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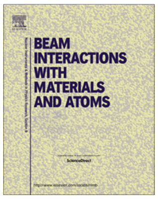

Negative ion-gas reaction studies using ion guides and accelerator mass spectrometry I: SrF_3^-, YF_3^-, ZrF_3^-, YF_4^- and ZrF_5^- in NO_2

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ABSTRACT

Typical accelerator mass spectrometry (AMS) ion sources readily produce useable currents of a wide variety of negative ions, including exotic species, and the sensitivity and dynamic range of AMS can be used for relatively unambiguous ion identification at low count rates. Difficulty producing negative ion currents with high fluxes (ex. when electron binding energies are small) and unambiguous identification of reaction products can be obstacles to negative ion-gas reaction studies. Thus, an AMS setup can be considered to be suitable for certain ion-gas reaction studies. Presented here are preliminary studies on interactions of SrF_3^-, YF_3^-, ZrF_3^-, YF_4^- and ZrF_5^- with NO_2 gas at <50 eV kinetic energies using a prototype radio-frequency quadrupole (RFQ) instrument installed before the accelerator on the low-energy side of an AMS system. The superhalogen anions SrF_3^-, YF_4^- and ZrF_5^- were found to be highly unreactive with NO_2, consistent with expected electron binding energies greater than 3.6 eV. YF_3^- and ZrF_3^- were found to have large overall attenuation cross sections in NO_2 of $7.6 \times 10^{-15} \pm 4.4\%\ \text{cm}^2$ and $1.5 \times 10^{-14} \pm 21\%\ \text{cm}^2$ respectively at the ion energies created under the experimental conditions. The major reaction channels were shown to be electron transfer and oxygen capture. A cluster $NO_2{\cdot}(YF_3^-)$ was also observed.

1. Introduction

The use of accelerators in mass spectrometry (AMS) has made possible ion identification with signals on the order of counts per day and thus the ability to measure abundance ratios of long-lived radioactive to stable isotopes down to the order of 10^{-16}. This is the first of two papers [1] that present a new application of AMS, gas-phase ion reaction studies. Advantages include the relatively unambiguous ion identification, large dynamic range and high sensitivity of AMS, as well as the wide variety of negative ions readily produced in AMS ion sources.

In the early 1990s, techniques using gases to remove isobars from low energy ion beams trapped in radio-frequency multi-pole instruments were developed for mass spectrometry [2]. A prototype radio-frequency quadrupole (RFQ) instrument produced by Ionics Mass Spectrometry Group Inc. (Ontario, Canada) was incorporated into a test bed at IsoTrace Laboratory (University of Toronto, Canada) to study the viability of such methods for AMS [3–8]. Since this work, IsoTrace has been closed and a 3 MV AMS facility at University of Ottawa (Canada) has been built to replace it [9].

Anion-gas reaction studies began while trying to understand isobar attenuation plateaus observed well above the IsoTrace AMS detection limits during proof-of-principle work [5–7,10–13]. Plateaus are often observed in ion-gas reaction experiments, but using conventional mass spectrometry the ion identifications are often only inferred (discussed at Fig. 7 of [14]). This and an accompanying paper [1] aim to demonstrate the power of AMS for identifying ions at the base of a plateau rather unambiguously over several orders of magnitude change in count rates, even in the presence of isobaric interferences accompanying the ions of interest.

In addition to the built-in power of ion identification, a wide variety of negative ions can also be readily produced by AMS Cs^+ sputter ion sources at useable currents for experiments, including those having small electron binding energies. This enables studies of novel reactions that are normally inaccessible with other systems. For example, the ion source used in this work readily produced the exotic anions KF_3^- (pA), ZrF_3^- (10 > 100 pA) and YF_3^- (>nA) for study. Our ability to produce and identify the previously unknown KF_3^- anion, and observe that it did not react strongly with gases in the RFQ [15] led to the surprising discovery that KF_3^-

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represents a new class of superhalogen anions [16] with electron binding stronger than the known superhalogen anion KF_2^- [17].

This paper describes an experimental system and the general methods for using AMS to study ion-gas reactions at the low range of hyperthermal energies (1–50 eV) in an RFQ instrument. Initial results using this method for the study of reactions between NO_2 gas and a series of fluoride anions of Sr, Y and Zr, will be presented.

2. Experimental

The system and procedures have been described in more detail elsewhere [5–7]. To be brief, Fig. 1 shows a sketch of the AMS system and Fig. 2 shows a sketch of the RFQ instrument and typical experimental settings. Table 1 lists other relevant parameters. Ions were generated in a Cs^+ sputter ion source similar to the Model 860[1] by 4 keV Cs^+ bombardment and accelerated to 15 keV axial kinetic energy for analysis in a wide gap (80 mm), 90°, $\rho = 500$ mm radius double-focussing magnet. Ion beams were collimated to ±12 mrad on-axis angular spread by a $\phi 2$ mm aperture located at the focal plane of the magnet and a $\phi 10$ mm aperture 500 mm upstream. A retractable Faraday cup ("FC2") located before the RFQ instrument was used for injection current measurements.

