimental cooling of negative ions

The apparatus used in our experiments consisted of the following components:

1. An electrospray ion source operated at atmospheric pressure that can generate both positive and negative ions.
2. A 170 or a 400 mm long segmented rf-quadrupole of 7 mm aperture (shown schematically in Fig. 1) both featuring a lateral rf- and a longitudinal dc-field. These quadrupoles were both operated with buffer gases of air at 0.013 and 0.005 mbar or of He at 0.1 and 0.045 mbar, respectively.
3. A 25 mm long segmented rf-quadrupole of 3.6 mm aperture, known from [10] as the molecular ion reactor (MIR). This MIR is operated at pressures of 0.3 mbar for air as well as for He and acts in the described experiments as a precooler in a fashion very similar to that of the 170 or the 400 mm long cooler quadrupoles. This MIR is positioned between the atmospheric pressure ion source and the cooler quadrupole.
4. A time-of-flight mass spectrometer (TOF-MS), as described in [11] in which the cooled ions are mass analyzed. Into this TOF-MS the ions under consideration are accelerated orthogonally to their initial velocity by a pulsed-grid extractor that formed bunches of a few nanoseconds duration of ions of 6000 eV energy.

In our experiments, the ions formed in the electrospray source were passed through the MIR and then as is shown schematically in Fig. 1 through a 1 mm diameter “entrance aperture” into the cooler quadrupole which they left through a 2 mm “exit aperture” of 2 mm diameter. Since the electrodes of the cooler quadrupole were at a potential U_0 relative to the potential of the entrance-aperture electrode, the ions entered the cooler quadrupole with an energy $K_0 \geq qU_0$ with q being the ion charge.

With this arrangement two measurements were performed:

1. For a special setup the exit-aperture electrode and the four quadrupole electrodes were connected electrically and used together as a total beam collector. In this case, the total ion current I_0 was observed.
2. During normal operation of the cooler quadrupole an ion current I_1—with I_1 being in the 0.1 nA range—was observed leaving the cooler quadrupole. This current I_1 was recorded downstream of the exit aperture (see Fig. 1) after a post-acceleration by a voltage difference of 6.8 V
   - As function of the potential U_1 at the retarding grid arrangement (see Fig. 1). This $I_1(U_1)$, shown in Fig. 2, reveals the energy spread ΔK of the cooled ions.
   - As function of the potential difference $U_0 \leq 150$ V between the entrance aperture and the

