A STUDY OF KF_3^- ATTENUATION IN AN RFQ GAS CELL FOR ^{41}Ca AMS

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ABSTRACT. Guided by simulations using SIMION 8.1, a series of modifications were made to an experimental version of an Isobar Separator for Anions (ISA). The resulting improved version of the ISA provides a means of re-energizing the ions after they are cooled by gas collisions as they pass through the gas-filled radiofrequency quadrupoles (RFQ), and also provides higher transmission efficiencies. Reinvestigation of the separation of CaF_3^- and KF_3^- with this refined apparatus resulted in a better balance between isobar suppression and analyte transmission. KF_3^- was attenuated at eV energies by 4 orders of magnitude while 40% transmission of CaF_3^- was retained, for a 20keV CaF_3^- beam of ϕ2mm and ±12mr. These results advance the possibility of an efficient small ISA-AMS system for both cosmogenic and medical applications of ^{41}Ca.

INTRODUCTION

Since the use of CaF_3^- for ^{41}Ca accelerator mass spectrometry (AMS) was first introduced by Kubik and Elmore (1989), it has been the preferred choice over CaH_3^-, as CaF_2 is more convenient to handle than CaH_2. Similar to the use of CaH_3^-, the use of CaF_3^- has benefited from the fact that the molecular isobars carrying ^{41}K are rare. However, small amounts of ^{41}K do enter the final detector together with ^{41}Ca, which then can only be separated by the rate of energy loss method, thus requiring a large tandem accelerator (>3 MV) to prepare ^{41}Ca positive ions with sufficiently high energies. Otherwise, the abundance sensitivity of $^{41}Ca/Ca$ would be limited in the range of 10^{-10}–10^{-12}, which is inadequate for many ^{41}Ca applications.

It became possible to attenuate the ^{41}K background by orders of magnitude for ^{41}Ca AMS using small accelerators when the main molecular isobar, KF_3^-, was clearly identified (Zhao et al. 2010). This molecular anion was previously unknown, but has now also been studied theoretically and found to belong to a new class of superhalogen anions with an electron vertical detachment energy calculated to be near 6.8 eV (Lo and Hopkinson 2011), not far from the calculated 8.62 eV for CaF_3^- (Anusiewicz et al. 2003). The main difference between KF_3^- and CaF_3^- is found to be in the binding energy of their last F and F^-, respectively, with the former calculated to be 1.0 eV (Lo and Hopkinson 2011) for KF_3^- while the latter 3.7 eV (AC Hopkinson, personal communication, 2012) for CaF_3^-. Thus, it is easier to destroy KF_3^- by removal of an F atom than an electron. It is conceivable that during collisions with gases, KF_3^- could receive enough internal energy to break apart into KF_2^- and F. If the gas contains H, exothermic chemical reactions leading to KF_2^- and HF could also result. These 2 processes, which might be complicated in the details, would have substantially different near threshold behaviors for KF_3^- and CaF_3^-. If the collision energy in the center of mass could be controlled well, it should be possible to attenuate KF_3^- to a desired level while still maintaining an adequate transmission of CaF_3^-.

As soon as the existence of KF_3^- was identified clearly, this low-energy method of Ca/K separation was attempted briefly (Zhao et al. 2010) using a novel experimental apparatus under development, known as the Isobar Separator for Anions (ISA). In recent years, the use of a radiofrequency quadrupole (RFQ) gas cell to separate isobars by anion-gas reactions has been shown to have great poten-

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tial for AMS measurement of ^{36}Cl, ^{90}Sr, and ^{135}Cs using small tandem accelerators (Eliades et al. 2010a,b, 2013; Eliades 2012). However, in comparison to the 5 or 6 orders of magnitude of isobar separation demonstrated for $^{36}Cl^-/(^{36}S^-,^{12}C_3^-)$, $^{90}SrF_3^-/(^{90}ZrF_3^-,^{90}YF_3^-)$, and $^{135}CsF_2^-/^{135}BaF_2^-$, the degree of KF_3^- attenuation relative to CaF_3^-, about 2 orders of magnitude, was somewhat disappointing. This was the case both in the initial attempt using Ar (Zhao et al. 2010), and in a follow-up attempt using NO_2 (Kieser et al. 2010). Up to the early stages of the current study, efforts had been concentrated on searching for a particular gas that could mediate a fast chemical reaction for the CaF_3^-/KF_3^- separation. Gases such as H_2, C_2H_2, CH_4, and CO were all studied, but the relative CaF_3^-/KF_3^- separation was always found to be limited to about 2 orders of magnitude, as it was with Ar and NO_2. During this period, a partial molecular stripping method at higher energies was also studied (Zhao et al. 2013). Again, a relative Ca/K separation by 2 orders of magnitude was achieved when CaF_3^- was stripped into CaF^+ in a dilute Ar gas at the high-energy terminal of a tandem accelerator. None of these efforts was spectacularly successful for the purpose of ^{41}Ca measurements. However, the observations in all cases were highly consistent with the computed KF_3^- property that the last F has the weakest bond (Lo and Hopkinson 2011), as KF_3^- breaking up to KF_2^- was always found in experiments to be the most probable fragmentation pathway. This is not surprising as the KF_2^- ion also belongs to a class of superhalogen anions with a large electron vertical detachment energy measured to be 5.61 eV (Wang et al. 1999) and a theoretical F^- binding energy of 2.15 eV (Gutsev and Boldyrev 1981). Thus, these earlier efforts continued to warrant an eventually successful exploitation of the weak F bond in KF_3^-, once the correct experimental conditions could be found and maintained.

The required experimental conditions have now been identified, and a relative CaF_3^-/KF_3^- separation by as much as 5 orders of magnitude has been observed. In this report, we describe the experimental steps that led to these findings, and discuss their implications for AMS applications.