Literature describing RFQs is extensive [14,18–20] and further considerations for AMS can be found in [5,13,21,22]. Assuming anions of mass M [amu] and applied peak-to-peak RF voltage V_{pp} [V], a convenient form for the RFQ ion guide stability parameter for the system used in this work can be written as follows (quoted in Table 1):

$$q_2 \approx 0.017 \cdot \left(\frac{V_{pp}}{M}\right) \tag{1}$$

For ion energy retardation, the RFQ instrument was housed in an electrically isolated vacuum chamber floated at V_{RFQ}, near but above the ion source deck voltage V_S. The voltage difference is quoted in Table 1,

$$\Delta V_{SRFQ} = V_{RFQ} - V_S \tag{2}$$

While ΔV_{SRFQ} represents a deceleration voltage, the actual instantaneous ion kinetic energy would depend on contributions from DC voltages applied to RFQ segments and apertures, radial momentum increases during deceleration, energy gained from the RF field, and energy transferred during collisions with gases [21]. Preliminary simulations for this system suggest that some ions could have been much more energetic than the deceleration voltage ΔV_{SRFQ} would suggest, with a small fraction >20 eV. Related simulations can be found in [21]. These contributions cannot be ignored for quantitative measurements and reactions known to be endothermic have been observed [1].

The RFQ instrument consisted of an initial deceleration region, two RFQ ion guide segments followed by a single RFQ collision cell for ion-gas interactions, another RFQ ion guide segment and a final region for re-acceleration by V_{RFQ}.

Each RFQ segment was composed of 4 symmetrically distributed, cylindrical stainless steel electrodes of outer diameter ϕ 16 mm and inscribed radius $r_0 = 6.9$ mm. Two RFQ segments shared one RF power supply operated at 2.45 MHz between $0\,V \leqslant V_{pp} \leqslant 2000\,V$. A further static voltage (V_{DC}) could be applied to RFQ segments separately for a potential offset between neighboring segments. All 4 rods of a segment were connected to the same V_{DC} so that the RFQs were not operated as mass filters. Gradient bars were inserted between the collision cell RFQ rods to maintain a slight forward axial gradient during ion-gas collisions. Apertures had separate V_{DC} supplies.

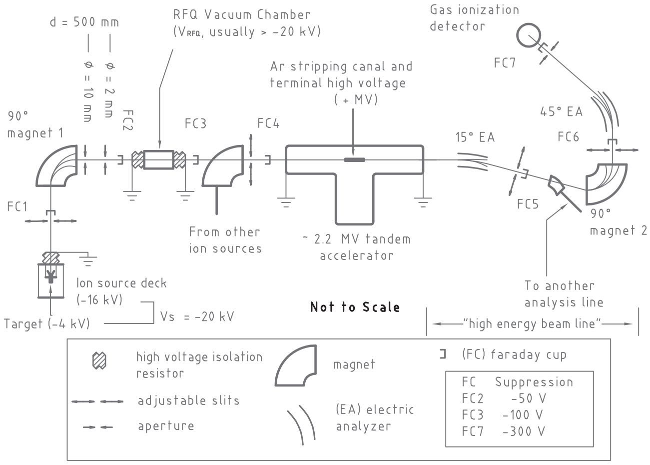

Fig. 1. Full AMS system.

Gas was conducted from external cylinders at ground potential to the vacuum chamber and silver wool was inserted in the NO_2 gas feed line to reduce contaminant compounds such as SO_x. Reaction cell pressure measurements had an uncertainty of ±0.005 mTorr, and vacuum chamber pressures were monitored separately typically showing about 2 orders of magnitude difference (e.g. 1–3 mTorr NO_2 RFQ cell pressure corresponded to 0.008–0.024 mTorr vacuum chamber pressure).

The high energy heavy element line at IsoTrace has been described elsewhere [23,24]. Electron stripping was in Ar gas with thickness of approximately 1.5 μg/cm^2. Following the tandem accelerator was a 15° (25 mm gap, $\rho = 2.5$ m, $K/\Delta K \sim 300$) electric analyzer, then a 90° (120 MeV amu, $M/\Delta M = 2600$) double-focussing magnet, followed by a 45° (42.5 mm gap, $\rho = 2.5$ m, $K/\Delta K = 900$) electric analyzer. Finally, either a Faraday cup or an ionization detector could be used for ion detection. Intermediate count rates of 40–40,000 c/s were also measured by a rate meter.

2.1. Analysis of reaction products

All ions exiting the RFQ instrument were focussed into the accelerator as there were no analyzing elements in between. A 'V_T scan' method, where V_T is the voltage applied to the accelerator terminal, was used to obtain relatively rapid mass spectra for the reaction products that contained a selected isotope by monitoring a selected charge state of the isotope of interest using the AMS system. First, the AMS system was tuned for a known parent negative ion to positive ion stripping fragment combination at a chosen V_T (ex. $^{89}YF_3^- \rightarrow {}^{89}Y^{+2}$ at 1.2 MV, Table 1). Then, V_T was scanned. If a peak from the same stripping fragment (i.e. $^{89}Y^{+2}$) was observed again at a different voltage when scanning V_T, then it had to stem from a different precursor molecule. Comparison of the tuned V_T and the V_T at which the same fragment was observed allowed for calculation of the precursor negative ion mass using the equations below.

With B the magnetic field of the "high energy beam line" magnet (magnet 2, Fig. 1), E the electric field of an electrostatic analyzer, ρ the deflection radius, and m and q^+ the mass and positive charge state of a stripping fragment, general expressions can be written:

$$B\rho = \frac{\sqrt{2 \cdot m \cdot [(q^+ + Q_{eff}) \cdot V_T + \delta]}}{q^+} \approx \frac{\sqrt{2 \cdot m \cdot [(q^+ + Q_{eff}) \cdot V_T]}}{q^+} \tag{3}$$

$$E\rho = \frac{2 \cdot [(q^+ + Q_{eff}) \cdot V_T + \delta]}{q^+} \approx \frac{2 \cdot (q^+ + Q_{eff}) \cdot V_T}{q^+} \tag{4}$$

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[1] General Ionex Corp, now produced by High Voltage Engineering.