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Discussions

Interactive comment on "A novel rocket borne ion mass spectrometer with large mass range: instrument description and first flight results" *by* Joan Stude et al.

Joan Stude et al.

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Received and published: 15 October 2020

Dear Referee #1 Thank you very much for your helpful review. Answers and actions to your comments are provided below.

"Line 30/31. Particles with masses of 'tens: : :of atomic mass units' are called MSP particles. I would think that these masses would fall under atomic or molecular ions, instead of MSPs"

CHANGED: hundreds to millions of atomic mass units [u]

We refer to Huntens bin sizes starting at 0.2 nm radius. With the different density

assumptions, this leads to a minimum of 40 u which is probably more a "molecular ion" than a MSP.

"Fig. 1. I find it strange to talk about the density of particles with masses down to 10u."

CHANGED: Figure reprinted to fit 0.2 to 10 nm. The line from Bacher et al. was adjusted to his actual measurements (start from 3022 u)

"Line 107. Perhaps it would be better talking about fractions (e.g. percentages) of ions passing through the quadrupole, instead of 'few ions'."

CHANGED: ... only small fractions of ions above 10e4 ...

"Line 134. The unit of data rate would be kbits/sec. Either call it data volume, or provide the actually rate."

CHANGED: ...the data volume per spectrum is about 10 kbyte."

"Line 144. m/z 5 – 2075. The = sign is missing."

CHANGED: ...peak height was determined with about 17.5 (5 u peak width for Kr) and the mass range from m/z 5 to m/z 2075.

"Line 160. It would be useful to provide some key information about the conditions for the launch. For example, the Sun elevation angle, or the orientation of the payload wrt to the Sun. Later in the manuscript scattered UV photons are mentioned."

ADDED: At the given time and location a solar zenith angle of $61.6°$ is calculated, the direction of the launch was $330°$ azimuth.

"Line 172. Maybe I have missed it, but was there a numerical analysis that considered the effect of the angle of attack on the transmission of ions through the quadrupole filter? This would be useful to discuss to some extent."

The simulations carried out should only show that the RF-only mode is not simply a high-pass mode. In general the increasing AoA reduces the amount of incident

ions (see eq. 3). More refined trajectory simulations would require more detailed assumptions on the incident particles properties and a higher geometric detail. Albeit this is very interesting, it would go beyond the scope of the paper.

"Fig. 6&7 and the text describing them present the data in the units of count rates. It would be useful to provide an estimate how to such rates convert to number density."

ADDED: additional section 3.5 Charge balance at 70 km altitude

In principle these count rates can be converted to ion densities (N=c/(A v). c as counts, A as intake area, v rocket speed. This leads to ion densities of N_+ = 32 cm-3 and N_- =379 cm-3, however some factors are not considered (see below).

"As a general comment, I have missed some level of discussion of how the CEM detection probability varies with the mass of the ions. Is there any information on this? Apologies if it is there and I have missed it."

ADDED: additional section 3.5 Charge balance at 70 km altitude

The working principle of a CEM detector is the generation of secondary electrons at the cone of the CEM. This mainly depends on the incident particle (mass, speed, angle) and the material of the cone (secondary electron yield). There are numerous publications on detection efficiency for atomic ions like noble gases, hydrogen and oxygen but little or none for heavy molecules. Thus for example C. A. Keller, and B. H. Cooper for positive and negative oxygen report 0.6 to 0.7 at 2 keV (ROMARA has 1.8 keV). Or Krems et al reporting similar values (2 keV) for oxygen 0.75 and 0.15 for xenon, reaching 1 with sufficient post acceleration. For micro channel plates, that use the same electron multiplying principle, Gilmore reported efficiencies of about 0.02 for 2352 u at 2 keV. For electrons a MgO coated CEM was tested by Manalio et al. to be about 3 times more efficient than uncoated.

"Lines 208 and 244: It appears that the instrument measures significantly more negatively charged ions/particles than positively charged ones. This is a potentially signifi-

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cant issue that in my opinion needs to be treated carefully. In particular, the quasineutrality of the plasma is not discussed. What would possibly be the cations or positive charge carriers that remain undetected?"

ADDED: additional section 3.5 Charge balance at 70 km altitude

For 69/70 km: Quasineutrality requires: $N+ = N- + Ne$. Measured electron densities: SAURA: $\sim$ 500 e/cm3 (Latteck 2019). With: $c+ \sim$26 kHz and $c- \sim$300 kHz (200 kHz light ions + 100 kHz heavy ions): $N+ = 32$ cm-3 and $N- = 379$ cm-3. Payload charging to positive values in the sunlight could explain this discrepancy, as the positivly charged rocket would attract negativly charged particles and repel positivly charged.

"I am not sure if I can agree with the statement starting on line 244 that the neutralization of positive MSPs due to free electrons is a viable mechanism. The large number of negative particles already suggest that the electrons are scavenged from plasma."

The electron density is measured to be about 500 e/cm3 (Latteck 2019) and thus electrons would be availabe for neutralization of positive MSPs.

"Several models have been published on the charge balance of MSPs that could provide some guidelines on how to interpret the observation for the given condition (solar elevation angle, for example). It is probably a good idea to briefly mention or discuss these models, just to provide a background for reader. If there is a significant disagreement between the models and the data, it should be stated."

In this instrument paper we wanted to focus on the instrument and first results. We are working on a follow-on paper, where we compare our measurements to the Sodankylä Ion Chemistry Model (SIC) See: Verronen et al. 2005, doi:10.1029/2004JA010932

"Another general comment: I am not sure if I have seen a discussion how heavy neutral MSP particles could possibly affect the measurements. Such particles may pass through the Q/m filter unaffected and be detected. Any information of this that is worth discussing? My guess is that at higher altitude and the corresponding higher angles of

attack this become less of an issue, but perhaps at the lowest ~2 degree angle they have a direct path to the detector from the orifice."

A neutral particle requires an angle of attack below $0.85°$ (angle between center and apertures) to pass the intake orifice and the exit aperture of the quadrupol. Heavy particles have a low angular spread at mesospheric temperatures. Thus the probability to enter is low for AoA>$1°$. Further, any neutral particle effects both, positive and negative ion measurements. Thus a neutral particle signal should be present during positive and negative ion mode. However, in negative ion mode secondary electrons from neutral particles might be detected. To briefly test that, we used UV LEDs to stimulate the CEM, independent on the applied voltages for the different ion modes. We measured a 3 times higher count rate in negative ion mode as in positive ion mode. As the photons generate secondary electrons in front of the CEM cone, these electrons are more easily captured in negative ion mode. However, we do not measure a heavy ion signature in positive ion mode that is in the order of 3 lower than in negative ion mode.