IMPROVEMENT OF ORIGINAL ISA-AMS EXPERIMENTAL SETUP AT ISOTRACE

The first experimental ISA was an extrapolation from a system used for low-energy ions from electro-spray or inductively-coupled-plasma ion sources, and for more conventional applications that are not jeopardized by sampling only a small portion of the ions produced. However, retardation of the 20keV anions from a Cs sputter ion source and their passage through the subsequent RFQs were found to be difficult, unless the phase space of the original beam was limited to unpractical levels for AMS. As a proof-of-principle instrument, the first experimental ISA has been successful in demonstrating the separation of a number of isobar pairs, but to make it a routine analytical tool for AMS, studies of many technical details were necessary to maximize the efficiency. The beam transport throughout the ISA setup has been simulated using SIMION 8.1, and the main sources of several transmission inefficiencies have been identified. Simple modifications of the first experimental ISA, based on these simulations, have resulted in much improved versions, which have allowed us to reinvestigate in more detail the case of CaF_3^-/KF_3^- separation. Three major aspects of the improvement are described below.

Provision of Some Ion Energy Control Through the RFQ Gas Cell

The original setup used a single gas cell wherein collisions with reaction gases resulted in both isobar separation and ion cooling (kinetic energy reduction). To maintain a forward momentum of the ions towards the exit of the cell, a set of gradient bars were added later (Eliades et al. 2010a) to create a drift gradient along the axis. The strength of this axial gradient, as well as many other useful quantities, can be obtained using SIMION 8.1 by firing an ion into the system and observing the calculated physical parameters that are experienced by the ion along its trajectory. However, the accu-

racies of these results depend on the maximum grid unit resolutions permitted by the amount of RAM in a PC. Resolutions of 4–10 grid units per mm (and time step of 1/80th the RF period) were used to compute the quantities quoted in this work, which are limited by the 26GB RAM available.

Usually, the optimum tuning of an analyte beam would result in a drift gradient of 10–30 mV/mm to be produced along the axis. Under these conditions, ions passing through the gas cell could not be re-energized significantly once cooled during collisions with gas atoms or molecules. This would not be a problem in cases when lower energies may be preferred, such as the destruction of WF_5^- in O_2, but to break apart KF_3^- into KF_2^- + F, the molecule must absorb more than 1 eV internal energy to overcome the binding energy of the last F atom (Lo and Hopkinson 2011), plus additional energy for any barriers that may be involved. If CH_4 gas is used, the maximum kinetic energy transferable to the internal energy of KF_3^- during a collision, in the center of mass, is $E_{cm} = M_{target} \cdot E_{lab}/(M_{target}+M_{ion}) = 0.14 \cdot E_{lab}$. The cross-section of the collisional fragmentation would then decrease rapidly when $E_{cm} < 1$ eV, or $E_{lab} < 7$ eV. Although the reaction $KF_3^- + CH_4 \rightarrow KF_2^- + HF + CH_3 +$ 0.36 eV is slightly exothermic, it would also involve threshold energies as the ground state geometry of KF_2^- is linear while that of KF_3^- has an isosceles-triangle shape (Lo and Hopkinson 2011), and there is also a geometrical difference between CH_4 and CH_3.

For the experimental ISA, it was found that the retarded anions were best transmitted through it by entering the gas cell at energies ≤10 eV when gas was present in the cell. Based on the theoretical 1.0eV F binding energy in KF_3^- (Lo and Hopkinson 2011) and 3.7eV F^- binding energy in CaF_3^- (AC Hopkinson, personal communication, 2012), CH_4 would be an ideal gas to use for attenuating KF_3^- by both types of reactions in a single gas cell. That is, when ions enter the gas cell with a typical energy of $E_{lab} \sim 10$ eV ($E_{cm} \sim 1.4$ eV), KF_3^- attenuation would begin with a significant cross-section, while at the same time the collisional destruction of CaF_3^- should be minimal. The loss of CaF_3^- in collision with CH_4 due to adduct formation should also be minimal because of the symmetry and saturation of the bonds in CH_4. As KF_3^- were attenuated, its product KF_2^- would be formed with a corresponding increase in flux. As the ion energy cooled after a number of non-destructive collisions, the cross-section would drop rapidly and the attenuation of the remaining KF_3^- would stall. This was exactly what had been observed many times, with the KF_3^- attenuation typically forming a plateau at ~1% of its original flux.

The need to re-energize ions during their passage through the gas cell as they lost energy by collisional cooling was then realized, and 2 ways of doing this were explored. The first was to apply a substantially larger DC bias on the gradient bars, resulting in a 40–80 mV/mm drift gradient along the axis. The second was to join 2 gas cells together so that a large acceleration gradient across a small gap between them (~130 mV/mm at the peak) could be applied to raise the ion energy once again above 10 eV. In both tests, significantly greater attenuations of KF_3^-, by as much as 5 orders of magnitude in the latter case, were achieved. However, the re-energized ions were more difficult to transmit through the RFQ gas cell as they required a number of collisions to cool down again (i.e. to reduce their transverse momentum) before being extracted out of the final ϕ3mm exit aperture. With the experimental ISA, it was not possible to achieve a better balance between the re-acceleration needed for KF_3^- attenuation across the single gap and the limited cooling possible following it. A longer segmented RFQ gas cell would provide a better means of variable ion energy control.

Towards Optimization of Ion Optical Matching with the ISA

The use of RFQs for low (eV) energy ion confinement and mass selection has been a well-known technology for decades. SIMION 8.1 provides an RFQ example and a short list of references; it is a convenient way to become familiar with the subject very quickly. A survey of the RFQ principles

and a detailed description of its first application in an ISA are provided by Eliades (2012). Basically, when an ion travels through a perfect hyperbolic RFQ field, its motion is determined exactly by the solutions of the Mathieu equation, resulting in the ion's trajectory under certain conditions seen as being composed of many micromotions superimposed on a well-characterized macromotion. The micromotions are rapid responses to the radiofrequency voltages where the ion experiences the largest gradients, and the macromotion is a longer-period repetitive sinusoidal motion in which an ion crosses the axis of symmetry periodically. The overall motion is determined by an important stability parameter. For singly charged ions, this parameter is calculated as

$$q = 4.888 \cdot V_{pp}/(m \cdot r_0^2 \cdot f^2)$$

where V_{pp} (in volts) is the RF peak-to-peak voltage, m (in amu) is the ion's mass, f (in MHz) is the RF frequency, and r_0 (in mm) is the inner inscribed radius of the RFQ rods. The rods themselves typically have radius of ~$1.148r_0$. In general, it requires $0 < q < 0.91$ in order for the ion's motion to remain bound. For adiabatic motion, that is, when the fluctuations in the ion velocity are relatively small compared to the larger average motion envelope, q should be restricted further to less than 0.3. Another way to comprehend the nature of adiabatic motion is to say that such motion reduces the maximum deceleration and acceleration an ion experiences from the RFQ field. This makes it more probable for the ion's motion to remain bound upon perturbations such as higher orders of harmonics, fringing fields, gas collisions, etc. A comprehensive study on this subject is provided by Gerlich (1992).