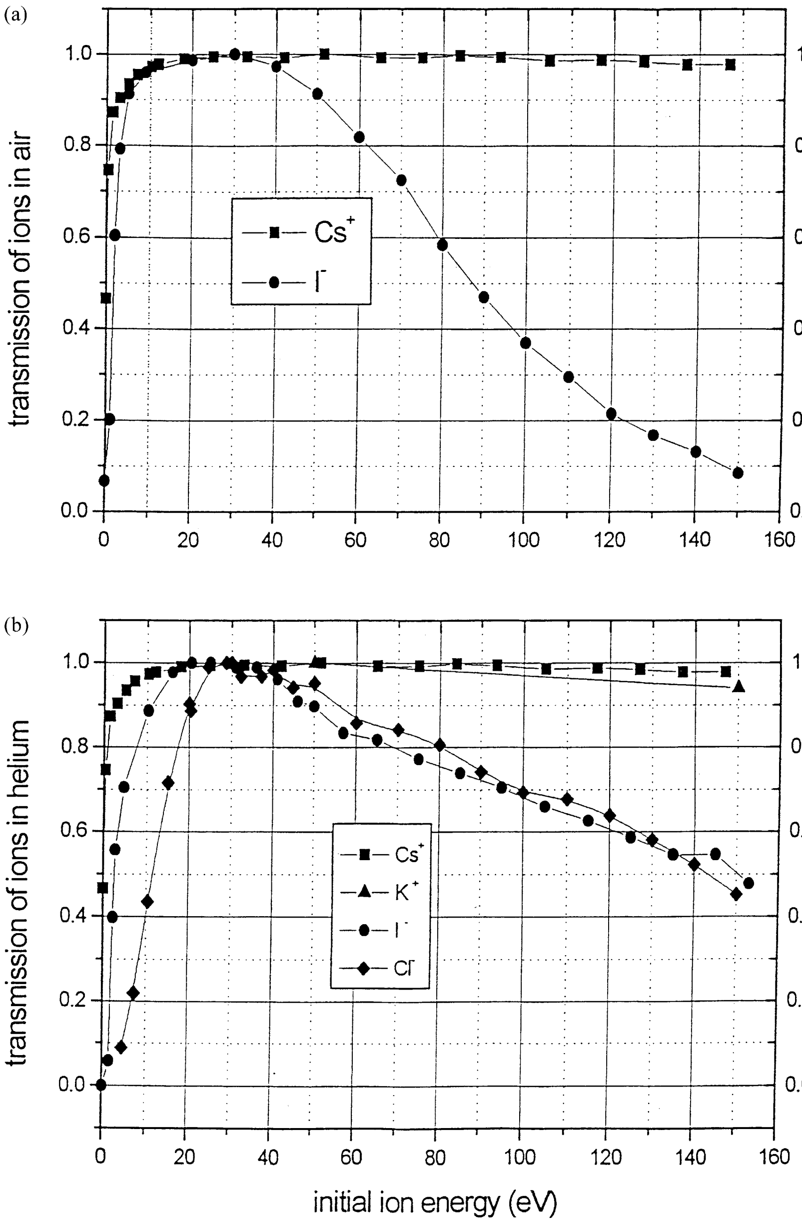

Fig. 3. Normalized transmission curves $I_1(K_0)$ measured downstream of the 170 mm long cooler quadrupole as function of initial ion energies $K_0 \approx qU_0$. Shown are the results (a) for Cs$^+$- and I$^-$-ions measured when air was used as buffer gas and (b) for K$^+$-, Cs$^+$-, Cl$^-$-, and I$^-$-ions measured when He was used as buffer gas.

first segment of the cooler quadrupole (see Fig. 1). This $I_1(U_0)$, shown in Figs. 3 and 4, demonstrates the ion transmission as function of the "initial ion energy" $K_0 = K_{00} + qU_0 \approx qU_0$, where $K_{00} \approx 1\text{eV} \ll qU_0$ is the energy to which the MIR had precooled the ions before they entered the cooler quadrupole through the entrance aperture shown in Fig. 1.

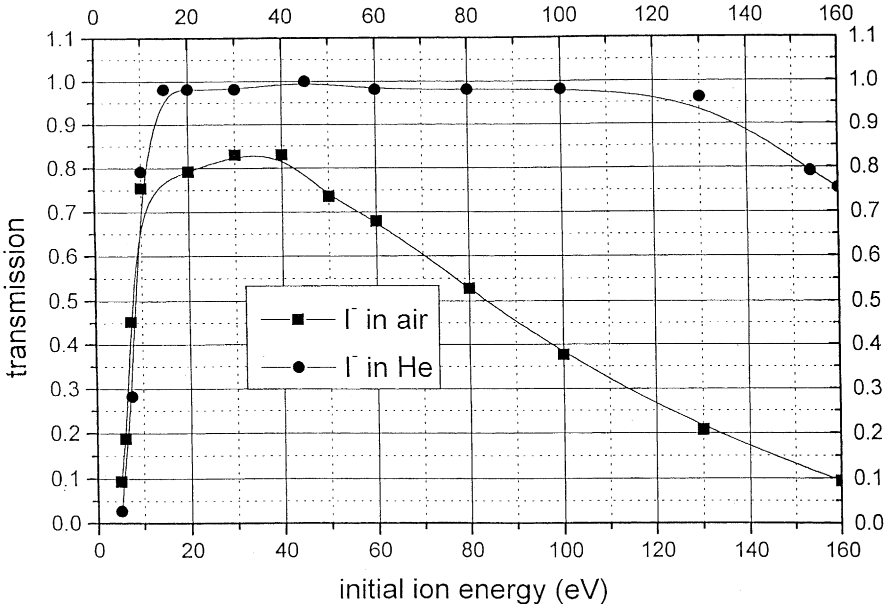

Fig. 4. Normalized transmission curves $I_1(K_0)$ for I$^-$-ions measured downstream of the 400 mm cooler quadrupole as function of their initial ion energies $K_0 \approx qU_0$. In a buffer gas of He these I$^-$-ions were transmitted with high efficiencies up to initial energies of ≈100 eV. In a buffer gas of air their transmission was reduced by at least 15% and even these values were achieved only for I$^-$-ions whose initial energies were kept between 30 and 40 eV.