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Received and published: 15 October 2020

Dear Referee #2 Thank you very much for your helpful review. Actions and answers to your comments are provided below.

"My only substantive question is around charge balance. The positive ion spectrum at 69 km in Figure 6 shows a much lower integrated countrate than the negative ion spectrum at 70 km in Figure 7. Do these counts needs to be scaled in some way to compare them directly?"

ADDED: additional section 3.5 Charge balance at 70 km altitude

Printer-friendly version

Discussion paper

In principle these count rates can be converted to ion densities (N=c/(A v). c as counts, A as intake area, v rocket speed. For 69/70 km: Quasineutrality requires: N+ = N- + Ne. Measured electron densities: SAURA: $\sim$ 500 e/cm3 (Latteck 2019). With: c+ $\sim$26 kHz and c- $\sim$300 kHz (200 kHz light ions + 100 kHz heavy ions): N+ = 32 cm-3 and N- =379 cm-3 (see chapter 3.5 for more details). Payload charging to positive values in the sunlight could explain this discrepancy, as the positivly charged rocket would attract negativly charged particles and repel positivly charged.

"One final point: the data availability needs to be specified – location and electronic address."

CHANGED: The data will be made available through HALO database: https://halo-db.pa.op.dlr.de

Minor points:

"line 5: major"

CORRECTED

"line 20: there are some more recent references (from the Leeds group) which might be appropriate here: Frankland, V. L.; James, A. D.; Feng. W.; Plane, J. M. C. (2015): The uptake of HNO3 on meteoric smoke analogues, Journal of Atmospheric and Solar-Terrestrial Physics, 127, 150-160, 127, 150-160. James A. D., J. S. A. Brooke, T. P. Mangan, T. F. Whale, J. M. C. Plane, and B. J. Murray (2018), Nucleation of nitric acid hydrates in polar stratospheric clouds by meteoric material, Atmospheric Chemistry and Physics, 18, 4519-4531."

ADDED: references

"line 59: presumably the payload detaches from the rocket motor at some point before measurements commence? This should be made clear here, since it sounds as though the motor is attached throughout flight."

[Printer-friendly version]

[Discussion paper]

CHANGED: ...supersonic speed of the payload...

"line 59 and elsewhere: supersonic is usually written as a single word"

CORRECTED

"line 65: the end of this sentence reads a little strangely. Perhaps rewrite to something like ": : cryopump also provides structural support.""

CHANGED: ... which serves also as structural support...

"line 67: on the ground"

CORRECTED

"line 68: ... transmission, independent bias potentials can be applied to the intake cone, lens and quadrupole ...

CORRECTED

"Figure 2 caption: what is "Bat." – presumably battery, but this should be spelled out."

CHANGED

line 111: "..). For the inline: : :"

CHANGED: For the line mode...

line 118: ": : :the ram direction"

CORRECTED

line 120: ": : :of a standard : : :"

CORRECTED

line 121: ": : :atmosphere with a composition: : :"

CORRECTED

line 170: ": : :operate up to 49"

CORRECTED

line 172: "Thus ions enter the instrument"

CORRECTED

line 173: "In contrast to 70 km,"

CORRECTED

line 182: "In contrast to the calibration"

CORRECTED

This list contains changes made to the document "AMT_20201016_markedup.pdf".

- Line 5: Major
- Line 18 - 22: added reference: Arnold_1980, Arnold_1981, Arnold 1989, Frankland_2015, James_2018, Crutzen_1986
- Line 32: deleted: thick
- Line 33: rephrased
- Figure 1: Bacher measured >3000 u
- Line 61: added references: Arnold_1971, Arnold_1977
- Line 64: rephrased
- Line 70: rephrased
- Line 74: rephrased
- Figure 2: Bat. To battery
- Line 77: added text
- Line 86 - 91: rephrased
- Line 111: added text
- Line 116: rephrased
- Figure 3 reprint for clarity, added m/z 100
- Line 118: rephrased
- Line 119: rephrased
- Line 120: updated numbers
- Line 128: rephrased
- Line 131: rephrased
- Line 144: rephrased
- Line 155: rephrased
- Line 167: changed section name
- Line 172: added text
- Line 173: added text
- Line 174 - 176: added text
- Line 183: rephrased
- Line 185: rephrased
- Line 186: rephrased
- Line 195: rephrased
- Line 197 – 198: rephrased
- Line 200 - 201: rephrased
- Line 206: rephrased
- Line 207: rounded, error removed
- Line 209: rounded, error removed
- Line 211 – 212: added and removed text
- Line 221: added text
- Line 231 - 234: rephrased
- Line 239: added section "Charge balance at 70 km altitude"
- Line 280: The data will be made available through HALO database: https://halo-db.pa.op.dlr.de
- Line 291: Acknowledgements changed

A novel rocket borne ion mass spectrometer with large mass range: instrument description and first flight results

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Abstract. We present a novel rocket borne ion mass spectrometer ROMARA (ROcket borne MAss spectrometer for Research in the Atmosphere) for measurements of atmospheric positive and negative ions (atomic, molecular and cluster ions) and positively and negatively charged meteor smoke particles. Our ROMARA instrument has, compared to previous rocket borne ion mass spectrometers, a markedly larger mass range of up to m/z 2000 and a larger sensitivity, particularly for meteor smoke particle detection. ~~Mayor~~ Major objectives of this first ROMARA flight included: a functional test of the ROMARA instrument, measurements between 55 km and 121 km in the mass range of atmospheric positive and negative ions, a first attempt to conduct mass spectrometric measurements in the mass range of meteor smoke particles with mass to charge ratios up to m/z 2000, and measurements inside a polar mesospheric winter echo layer as detected by ground based radar. Our ROMARA measurements took place on the Arctic island of Andøya/Norway around noon in April 2018 and represented an integral part of the PMWE rocket campaign. During the rocket flight, ROMARA was operated in a measurement mode, offering maximum sensitivity and the ability to qualitatively detect total ion signatures even beyond its mass resolving mass range. On this first ROMARA flight we were able to meet all of our objectives. We detected atmospheric species including positive atomic, molecular and cluster ions along with negative molecular ions up to about m/z 100. Above m/z 2000, ROMARA measured strong negative ion signatures, which are likely due to negatively charged meteor smoke particles.