The beauty of the RFQ technology is that, once an ion is captured and eventually settles into a stable trajectory of adiabatic motion, it can no longer be lost unless it is removed by collision with an aperture, by reactions during gas collisions, or by "bad" scattering if the mass of the gas atoms or molecules is not sufficiently small compared to the mass of the analyte ion. For an ISA, there are 2 major efficiency concerns that must be addressed satisfactorily. Firstly, it is highly desirable to pass the retarded anions into the RFQ and actually capture them within the boundaries of that RFQ segment, with the highest entry efficiency. Secondly, it is equally important to achieve high and stable transmission of the captured analyte anions through the RFQs under the gas-collision conditions that are needed to produce the required degrees of cooling and isobar attenuation.

The RFQ entry issues are an important place to start. If a mono-energetic beam entering an RFQ begins as spatially concentrated near the axis (i.e. beam waist radius <10% of the r_0), and at the same time has a small transverse momentum spread (i.e. beam divergence less than ±15°), then the macromotions of all ions of the same mass/charge ratio in the beam would form a nearly equal wavelength in vacuum. Such a beam would be easily transmitted through the RFQ without loss, and the stability of all ions in the beam could be well described by the single stability parameter q. Such a well-prepared beam is usually a prerequisite condition for an RFQ to function as a high-resolution mass spectrometer, the mass analysis function of which is achieved through adjustment of DC/RF voltages applied to the rods, so that only ions of the chosen mass/charge ratio could remain bound with $q \approx 0.70$ throughout the RFQ of a sufficient length. To prepare such a beam, the use of skimmers and small entrance apertures to sample just a usable portion of the original beam is a common practice. Thus, for high mass resolution RFQ-MS, the beam entry efficiency is generally not the prime concern. However, if an RFQ is used for ISA-AMS and the study of very rare radioactive atoms, high beam entry efficiency would be desirable because of the rarity of the ions being measured. Fortunately, this is possible, because in an ISA the RFQ is used only as an ion guide operated in the RF only mode, so the extreme starting conditions required for RFQ-MS can be relaxed. The size of the entrance aperture can thus be much larger as long as there is sufficient gas pressure partitioning (i.e. differential pumping).

Given the size of the entrance aperture, the r_0 of the RFQ and the phase space of an AMS beam before retardation, the RFQ entry efficiency of the retarded beam, as well as the entry quality (magnitude of the transverse momentum spread and extent of the RFQ radial filling), depend critically on the design of the transfer optics of the DC retarder preceding the RFQ. The aim is for the retarded beam to be fully captured by the RFQ with the finally settled average energy, energy spread, and radial waist to be as small as possible, before a significant number of gas collisions take place. To achieve these subtly related goals, the design up to the beginning part of the RFQ is very important, and appears to be only possible by means of simulations that include all the preceding DC components as well as the receiving RFQ itself. To describe the stability of all ions captured by the RFQ, it is no longer sufficient to rely on the single stability parameter q alone, though it is still a very useful benchmark.

In order to improve the optical matching in the experimental ISA at IsoTrace, a series of modifications were made to enhance the beam transport before, after, and through the RFQ. However, because the basic beam line structure could not be altered without extensive and time-consuming modifications, the remedies were limited to several simplifications and additions to the original assembly. In particular, the number of apertures used in the earlier ISA assembly was reduced, and the gas cell entrance was enlarged. An extra einzel lens was added before the ISA and was used together with the DC deceleration-lens to operate in a telescopic mode, so that the DC deceleration-lens alone was less filled by the same beam as in the earlier case. Finally, by using a pair of apertures between the magnet and the ISA to limit the original beam to a phase space of ϕ2mm and ±12mr before retardation, the highest entry efficiency into the first RFQ was achieved for this beam. SIMION simulations demonstrating this result are given in Figures 1 and 2.

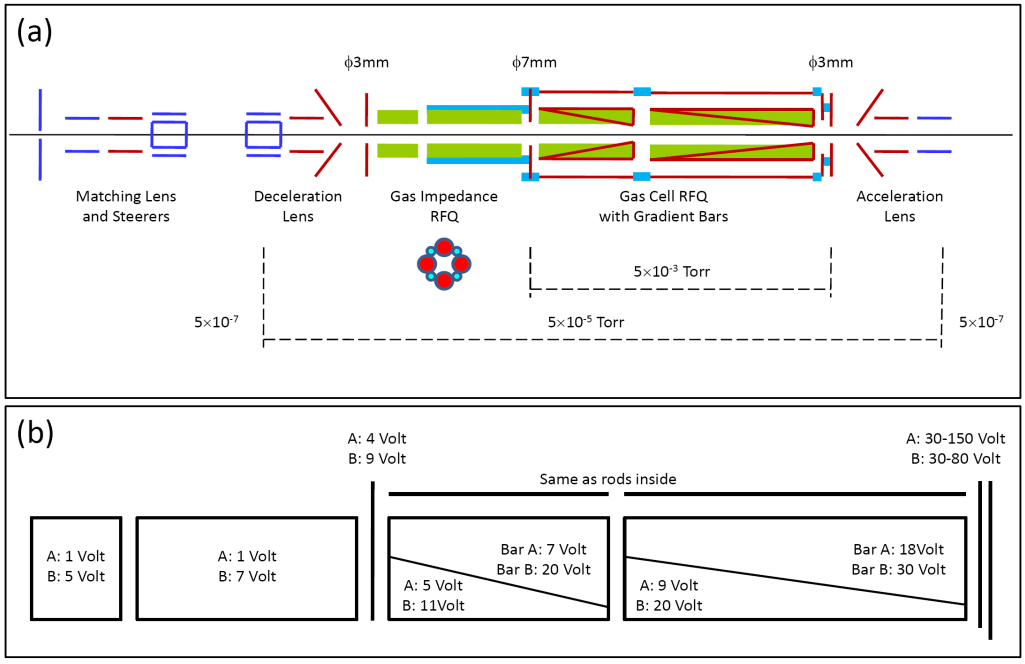

Figure 1 (a) The layout of an optimized experimental ISA; (b) Two sets of DC bias used for obtaining the results shown in Figures 2 and 3. In both cases, the RF frequency was 2.48 MHz, the target potential was –20007.5 V, and the ISA deck potential was –20001.2 V. The stability parameter was $q \approx 0.12$ (V_{pp} = 700 V) in Case A and $q \approx 0.13$ (V_{pp} = 750 V) in Case B for all the RFQ sections.