4. Results and conclusion

From the ion transmission I_1/I_0 as well as the energy spread ΔK measured downstream of the exit aperture, we concluded whether the ions were cooled sufficiently and whether the gas pressure in the cooler quadrupole needed to be further optimized.

4.1. *Energy spread of cooled ions*

The energy spread ΔK of the cooled Cl$^-$- and I$^-$-ions was determined directly by measuring the ion transmission of a retarding potential U_1 applied to the double grid arrangement located downstream of the cooler quadrupole and its exit aperture (see Fig. 1). As is shown in Fig. 2 more than 80% of the ions have energies below 0.3 eV and 90% below 0.5 eV. In other words, the ions have a FWHM energy spread of ≈0.26 eV. This measurement was repeated for different initial ion energies $K_0 \approx qU_0$ with 20 eV $\leq K_0 \leq$ 150 eV producing, in all cases, the same final energy distribution. This result was also independent of the type of buffer gas used.

4.2. *Transmission efficiency*

Relative transmission curves $I_1(K_0)$ for ions of different initial energies $K_0 \approx qU_0$ were measured for air-filled and or He-filled rf-quadrupoles of 170 and 400 mm length.

1. We conducted experiments that used air as cooling gas at 0.013 mbar in the 170 mm long quadrupole and at 0.005 mbar in the 400 mm long quadrupole. In both systems, the transmission was approximately energy independent for Cs$^+$- and K$^+$-ions as long as their K_0 stayed below ≈150 eV. However, for I$^-$- and Cl$^-$-ions the transmission fell off in both systems when the ion energy K_0 was increased to values above ≈40 eV and reached ≈10% for $K_0 \approx$ 150 eV. These dependencies are illustrated for Cs$^+$- and

for I^--ions in Fig. 3a for the case of the 170 mm long quadrupole and by the lower curve in Fig. 4 for the case of the 400 mm long quadrupole.

2. We conducted experiments that used He as buffer gas at 0.01 mbar in the 170 mm long quadrupole and at 0.0045 mbar in the 400 mm long quadrupole. Again the transmission was approximately energy independent for Cs^+- and K^+-ions in both systems as long as K_0 stayed below ≈150 eV. For I^-- and Cl^--ions the transmission fell off in both systems:
   - in the 170 mm long cooler quadrupole the transmission started to fall off when the ion energy K_0 was increased to values above ≈40 eV and reached ≈50% for $K_0 \approx 150$ eV as is illustrated in Fig. 3b;
   - in the 400 mm long cooler quadrupole the transmission started to fall off when the ion energy K_0 was increased to values above ≈120 eV and reached ≈80% for $K_0 \approx 150$ eV as is illustrated for I^--ions by the upper curve in Fig. 4.

Though for the operation in air the two cooler quadrupoles performed similarly, the 400 mm long cooler quadrupole performed considerably better for negative ions when filled with He.

In all our measurements, we also observed a reduced ion transmission for negatively charged ions when the initial ion energy was kept below 10 or even 20 eV. Using the 400 mm long cooler quadrupole and an ion beam with a 30% smaller phase-space area, 100% transmission efficiencies were observed for I^--ions with energies up to ≈150 eV (see Fig. 4).

Though we were able to determine the transmitted intensities of the negative ions of interest very precisely with both cooler systems, we had difficulties in determining the intensity of the incoming ion beams since they also contained small amounts of other ion species. These contaminations we determined, however, by measuring the mass distribution of the transmitted ion beam. From these measurements we concluded that the ions of interest constituted more than 50% of the total ion beam. Since furthermore the intensity of the total incoming beam was found to be 2.5 times larger than the recorded intensity of the cooled beam of the desired species we conclude that there were more than 1.25 times as many ions coming in of this species than were going out so that the overall transmission should be well above 50%. This finding is correct in all case in which the energy of the injected ions was kept below 50 eV and with a reduced certainty when this energy was kept below 100 eV.

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