1 Introduction

Meteor smoke particles (MSPs) are of considerable current interest, since they have several interesting atmospheric roles: MSPs may act as sites of heterogeneous reactions involving atmospheric trace gases and ions. Moreover, MSPs act as nuclei in the formation of mesospheric water ice clouds(Rapp and Thomas, 2006) and as nuclei in the formation of the stratospheric sulphuric acid (Arnold and Fabian, 1980; Arnold et al., 1981; Hervig et al., 2017) and nitric acid aerosol layers (Arnold and Knop, 1989; Arnold et al., 1989; Voigt et al., 2005; Frankland et al., 2015; James et al., 2018; Curtius et al., 2005), which have an impact on ozone and climate ~~(Rapp and Thomas, 2006; Hervig et al., 2017; Voigt et al., 2005; Curtius et al., 2005)~~ (Crutzen and Arnold, 1986). MSPs may also influence the charge balance of the lower ionosphere, by acting as scavengers of

free electrons and ions (Rapp and Lübken, 2001; Friedrich et al., 2012)

(Schulte and Arnold, 1992; Rapp and Lübken, 2001; Friedrich et al., 2012). Furthermore, electrically charged MSPs have been

25 proposed to play a potential role in the formation of polar mesospheric winter radar echoes (PMWE) (Rapp et al., 2011; La Hoz and Havnes, 2008).

MSPs are formed by the ablation of meteors or interplanetary dust particles in the upper atmosphere, leading to meteoric vapours, which ultimately recondense to secondary aerosol particles, as was originally hypothesized by Rosinski and Snow (1961). The meteoric vapours are released, mostly at altitudes around 90 km in the mesopause region, during the entry of the

30 atmosphere at high velocities (Kalashnikova et al., 2000; Plane, 2003). Hereafter, such vapours undergo gas phase reactions with atmospheric gases and ions and ultimately recondense, leading to tiny aerosol particles (Plane, 2012). Hunten et al. (1980) termed these particles meteor smoke particles and conducted model simulations, predicting a ~~thick~~ MSP layer to be present between 70 and at least 100 km, peaking around 85 km. Predicted MSP radii range from 0.2 to 10 nm, corresponding to ~~some tens to some hundred thousands~~ hundreds to millions of atomic mass units (u) (Fig. 1). For example, at 85 km, MSPs with radii

35 larger than 0.2 nm have a predicted number concentration of $7 \cdot 10^4$ cm^{-3}. The meteor vapours, which lead to MSP formation, are to a large part composed of metal and silicon atoms, formed mostly via ion-molecule reactions with atmospheric positive ions. Early rocket borne ion composition measurements of the whole suite of the most abundant meteoric positive ion species Fe, Mg, Si and their isotopes revealed an ion composition similar to the elemental composition of chondrites (Krankowsky et al., 1972). The mass density of ordinary chondrites is about 3.5 g cm^{-3} (Britt and Consolmagno, 2003), however the

40 ablation process might form particles of lower densities with 2.0 g cm^{-3} as assumed by Hunten et al. (1980) and Plane et al. (2014).
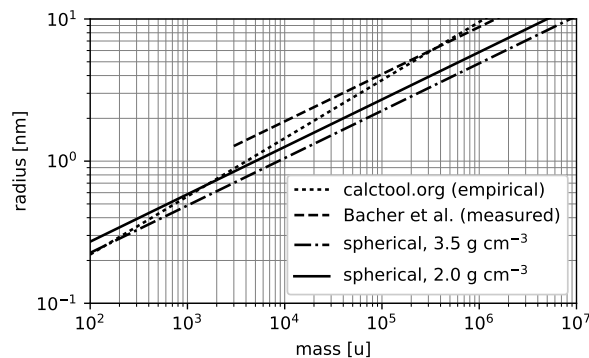
Figure 1. Comparison of different relationships between molecule mass and size with data from Bacher et al. (2001) and (Shipway, A. and Shipway, S., 2008).

Using the above values in Fig. 1 and assuming a spherical MSP particle of 0.3 nm radius, one would estimate an effective mass of about 135 u to 240 u. First observational indications for the presence of such negatively charged nascent MSPs (>473 u) have been obtained from rocket borne measurements of ion mass spectrometers by Schulte and Arnold (1992) under

45 twilight conditions. Meanwhile several rocket borne electrostatic probe measurements provided evidence for larger MSPs than

measured by the ion mass spectrometers (Gelinas et al., 1998; Rapp et al., 2005; Lynch et al., 2005; Strelnikov et al., 2012; Robertson et al., 2014; Havnes et al., 2015; Asmus et al., 2017). Even some first direct information on the chemical nature of MSPs was obtained by rocket borne photo ionisation measurements. It was found that the ionisation potential ~~from~~ of MSPs is somewhat similar to that of Fe and Mg hydroxide clusters (Rapp et al., 2012). Besides those direct in-situ measurements, more indirect measurements of MSP-signatures in the spectra of incoherent scatter radars were reported by several investigators: Rapp et al. (2007); Strelnikova et al. (2007); Fentzke et al. (2009, 2012). Also satellite measurements with the Solar Occultation For Ice Experiment (SOFIE) have provided clear evidence of MSP in solar occultation extinction measurements (Hervig et al., 2009) .

The present paper reports on a search of MSPs using a novel rocket borne ion mass spectrometer, having an increased mass range of up to m/z 2000 and an increased sensitivity. Importantly, the rocket flight was determined to penetrate a PMWE layer, which could indeed be realized. Details about the PMWE campaign as such will be given in a future publication by Strelnikov et al. (in preparation). Here we give a thorough description of the ROMARA instrument and a brief presentation of ion and MSP data.

2 Instrument description

The instrument ROMARA is a cryogenically pumped quadrupole mass spectrometer based on earlier designs at Max-Planck-Institute for Nuclear Physics (MPIK) ~~(Krankowsky et al., 1972)~~(Arnold et al., 1971; Krankowsky et al., 1972; Arnold et al., 1977b) . A cross-section of instrument and mass spectrometer is shown in Fig. 2. Ions enter the instrument through a knife edge intake orifice with a radius of 0.5 mm on the tip of a double cone. The design allows to sample the atmosphere in front of the shock due to the ~~super sonic~~ supersonic speed of the ~~rocket~~payload. A quadrupole lens (Brubaker, 1968) of 36 mm length is mounted between intake orifice and quadrupole, with skewed tips for a placement as close as possible to the intake cone. The quadrupole mass filter has a length of 115 mm and uses cylindrical rods of 2.4 mm radius. The field radius r_0 between the rods is given by a ratio of $r_{rod}/r_0 = 1.128$ as recommended by Douglas (2009).