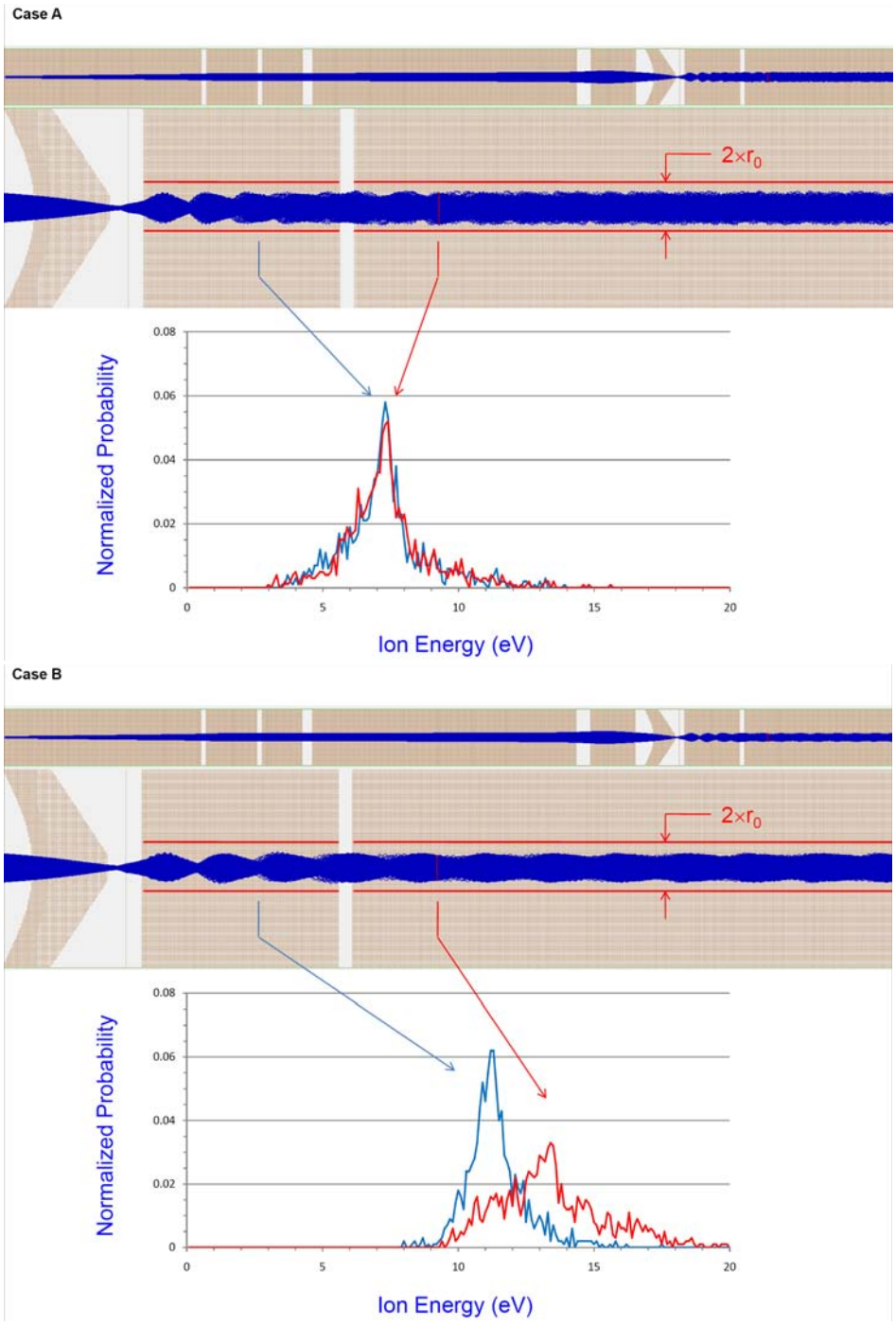

Figure 2 SIMION simulations of beam transport up to the onset of gas collisions for both cases as shown in Figure 1. Simulated ion energy dynamic ranges and probability distributions on 2 axial planes are also shown. These results are based on 1000 $^{40}CaF_3^-$ ions of mono-energetic 20007.5 eV, ϕ2mm and ±12mr, fired randomly throughout all phases of a RF cycle. In both cases, the DC retarder cone was biased at 600 V above the ISA deck potential. The RFQ entrance aperture was biased at 40 V in Case A and 55 V in Case B, above the ISA deck potential.

Possible Processes of Ion Losses in Gas-Filled RFQs and Methods of Minimization

For nearly mono-energetic beams, as could be the case with lower current superhalogen anions (Gnaser and Golser 2011), it does not appear to be a difficult task to just simply pass a retarded beam through an aperture comparable to the original beam waist, into an RFQ in vacuum with high entry efficiency. Atomic anions from Cs sputter ion sources, however, typically have a much larger intrinsic energy spread and present a more difficult case for good entry efficiency, regardless of the current. In the experimental ISA, the beam energy spread was constrained to ~50 eV, as the beam was limited to ϕ2mm and ±12mr following the double-focusing magnet (ρ = 500 mm). Under these conditions, efficient entry of atomic anions such as Cl^- into the RFQ in vacuum was still achieved with no major obstacles. This is consistent with SIMION simulations, which suggest that 35keV ions with up to 80eV energy spread (covering ~99% of a sputtered atomic beam, a detailed spectrum for which was also given by Gnaser and Golser 2011), could all be captured through adequate matching optics by the same RFQ as used in the experimental ISA. Ions in the high-energy tail would result in both greater transverse and longitudinal momentum into the RFQ, thus forming larger beam waists and longer macromotion wavelengths. These ions require the receiving RFQ to be operated with somewhat larger q, or higher effective potential calculated by $V_{eff} = (1/8) \cdot q \cdot V_{pp} \cdot (r/r_0)^2$, while for most molecular anions the use of $q < 0.15$ is optimal. By and large, the intrinsic energy spread of sputtered ions should not prevent the majority of them to be captured by an RFQ in vacuum, at least initially.

However, if an ion that has successfully entered the RFQ in vacuum has a large transverse momentum or has resulted in a trajectory that overfills the RFQ (occupying a radial volume $>0.6r_0$), the ion is not necessarily transmitted for any distance, especially when gases are present in the subsequent gas cell. The main difficulty in ISA-AMS comes from the fact that the negative ion beams, especially atomic anion beams produced from Cs sputter ion sources, usually already occupy quite large phase space volumes. In addition to that, because anions are often very fragile, the beams must be retarded down to a few eV in the center of mass frame before gas collisions take place. When these requirements are met, some of the retarded ions would settle inside the RFQ with transverse momentum and trajectory envelope much too large compared to those of ions that are well prepared for injection with skimmers and small entrance apertures. Consequently, even if the receiving RFQ is operated with the stability parameter $q < 0.3$ (also the adiabaticity parameter $\eta < 0.3$, Gerlich 1992), a fraction of the retarded AMS beam would still not undergo adiabatic motions within the RFQ. These ions could not be smoothly transmitted through the RFQs, especially gas-filled RFQs, which were originally designed for better prepared ion beams. The existence of ions undergoing non-adiabatic motions and the (consequent) trajectory overfills are the 2 major root causes for a number of observed ISA inefficiencies, as assessed in detail below.

The angular spread of an AMS beam, especially a high current atomic anion beam of initial kinetic energy E_i, is typically quite large (>15 mr). When such a beam is retarded to a final kinetic energy E_f and fully passed into an RFQ, the angular spread of the retarded beam increases roughly by $\sim(E_i/E_f)^{1/2}$ assuming unit magnification. The angle can become too large if too small a final energy E_f is attempted directly. To avoid excessive angles, the retarded beam must still be relatively energetic immediately after entering the RFQ field. An AMS anion beam usually starts from a sputter target potential of –20 to –75 kV with respect to laboratory ground. To retard such a beam into the RFQ entrance aperture with a reasonable near-unit magnification waist size while avoiding excessive angular spreads much beyond ±45°, the DC bias of that aperture cannot be much less than 50 V above the ISA deck (the latter at nearly the same potential as the ion source target). It can be shown by SIMION simulations that the retarded ions could still have energies well over 100 eV upon cross-

ing that 50V-biased aperture because of the curvature of its equipotential surface. These energies are too large for the intended anion-gas reactions.

The problem can be even more complex with actual beams. For example, SIMION simulations show that the lowest ion energy when retarded solely by DC potentials from the original tens of keV, depends more profoundly on the waist size than the angular divergence of the original mono-energetic ion beam. For a receiving RFQ with r_0 = 6.9 mm as in the experimental ISA, the DC bias on the RFQ entrance aperture can be set close to 50 V only for beams with a waist size of no more than ϕ3mm. If the beam waist is ϕ5mm, that DC bias would need to be ≥1000 V in order for the beam to enter the same RFQ with acceptable angular spread. In that case, the receiving RFQ must also be functioning as the final part of the energy retarder. This is in fact empirically a very good general solution for RFQ entry in vacuum for beams with large phase space volumes, but the design of such a retarder system can only be done through simulations with all the relevant DC and RF components working together.

To prevent significant anion losses in gas collisions, the average energy of the beam upon crossing the entrance aperture of the receiving RFQ must be further reduced prior to entering the region of higher gas pressure, regardless of whether the beam can be DC retarded directly down to 50 to 100s eV, or only down to ≥1000 eV. The final average ion energy is determined by the DC bias of the RFQ rods with respect to the ISA deck. Usually, the lower the final retarded average energy can be, the safer it is for anions to avoid collisional losses. However, the transverse momentum spread also increases as lower average energies are attempted. Just how low it can be without the retarded anions suffering a significant probability of escaping the RF field or being reflected by the RF field depends on: (a) the phase space, ion energy, and energy spread of the original beam; (b) the aberrations of the matching optics and the DC retarder when operated with the final DC bias applied on the RFQ entrance aperture; and (c) the r_0 of the receiving RFQ and the available range of both f and V_{pp} from the RF power supply. For the experimental ISA used in this work and the chosen limited phase space of the beam, 3 to 10eV final retarded average energies in the first RFQ could be achieved. This appeared to be satisfactory for strongly bound superhalogen anions such as CaF_3^- incident on CH_4. For more fragile and delicate anions, a level <3 eV may be needed, which could be very challenging to prepare with high efficiency.

The above overall picture of RFQ entry implies that there are 3 general processes that could lead to ion losses when gases are introduced into the gas cell, even if an ion has already entered the RFQ and appears to have been captured successfully in vacuum (Figure 2):

(**I**) If there is a significant gas pressure immediately behind the first RFQ entrance aperture, the final ion energy retardation from over 100 eV down to the ≤10eV level means that there will inevitably be collisions that occur at still quite large energies so that almost all anions could suffer losses due to electron detachment or molecular fragmentation. Thus, it is highly desirable to create a pressure gradient inside a sequence of RFQs, so that the pressure within several centimeters behind the first RFQ entrance remains as close to a good vacuum as possible.

(**II**) The final stage of ion retardation, from having just entered the RFQ to the finally settled average energy of ≤10 eV, causes a profound expansion of the beam envelope. This expansion is particularly large if gases are present, and in fact chaotic in heavy gases when the probability of large-angle (and even back-) scattering is greater. Even in vacuum, this expansion is significant (Figure 2). For example, a ϕ3mm aperture (which matches the beam waist there) is used as the RFQ entrance in the experimental ISA, in which the $2\times r_0$ of the RFQ is 13.8 mm, so the beam waist upon crossing that aperture is already 22% of the $2\times r_0$. When the ions are further retarded down to the ≤10eV level in

vacuum, the beam waist expands to ≥ϕ8 mm, or ≥60% of the $2\times r_0$. This was shown by SIMION simulations, and was also confirmed by actual tests with the various aperture sizes once used between 2 RFQs. Only when the aperture at the gas cell entrance was enlarged to ϕ7mm, a ~90% transmission for up to ~1μA Cl^- beams was measured in vacuum (which had to be aided by a >200V acceleration bias applied to the small gas cell exit aperture due to the lack of collisional cooling). This is consistent with the ≥ϕ8mm assessment on the ions' outer reaches of trajectories.