Ions passing the mass filter are detected by a channel electron multiplier (CEM), placed in the centre of the instrument, in line of sight of the intake orifice. Quadrupole and detector are almost completely surrounded by the cryopump which serves also as ~~structure~~mechanical support. A cap seals the instrument intake during storage and launch and is jettisoned before the measurements begin. For this purpose a spring loaded bayonet ring is turned by pyro-actuators to release the cap. Inside the cap a commercial ion source (electron ionisation, Hiden Analytical 205011) allows to calibrate and test the instrument on the ground and monitors operation during launch until the cap together with the ion source is removed. To increase ion transmission, ~~intake cone, lens and quadrupole can be applied with independent bias potentials~~ independent bias potentials can be applied to the intake cone and the quadrupole lens and rods (see 2.4). To maximize detection efficiency, especially for heavy ions, the CEM (Photonis 4830-MgO) is coated with magnesium oxide and biased to ±1800 V with a constant voltage across the CEM of about +2700 V. Measuring positive ions requires all bias voltages to be negative and vice versa~~, thus~~. For
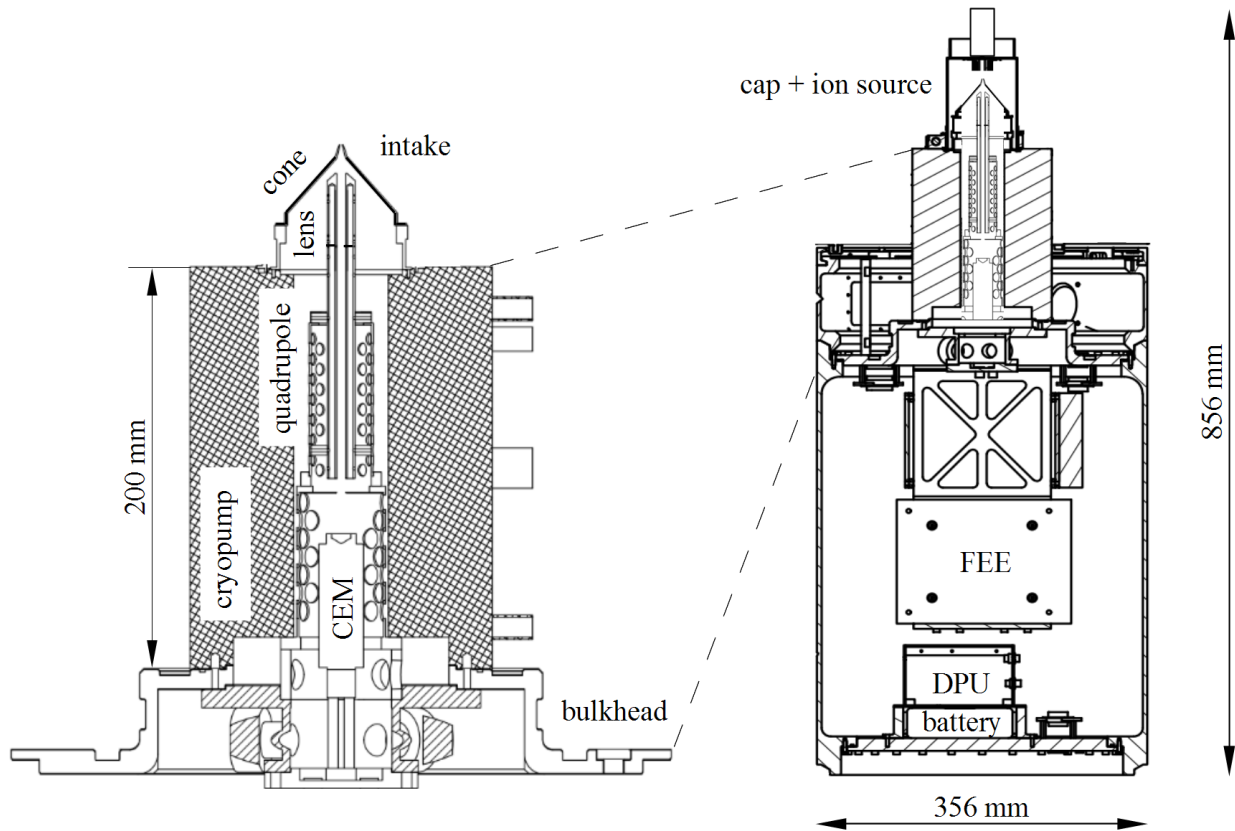
Figure 2. LEFT: detailed cross-section of ROMARA mass spectrometer in flight configuration. RIGHT: cross-section of complete ROMARA instrument in launch configuration. CEM: channel electron multiplier, FEE: front-end electronics, DPU: data processing unit.

an alternating operation of the instrument between positive and negative ions, the bias voltages are switched in the dead time between the spectra.

80 The cryopump is a bath type design using gold plated cooling surfaces. A heat shield, cooled by the evaporating cryogen is placed between reservoir and outer shell. As cryogen, liquid helium is most readily available, however liquid helium evaporates rather quickly and the reservoir would be depleted in about an hour. Longer standby times can be achieved using neon because of its higher vaporisation enthalpy. Thus the rocket can be safely prepared for launch and the probability to meet the desired atmospheric conditions during a day of work is higher. On the day of launch a total standby time of $\approx 7\ h$ with subsequent

85 successful operation was achieved. We produced liquid neon at the launch site through liquefying neon gas with liquid helium. A disadvantage of ~~a cryopump is the inability to efficiently pump gases with a lower boiling point as the cryogen . In our~~

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~~ease this means that~~ using neon as cryogen is the inefficient pumping of hydrogen, helium and neon itself ~~can not be pumped effectively which could lead to~~ due to their boiling points below that of neon. While parts of these gases are trapped in the frozen air building up on the cooling surfaces, the remaining gas (mostly helium) could accumulate above a critical pressure~~increase~~

90 ~~by the accumulation of such gases~~. However, for our combination of intake size and ~~the duration of the flight in the order of minutes,~~ duration of flight this is not of concern.

A reinforced bulkhead holds the complete construction of electronics, quadrupole and cryopump. The bulkhead further seals the main structure against atmosphere and water during splashdown. Front-end electronics (FEE), data processing unit (DPU) and batteries are housed in the main structure at 1.5 bar absolute nitrogen pressure to safely handle high voltages. The whole

95 instrument is 856 mm in length with a diameter of 356 mm at a total mass of about 50 kg.

2.1 Principle of operation

A quadrupole mass spectrometer separates ions by their mass-to-charge ratio (m/z) in applying electrical fields along a central drift path of ions. These fields are ideally hyperbolic but are often approximated by cylindrical electrodes, the rods, circularly arranged along their length. The required fields are formed by radio frequency (V_{RF}) and static (V_{DC}) potentials with opposite

100 polarity at neighbouring rods. Thus opposing rods are electrically connected and form two pairs of rods. Ions of a certain m/z retain stable trajectories, pass the quadrupole and can be detected at the exit, while other ions collide with the rods and are lost. To pull ions in between the rods a constant bias voltage V_B is applied to all rods, i.e.,

$$V_{rod} = V_B \pm [V_{DC} + V_{RF}\cos(\omega t)] \tag{1}$$

The quadrupole allows 2 modes of operation: an RF-only mode and a line mode. In RF-only mode, V_{DC} is set to zero.

105 With increasing V_{RF} lower masses are rejected, until a maximum V_{RF} is reached. The count rate in the detector will thus eventually drop for each ion mass and produce a step in the recorded mass spectrum, which can be analysed for width and height. Ions with masses above the mass given by the maximum V_{RF} still pass the quadrupole but can not be mass analysed. This is often described as a high pass mass filter, although it is actually a wide bandpass as illustrated in Fig. 3. We simulated transmission curves for different mass settings of the quadrupole and different ion masses using SIMION® (Dahl, 2000) to

110 model the electrical fields and individual ion trajectories. Collisions with the background gas or charge exchange processes were omitted. For each ion mass ~~and mass setting~~per charge and mass per charge setting of the quadrupole, a population of 3000 ions is started inside the intake orifice with a constant velocity of 980 m s^{-1} (= rocket velocity, v), an angle of attack of 2.2° and a uniform conical direction distribution with an opening angle δ defined as:

$$\delta = 2 \operatorname{atan}\left(\frac{3kT}{mv}\right) \tag{2}$$

115 with k as the Boltzmann constant, T as temperature (180 K), m as ion mass.

It is evident that for low V_{RF} values and hence mass settings of the quadrupole, only ~~few~~ small fractions of ions above 10^4 u (≈ 1.2 nm radius) pass the quadrupole to the detector. Ions with sufficient masses and thereby sufficient kinetic energy do not respond efficiently to the small applied fields. In this case the intake orifice and exit aperture act as ~~collimators~~ collimator and
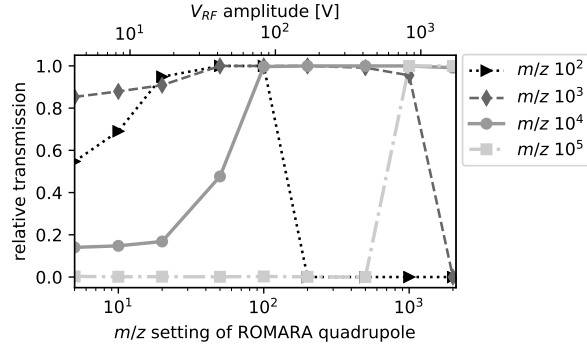
Figure 3. SIMION® simulation of ROMARA quadrupole for heavy ion transmission in RF-only mode for an angle of attack of $2.2°$.

limit the detector flux to ~~straight trajectories~~ trajectories smaller than $0.85°$ from the central axis. The instrument thus mass
analyses particles up to m/z 2000 and detects the presence of particles up to about m/z $3 \cdot 10^5$ ($\approx$ ~~2.5~~ ≈ 3 nm radius). ~~In~~ For
the line mode with an additionally applied V_{DC}, this effect is much smaller and can be neglected. For the quadrupole to operate
in line mode V_{DC} is set to a constant ratio to V_{RF} and thus forms a narrow band pass mass filter. With increasing voltages
the band pass window is moved from low to high masses and a line spectrum can be recorded. The ratio of V_{DC} to V_{RF}
determines the size of the band pass window and thus resolution and sensitivity. The voltage applied to the quadrupole lens
always corresponds to V_{RF} only. This minimizes ion losses at the entrance to the rod system, when the quadrupole is operated
in line mode.

2.2 Ion sampling from the atmosphere

The payload moves at ~~super sonic~~ supersonic speeds through the atmosphere, developing a shock in the ram direction. The
knife-edge double cone is designed to sample ions in front of the shock, avoiding perturbations and possible brake up of
weakly bound ions. The shock was simulated with the direct Monte Carlo simulation software DS2V (Bird, 1988, 1994) under
conditions of ~~standard atmosphere for~~ a standard atmosphere with a composition of nitrogen and oxygen (NRLMSISE-00)
and rocket speeds appropriate for our flight. The left panel of Figure 4 shows rocket speed, temperature and number density
for different altitudes used in the simulation. The right panel of Figure 4 shows the relative air speed and the increase of
temperature and number density 1 cm upstream the intake orifice. Up to 80 km the ratios stay about unity. Above 80 km the
shock starts to detach from the payload and number density and temperature begin to increase, while the relative air speed
decreases. Values change roughly by a factor of 2 at 100 km altitude as compared to undisturbed conditions. Heavier particles
will be less affected (e.g. Hedin et al. (2007); Asmus et al. (2017)).

6
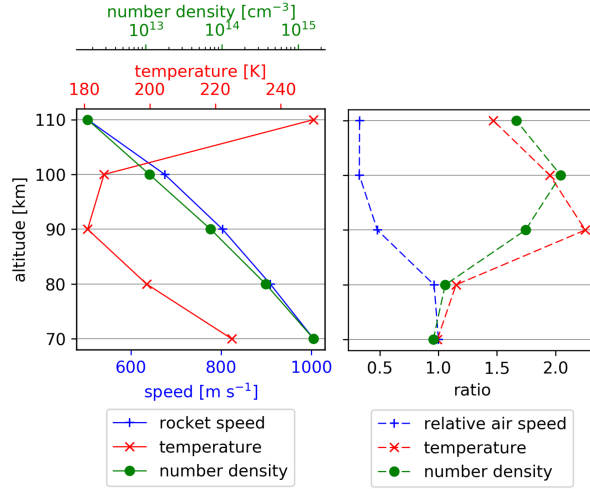
Figure 4. LEFT: DS2V simulation input parameters from NRLMSISE-00 Atmosphere Model, RIGHT: DS2V simulation results, 1 cm upstream of inlet orifice, plotted as ratio to ambient values of relative air speed, atmospheric temperature and number density.