With such a large radial overfill, the macrotrajectory envelope of analyte ions cannot form more than 1 or 2 notable waist nodes in which the ions are concentrated in a relatively small radius, even for mono-energetic anions (see Figure 2). Instead, it forms a uniform-radius envelope shortly after the RFQ entry. If a small aperture is to be used, for example, an exit aperture of the gas cell to restrict gas flows, the beam must be concentrated near the axis first, and the only means practically possible is by gas collisional cooling. If ions are not adequately cooled arriving at the exit aperture, a large acceleration voltage must then be used to compress the trajectories, which would cause some collisional losses. In principle, it is always possible to achieve a needed degree of ion energy cooling with a sufficient number of collisions with light non-reactive gases. If only reaction gases are used in the gas cell, however, significant losses at the cell exit could occur if the gases are too heavy, or the anions of interest could not afford to be adequately cooled due to reaction losses. In these cases, it is desirable to either further open up the exit aperture, or to mix into the reaction gases with higher pressures of He to assist in collisional cooling. This problem is still being studied. Before the benefit of collision-induced transmission enhancement is invoked, however, a large radial overfill by the ions' trajectories poses 2 immediate problems to their RFQ confinement.

First, when ions are furthest from the axis, where the fields are the strongest, trajectories can be significantly affected by the first few gas collisions for it is always possible that part of the ion's longitudinal momentum is converted and added to its transverse momentum. Usually at this point, there is already barely a single value of q (or the resulting V_{eff}) that can keep all ions bound in vacuum. Then, when the gases are leaked in, some of the ions' trajectories are readily pushed beyond the RFQ trapping region, inevitably causing a fraction of the beam to be lost. The degree of this loss depends on the mass of the collision gas and the size of the RFQ with respect to the uniform waist size of the retarded beam. SIMION simulations indicate that major difficulties only arise when the beam's radial waist surpasses ~60% of the r_0. For a typical retarded AMS beam, RFQs with $r_0 \geq$ 10 mm could be more desirable as they could provide greater unoccupied radial volumes for saving ions that have suffered a large velocity change. This scatter induced loss can also be reduced if the lightest non-reactive He is used as the first buffer gas to minimize ion velocity disturbances.

Second, the presence of conducting apertures between RFQ segments for gas restriction and/or RFQ field isolation weakens the RFQ confinement ability due to the presence of both DC and RF fringing fields, which could be highly destabilizing. Losses by the first few gas collisions are more probable near apertures if the beam waist is close to filling them up. It is particularly problematic behind the first RFQ entrance aperture where the ions' energies are still in the tens of eV range. This is again a reason for avoiding gas collisions near the first RFQ entrance, and ideally avoiding the use of small apertures anywhere in an RFQ ion guide where the beam has not yet been adequately cooled.

(**III**) If ions that have entered an RFQ have large transverse momenta, they subsequently approach the RFQ rods and are reflected from them with high transverse velocities. Therefore, they experience greater alternating deceleration and acceleration from the RFQ field. As a result, these ions acquire a broader kinetic energy spread around the average value. When all retarded ions inside an RFQ are considered, there exists a kinetic energy distribution that is dynamic throughout the sequence of RFQs. Knowledge of this is highly relevant to the tasks of an ISA; it is practically useful

to be shown as a statistical "snap shot" of all ions crossing an axial plane (Figure 2). Such a "snap shot" has a characteristic "Christmas tree" shape, which is not necessarily symmetrical.

To correctly prepare the ions for the intended reactions, it is particularly important to determine the energy spread crossing the axial plane, where the retarded ions have just settled inside the receiving RFQ before entering the region of higher gas pressure. This energy spread is mainly due to the RFQ's amplifying response to the transverse momentum spread of the retarded ions that have entered it, which, in turn, is determined by the original beam phase space and the coupling details of the matching optics and DC retarder to the receiving RFQ. The stability parameter q has the most profound effect on the maximum kinetic energy that can be reached inside an RFQ, which could be >10 times the average for $q \approx 0.9$, but ≤3 times the average with $q \leq 0.3$. Therefore, the receiving RFQ is ideally operated with smaller q values as long as r_0 and V_{eff} are still sufficiently large for trajectory filling and containing. For AMS beams that are retarded into the same RFQs (operated with $q \approx 0.15$) as used in the experimental ISA, a SIMION example shows that when the average energy settles at 15 eV, some ions' energies could from time to time actually reach >40 eV. This is important to bear in mind when it comes to choosing the first collision gas. For example, CaF_3^- could start to suffer collisional fragmentation in CH_4 gas if the maximum kinetic to internal transferable energy becomes $E_{cm} \geq 3.7$ eV (AC Hopkinson, personal communication, 2012), or $E_{lab} \geq 26.4$ eV. This problem has probably been avoided in this particular work on CaF_3^-, as the phase space of the experimental beam was chosen to be limited to ϕ2mm and ±12mr, so that a ~10eV average kinetic energy with 2–20 eV dynamic range (Figure 2) could be achieved before gas collisions begin. It could become a significant issue to deal with when the full phase space acceptance of an AMS beam is attempted, or when more fragile anions of interest are transmitted. If, in spite of great efforts in system designs, the kinetic energy range is still too large for the survival of the analyte anions, the use of He as the first buffer gas is once again a possible solution to minimize losses.

It should be further noted that this dynamic range of ions' kinetic energies as amplified by the RFQ field in response to an initially large transverse momentum spread, is a fundamental problem even with originally mono-energetic beams. The original intrinsic energy spread of the sputtered atomic anions certainly adds to the problem. These issues are more challenging than just simply passing retarded ions into an RFQ. The ion energy distribution analysis, such as those shown in Figure 2, should also be used to evaluate ISA designs for a given beam, in addition to the design goals of high entry efficiency and minimized (ideally ≤60%) r_0 radial filling.