2.3 Electronics

As front-end electronics we used modified electronics from MPIK, originally developed for aircraft operations e.g.: the
140   quadrupole power supply. The electronic pulses from the CEM are transformed by an Amptek A111F charge amplifier to digitally countable pulses. To control the front-end electronics and process the data we use a microprocessor/FPGA system from National Instruments (sbRIO-9637). During ground preparation the system can be remotely controlled and updated if necessary. After launch the system is controlled by a time-line program that does not allow further interactions. The data are transmitted via the rocket service module but are also stored on an internal SD card. The data ~~rate is about 100 kbit~~ volume is
145   about 10 kbyte per spectrum. The instrument is self powered using lithium iron phosphate batteries which allow approximately 1.5 h of operation.

2.4 Calibration

The bias voltages of the quadrupole lens and the rods were calibrated using positive xenon ions. The intake cone was connected to ground potential. We found an optimum transmission if the rods have a potential of -50 V and the quadrupole lens -20.5 V. For
150   negative ions the same absolute values were used. During tests we observed a significant loss of transmission if both voltages were equal. For the mass calibration of the instrument we used 4 eV ions of neon, krypton, xenon and perfluorotributylamine (PFTBA, Heptacosa, FC-43), allowing a calibration up to m/z 502. In Fig. 5 we show in the upper panel measurements of Kr and Xe ions, the cumulative distribution function (CDF) fits of the ion mass steps, the reconstructed Gaussian peaks and the respective isotopes lines from the National Institute of Standards and Technology (NIST). The mass resolution $m/\Delta m$
155   at 50% peak height was determined with about 17.5 ($\approx$ 5 u peak width for Kr) and the theoretical mass range ~~to~~ from m/z 5

7

to m/z 2075. In the lower panel we show the standard spectrum of PFTBA from NIST data and the measured spectrum of ROMARA. The NIST spectrum was converted to an RF-only version by summing up all single peaks in the NIST data. The measured spectrum was normalized to the m/z 69 peak and shows good agreement for the major peaks of PFTBA up to m/z 502. In cases where there are many small peaks close to each other the RF-only spectrum turns into a continuous slope because of the limited mass resolution. Each spectrum takes 1.274 seconds to complete with 4096 mass channels. The dead time between 2 spectra is 45 ms. The quadrupole frequency is about 1.4 MHz with a maximum amplitude (V_{RF}) of $\approx$ 1750 V.
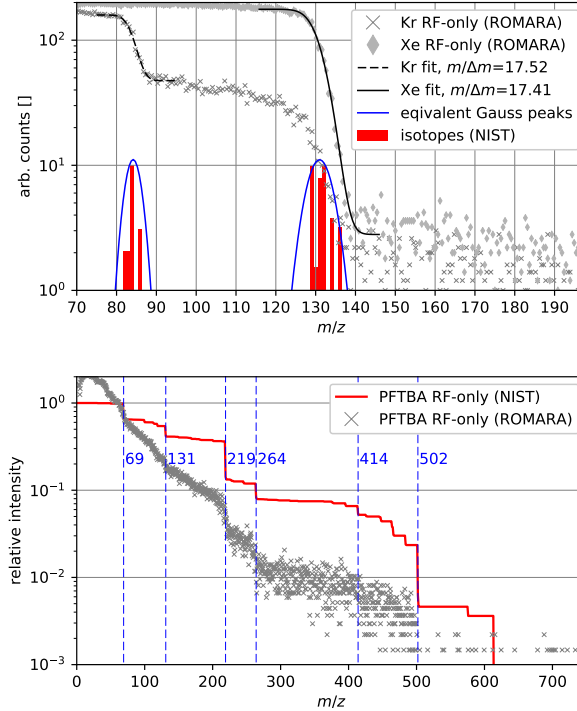
Figure 5. UPPER panel: RF-only spectrum of Kr and Xe, CDF fit and equivalent Gauss peak, LOWER panel: ROMARA RF-only measurement of PFTBA and NIST data of PFTBA

The noise level of the instrument is mostly determined by the oscillator and the switching between positive and negative ion mode leading to increased counts at the beginning and at the end of each spectrum, especially in the negative ion mode. On the launch pad with the instrument operating nominally and the ion source switched off, the average noise floor over a whole spectrum was 9 Hz in positive ion mode and 240 Hz in negative ion mode, well below our 1 count limit of 3.3 kHz.

3 Measurement and discussion

3.1 ~~Electron density and radar measurements~~Launch conditions

The main launch criteria were determined by the MAARSY radar (Latteck et al., 2012; Rapp et al., 2011; Latteck et al., 2019), looking for polar mesospheric winter echoes. The radar pointed alternately along the rocket trajectory and to zenith (see Latteck et al. (2019) for details). The days before launch several echoes were detected but other launch criteria for e.g. the sea recovery were not met. On 13 April 2018 at 09:44:00 UTC, ROMARA was launched directly into an echo between 78 km and 80 km altitude, reaching an apogee of 121.4 km. The rocket hit the echo at its decaying tail. At lower altitudes smaller and thinner echoes were present as well. The electron density was measured with the on-board wave propagation experiment (Friedrich et al., 2013) but ~~will be reported elsewhere~~also with the Saura MF radar (Latteck et al., 2019) about 20 km south of the launch site. The ionosphere was moderately disturbed with a simulated riometer absorption of 0.26 dB at 27.6 MHz. At the given time and location a solar zenith angle of 61.6° is calculated, the direction of the launch was 330° azimuth (Northwest by north).

3.2 Ion measurements

The instrument was operated in RF-only mode throughout the flight and measured natural ions during ascent from 54.4 km to apogee at 121.4 km but also on the downleg in the rocket wake. The intake cone was applied with a constant 0 V bias and thus was at payload potential during the whole flight. In this instrumentally oriented paper, we present 8 exemplary mass spectra, obtained during rocket ascent: 4 positive and 4 negative. These include 2 test spectra, obtained just prior to cap-ejection and 6 ambient ion spectra. A more detailed analysis of the ion measurements will be presented elsewhere. The internal ion source was operated ~~until~~ up to 49 km altitude and was switched off before the ejection of the cap. Other spectra were chosen around 70 km and 106 km. At 70 km the sampling conditions are ideal with the shock wave being well attached to the intake cone as the simulations of Fig. 4 show. Thus ions ~~entering~~ enter the instrument with minimum disturbance and under small angles of attack ($\alpha \approx 2.2°$). ~~Contrary~~ In contrast to 70 km, the spectrum at 106 km is much more affected by the shock, now completely detached and angles of attack are considerably larger ($\alpha \approx 11.4°$).