IMPROVED KF_3^- ATTENUATION RESULTS AND DISCUSSIONS

Following the considerations as described above, and after a series of iterations of SIMION simulations and experimental tests, a modified version of the ISA (Figures 1 and 2) was chosen for a renewed study of the CaF_3^-/KF_3^- separation. The new setup uses 4 RFQ sections created by rearranging existing components used from the earlier ISA configurations. The first one (55 mm) that follows the ϕ3mm primary entrance aperture is only for vacuum pumping. The second one (150 mm), which is closed to gas by Teflon® rods filling the spaces between the quadrupole rods, makes up a gas impedance section with conductance equivalent to a ϕ4mm aperture. The third (150 mm) and fourth (230 mm) are inside the gas cell, but because of the use of a gas impedance section, the gas cell entrance aperture was expanded to ϕ7mm from the original ϕ3mm, so the gas pressure diminishes gradually as it extends towards vacuum.

The use of insulators to seal the gaps between the RFQ rods introduces dielectric surfaces near electrodes, which are prone to causing instabilities. Although we routinely experience stable RFQ oper-

ation over the typical length of time for daily experiments, the techniques of implementing a closed RFQ require further development. The practice used here was meant to be a quick solution for demonstrating the benefit of including a gas impedance RFQ section. It makes highly efficient entry into the vacuum RFQ, followed by similar entry efficiency into the gas cell, very much easier to obtain for a retarded AMS beam. The ϕ7mm gas cell entrance aperture should ideally be even larger or not used at all, but to cope with the restricted differential pumping in this experimental ISA, and to prevent strong capacitive coupling between the 2 output channels of the RF power supply that control the first and second pair of RFQ segments separately, the use of a ϕ7mm aperture here was still necessary. The total gas conductance is somewhat larger than the original setup (Eliades et al. 2010a), with which the gas cell could be filled up to 10 mTorr. The new setup can only hold up to about 5 mTorr in the gas cell before the vacuum in the chamber containing the ISA approaches 5×10^{-5} Torr. However, the open structure of the new setup has avoided much inefficiency related to the RFQ and gas cell entries. It also ensures a better vacuum immediately behind the ϕ3mm primary entrance aperture, so the losses there due to disturbances by the first few collisions are reduced as well.

The new setup provides 3 gradient gaps and 2 sets of gradient bars for re-accelerating the ions. However, the gradient applicable to the gap across the ϕ7mm aperture is very limited as the RFQ's ion confinement ability is weakened there. In any case, major re-acceleration should be avoided before the ions have been concentrated enough near the axis through cooling.

Using the 2 sets of axial gradient profiles as shown in Figures 1 and 2, the transmission of $^{40}CaF_3^-$ and the attenuation of $^{39}KF_3^-$ were measured as a function of CH_4 pressure inside the gas cell. The results are summarized in Figure 3. Each data point was obtained using the final detectors of the IsoTrace AMS system by counting the $^{39}K^{+2}$ ions in the ionization chamber and by measuring the $^{40}Ca^{+2}$ current in the Faraday cup in front. $^{40}CaF_3^-$ entering the ISA was typically a steady beam of 50–100 nA from sputter targets made of CaF_2+KF+PbF_2 mixtures. Absolute transmission through the ISA was measured using Faraday cups inserted before and after the external ISA chamber at laboratory ground. The transmission of the sub-pA $^{39}KF_3^-$ (Zhao et al. 2010) through the ISA was about the same as that of $^{40}CaF_3^-$ because these RFQs were operated in the RF only mode (SIMION simulations indicate that a mass/charge range of 20 to 600 could all be transmitted more or less in vacuum under the same conditions used), and the rest of the data points were normalized accordingly. Before the gas cell pressure scans took place, the entire ISA-AMS system was first tuned with $^{40}CaF_3^- \rightarrow {}^{40}Ca^{+2}$ at 4 mTorr gas cell pressure. After that, the gas cell was pumped down to vacuum again. Then, $^{40}Ca^{+2}$ or $^{39}K^{+2}$ was measured quickly at each increment of the gas cell pressure. The data were later corrected for any small and slow $^{40}CaF_3^-$ current drifts as monitored in the Faraday cup before the ISA just before and after each pressure scan. Other system details and experimental procedures were identical to those described earlier (Eliades et al. 2010a).

The lower gradient profile was chosen for the optimum transmission of the wanted beam, CaF_3^-. Under this condition, the average energy of the retarded beam having entered the RFQ, but still before the onset of significant gas collisions, was E_{lab}~7.3 eV (E_{cm}~1.0 eV). This was subsequently cooled down to below 5 eV after several collisions, and was unable to go above 5 eV again as the rest of the axial gradient was very limited. The survival of KF_3^- reached a minimum and then settled at the 10^{-2} level with respect to that of CaF_3^-. Clearly the attenuation of KF_3^- in CH_4 reached a plateau when the average ion energy dropped well below 5 eV in the laboratory (E_{cm}<0.7 eV). The characteristics of both the CaF_3^- and KF_3^- curves suggest that the first few collisions did cause considerable transmission losses. Part of this was irreversible, although much of those originally lost on the gas cell exit aperture could be recovered after a sufficient number of collisions when the beam were cooled and more concentrated near the axis arriving at that aperture.