Raw count rates c_{raw} were corrected for detector dead time τ and angle of attack α. The angle was provided by the rocket operator and the dead time was taken from the A111F data sheet with $\tau = 350$ ns, giving the corrected count rate c:

$$c = \frac{c_{raw}}{(1 - c_{raw}\tau) \cdot \cos(\alpha)}. \tag{3}$$

In Fig. 6 and Fig. 7 we included an 8 channel mean, as the original data is noisy. The count rates given hereafter refer to the 8 channel running mean count rate.

3.3 Positive ions

Figure 6A depicts a positive test spectrum obtained at 46.6 km, prior to cap ejection with the internal ion source in operation. ~~Contrary~~ In contrast to the calibration data of Fig. 5 where a laboratory power supply for the ion source is used, the internal power supply provides a less stable current and typical residual gas steps are not clearly visible. However the count rate clearly

decreases from about m/z 28 up to m/z 300, typical for ~~residual gas and an unclean ion source~~ leaking air and contaminations in the ion source and cap, e.g. ~~hydrocarbon contaminations~~hydrocarbons. The maximum count rate is 636 kHz for below m/z 28.
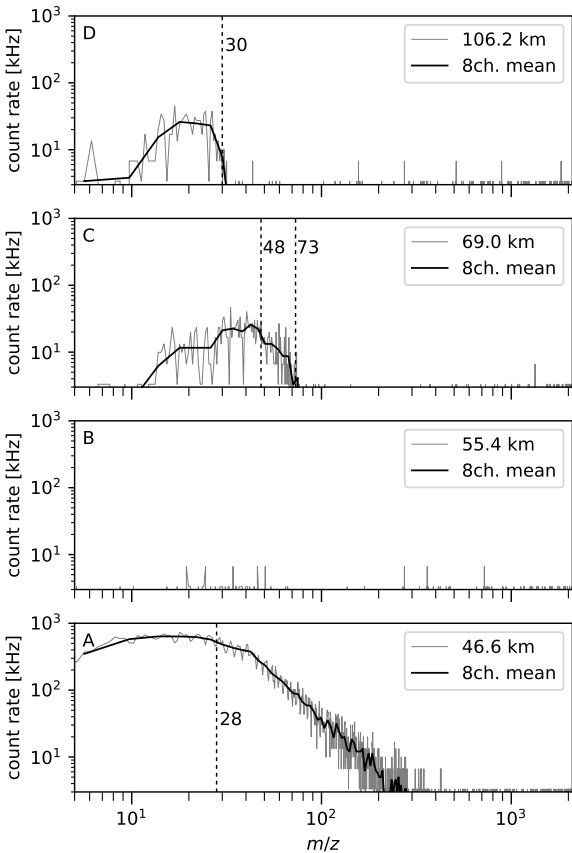
Figure 6. Positive ion mass spectra at 4 different altitudes during ascent in logarithmic scales. Spectrum A shows the residual gas spectrum from the internal ion source before ejecting the cap. Spectrum B, C and D show natural ambient ions.

Figure 6B depicts the spectrum at 55.4 km, just after ejecting the cap, and serves to show that no ~~residual peaks~~residuals are present in the mass spectrum~~are present~~. Some counts ~~in the same mass channels~~ of the same type as in the ~~selected~~ spectrum of Fig. 6C are already visible.

Figure 6C depicts a spectrum starting at 69.0 km altitude with ambient atmospheric positive ions. It has a maximum mean count rate of about 26 kHz and a maximum of m/z 76, which is most likely due to the expected proton hydrate $H^+(H_2O)_4$[73 u]. This proton hydrate of 4th order has been measured previously (Arnold et al., 1977a; Kopp et al., 1984) often together with $H^+(H_2O)_3$[55 u] and higher orders. However, in this ~~spectrum a substantial~~ particular spectrum a step is

found at around m/z ~~48.6 ±1.2~~ 49 which is thus more likely due to $NO^+(H_2O)$[48 u]. A less defined step around m/z 58 with only few counts per mass channel, corresponds likely to $H^+(H_2O)_3$[55 u].

In Fig. 6D a spectrum at 106.2 km is shown with a similar maximum count rate of 26 kHz with a step around m/z ~~28.1 ±3.3.~~ 28. This is consistent with NO^+[30 u] or O_2^+[32 u] as the most dominant ions at that altitude.

It is noticeable that the spectra do not start at maximum count rates. This is qualitatively the same effect as shown ~~for heavy ions~~ by the 100 u curve in Fig. 3~~and can be reproduced in the SIMION® simulations for smaller masses~~.

None of these positive ion spectra indicate the presence of heavy positive ions.

3.4 Negative ions

In Fig. 7 we show characteristic negative ion spectra for similar altitudes as in Fig. 6. The spectrum in Fig. 7A is taken before cap ejection at an altitude of 48.3 km with the ion source operating. As expected, negative ions are not present, as they are not formed by the ion source (electron ionisation) in the cap.
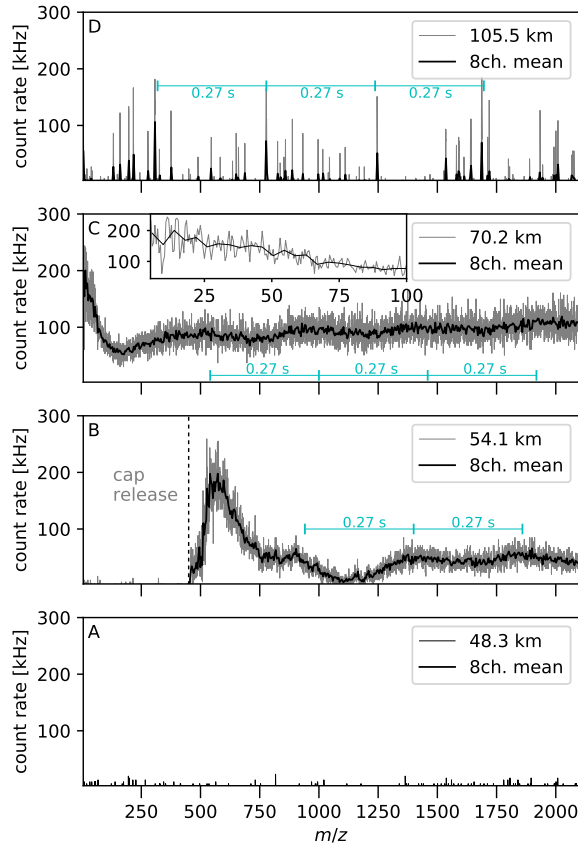
Figure 7. Negative ion mass spectra in linear scales during ascent, at similar altitudes as the positive ion mass spectra. In spectrum A the instrument is still sealed to the environment, while in spectra B,C and D natural ambient ions are present.

Figure 7B shows the spectrum beginning at 54.1 km altitude, in which the cap was ejected. Before cap ejection the count rate is at the same low noise level as in Figure 7A. Instantaneously with cap ejection around m/z 400, the count rate increases to a plateau around m/z 560 with a maximum count rate at 200 kHz. Hereafter the count rate decreases to about 50 kHz showing periodic minima and maxima. The maxima are about 0.27 s apart, indicating a dependence on rocket spin (3.6 Hz). To the end of the spectrum the count rate remains at about 50 kHz indicating ions beyond our mass range of m/z 2000.

Figure 7C at 70.2 km altitude contains light negative ions with a maximum count rate of 200 kHz exceeding the positive count rate almost tenfold. The count rate in the end of the spectrum is about 100 kHz. The inset is a blow up of the small ion mass range to m/z 100, indicating the presence of numerous unresolved mass steps. Potential mass steps can be found around: m/z 24, m/z 48, m/z 58, m/z 65 and m/z 79. These steps could be caused by CN^-[26 u], $Cl^-(H_2O)$[53 u], CO_3^-[60 u], HCO_3^-[61 u], NO_3^-[62 u], CO_4^-[76 u], of which some have been measured previously by Arnold et al. (1971, 1982) and Kopp (1992). Similar to Fig. 7B is the heavy ion signature modulated by the rocket spin, requiring 4.5 modulations of the incident ion flux for a full spectrum. This can only be caused by asymmetries in the ion optics or at the intake orifice under angles of attack larger than zero. We therefore interpret ~~the~~ this signal as negative ions with masses above our mass range of m/z 2000. Other origins of ~~the~~ this signal such as stray UV-light, neutral particles or a pressure effect inside the instrument ~~are~~ can most likely be ruled out: while UV-light or neutral particles could trigger false counts, this would also be visible in the positive ion mode ~~which was tested~~ as well and was tested for UV-light in the laboratory. A pressure effect inside the instrument due to the higher voltages ~~in~~ of the negative ion mode would lead to counts that directly correlate to decreasing ambient pressure but instead we measured an increase from about 50 kHz in Fig. 7B to about 100 kHz in Fig. 7C.

In Fig. 7D at 105.5 km altitude, increased levels of noise can be seen with no obvious small or large ion signatures. However, the largest spikes at: m/z 1688, m/z 1245, m/z 778 and m/z 308 are 0.27 s apart and thus indicate some heavy ions, again modulated by the rocket spin.

3.5 Charge balance at 70 km altitude

It is usually assumed that the atmosphere is quasineutral, such that the positive ion density, balances the negative ion and electron density: $N^+ = N^- + N_e$. At around 70 km we measured a maximum count rate of 26 kHz for positive ions and around 300 kHz for negative ions (light ions + heavy ions). Count rates may be converted to ion densities by the air column swept out through the intake orifice and rocket velocity: $N = c/(\pi r^2 v)$. This leads to ion densities of N^+ = 32 cm^{-3} and N^- = 379 cm^{-3}. In Latteck et al. (2019) the electron density at 70 km was about 500 cm^{-3}, suggesting about 27 times more negative charges than positive. The simple conversion of counts to ion density however does not consider the transmission efficiency of ions between intake and CEM, the absolute detection efficiency of the CEM and the payload potential. The transmission efficiency of the quadrupole in RF-only mode is assumed to be close to unity (Schulte and Arnold, 1992) and should be equal for both charge states as the potential amplitudes are identical between positive and negative ion mode. The absolute detection efficiency across the mass range of our MgO coated CEM is presently unknown. For the same CEM model but without MgO coating and similar ion energies Keller and Cooper (1996) found the absolute detection efficiency for oxygen to be about 0.6 for positive ions and 0.7 for negative ions. Heavier atomic ions generally have a lower detection

efficiency (Krems et al., 2005), e.g. xenon: 0.15 at 2 keV but publications are scarce for heavier molecules. Measurements from Gilmore and Seah (2000) on micro channel plates, indicate a rather low detection efficiency of around 0.02 for molecules of 2352 u at 2 keV. The payload potential is the result of currents to and from the payload, mainly dominated by free electrons (Darian et al., 2017; Friedrich et al., 2013). At 70 km the electron density is low and the emission of photoelectrons could enable a positive payload potential, thus increasing negative and decreasing positive ion count rates.

4 Conclusions

With our rocket borne mass spectrometer for research in the atmosphere (ROMARA), we successfully re-vitalized an instrument concept to make mass spectrometric measurements in the mesosphere and lower thermosphere. With its extended mass range for MSPs, ROMARA detects ambient atmospheric positive and negative ions up to m/z 2000 and in addition, ROMARA measures the total count rate of ions with masses above m/z 2000. We have simulated the instruments aerodynamic and ion-optical behaviour and conducted laboratory measurements for the characterisation of ROMARA. The first ROMARA flight, which took place at noon on April 13th 2018 and reached an apogee of ~~121~~121.4 km, was successful in detecting ambient atmospheric positive and large negative ions. After the flight the instrument was recovered nearly undamaged. Six exemplary mass spectra of ambient atmospheric positive and negative ions, measured during rocket ascent, are shown in the present paper and demonstrating the successful application of an instrument to conditions in the middle atmosphere.

The most important scientific results of the ROMARA data presented here concerns the detection of large negative ions and a strong indication for the absence of large positive ions. Most likely, the large ions are actually negatively charged meteor smoke particles with radii of about 0.6 nm to 2.5 nm (m/z 2000 - m/z 10^5). Besides large negative ions also small negative ions with masses mostly below m/z 150 have been detected at 70 km. At 106 km, no negative ions have been detected. These findings are consistent with previous measurements. Positive ions measured at 70 km are mostly hydrated cluster ions up to m/z 73. At 106 km the detected small positive ions have mass numbers around m/z 30. Again, this is consistent with previous measurements, which found $H^+(H_2O)_3$[55 u] and $H^+(H_2O)_4$[73 u] to be dominant at 70 km and NO^+[30 u] and O_2^+[32 u] to dominate at 105 km. Large positive ions have not been detected, neither at 70 km nor at 105 km above our measurement threshold. From our large ion measurements at 70 km the following conclusions may be drawn: The presence of large negative ions suggests that at 70 km, electron attachment to neutral MSPs was sufficiently fast and neutralisation of negative MSPs by photo detachment and recombination with positive ions was sufficiently slow to allow a substantial fraction of MSPs to be negatively charged. The absence of positive MSPs suggests that, neutralisation of positive MSPs by collisions with free electrons was faster than positive MSP formation by uptake of positive ions.

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