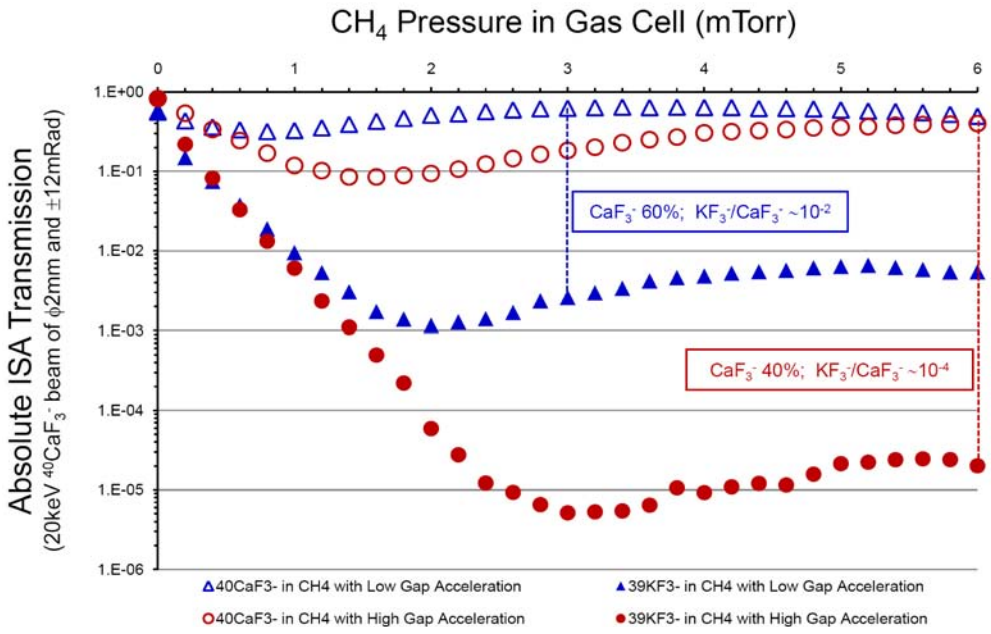

Figure 3 Results of the CaF_3^- transmission and KF_3^- attenuation as a function of CH_4 pressure in the gas cell, corresponding to the 2 sets of axial gradient conditions as described in Figures 1 and 2.

When the higher gradient profile was used, the average ion energy of the retarded beam was $E_{lab} \sim 13.3$ eV ($E_{cm} \sim 1.9$ eV) upon crossing the first gradient gap, where gas collisions were just about to take place. After cooling down to below 5 eV, the ions were once again re-energized to $E_{lab} \sim 5–10$ eV ($E_{cm} \sim 0.7–1.4$ eV) upon crossing the last gradient gap. These relatively small differences in ion energy control were enough to cause the KF_3^- attenuation to continue by 2 more orders of magnitude. However, the re-energized ions suffered further losses at the exit aperture, and more collisions were subsequently needed to recover some of the lost transmission. At 6 mTorr, however, the recovery of CaF_3^- transmission began to run into other losses possibly due to excessive deterioration of vacuum outside the gas cell and/or unknown reactions. Thus, a compromised result could be quoted for the new experimental ISA: 4 orders of magnitude of KF_3^- attenuation, at 40% of CaF_3^- transmission. The new setup has also shown much better transmission stability. Not only was the tuning much simpler, but the tuning parameters also stayed essentially the same at different pressures and over the course of several experiments. This indicates a good potential for the ISA to evolve into a reliable analytical tool.

These results have demonstrated a technique for CaF_3^-/KF_3^- separation using the ISA, with which the degree of KF_3^- attenuation depends on the ability to re-energize the ions after collisional cooling. The transmission of the wanted beam, CaF_3^-, can also be negatively affected, but the degree is largely dependent on instrument design. The 40% absolute transmission using the higher gradient profile with the new ISA configuration is still several times better than that with the original ISA setup (Zhao et al. 2010). This suggests that the efforts to reduce the potential losses in gas-filled RFQs as discussed above are probably in the right direction. However, the inefficiency issues are not yet completely solved, or even well understood (especially the degree of losses due to unknown reactions). There are still many other aspects of the experimental ISA that clearly need improvement. For example, the ion energy control is far too coarse, and the length of the last RFQ rods is not

long enough or the gas pressure cannot be raised high enough to cool the ions down sufficiently before the exit aperture. Or, the ϕ3mm exit aperture could be made larger, if aided by better differential pumping, to provide higher extraction efficiency for ions with variable degrees of cooling. Furthermore, the fraction of non-adiabatic ions and the trajectory overfills could be reduced if r_0 = 10 mm is used so that the RFQs can be operated with somewhat smaller q values by the same RF power supply. These and many other problems could be addressed with further advanced systems in the future, with which the reaction details and their cross-sections could also be quantitatively studied. For example, the nature of KF_3^- reactions can be studied in greater details with He and D_2 in comparison using turbine pumping.

CONCLUSION AND PROSPECT

The unexpectedly rugged superhalogen anion KF_3^- has been attenuated at eV energies by over 2, 4, and 5 orders of magnitude while attaining 60%, 40%, and 20% CaF_3^- transmission, respectively, using an improved experimental ISA, for a 20keV CaF_3^- beam of ϕ2mm and ±12mr. It has been found that SIMION simulations could be quite useful for guiding and evaluating the designs of ISA systems, and have indeed led to substantial improvements of the experimental version, although the quantitative correctness of the simulated results is yet to be assessed more carefully. Better ISA performance without arbitrary phase space limitations could be expected with gently sustained reactions in a longer RFQ gas cell using segmented rods, with improved vacuum pumping, and with a more modern Cs sputter ion source followed by an optically well matched DC retarder, ISA, re-accelerator, and tandem accelerator. Ultimately with the use of He buffer gas in a separate cooling cell and/or in addition to reaction gases in a single long cell, and with the use of properly dimensioned and shaped RF components that provide a tunable range of RF inputs for flat-top transmission under the working gas-collision conditions, this should eventually lead to an efficient small ISA-AMS system that is capable of detecting cosmogenic ^{41}Ca in natural samples. The system could also make routine measurement of biomedical samples with less concern for K contents in sample preparation. However, due to other practical considerations not discussed in this paper, an eventual commercial version of the ISA may be designed differently. A further step is to assess the isobar attenuation of other mass 98 amu molecular anions that also carry ^{41}K, such as $^{41}K^{57}Fe^-$, $^{41}K_2{}^{16}O^-$, etc., and to address the issues of isotope sequencing and phase space sampling on intense beams of major isotopes. Such a small ISA-AMS system would also have the potential, at least from the point of view of sufficient isobar separation, to measure $^{36}Cl^-$, $^{90}SrF_3^-$, and $^{135}CsF_2^-$. More cases of isobar separation using the ISA are also being studied, such as the cases of $^{182}HfF_5^-/^{182}WF_5^-$ and $^{238}PuF_4^-/^{238}UF_4^-$ separations, for which the use of anion-O_2 reactions have shown some promising preliminary results. The details of these developments will be published separately.

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