

## First Mass Spectrometric Measurements of Atmospheric Ions at Ground Level

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Naturally occurring positive and negative ions in the troposphere have been mass identified at Sapelo Island, Georgia, and Mt. Evans, Colorado. These measurements were made at ground level under a variety of weather conditions. Over the course of the experiment, positive ions were seen at masses 54, 60, 80, and 94 AMU. Mass 54 AMU is believed to be  $\text{NH}_4^+ \cdot 2(\text{H}_2\text{O})$ . In the negative spectrum, ions were observed at masses 62 and 125 AMU and are believed to be  $\text{NO}_3^-$  and  $\text{NO}_3^- \cdot (\text{HNO}_3)$ . Several ions that appear to be  $\text{H}_2\text{O}$  clusters of the above ions were also observed. These are the first measurements of the mass identity (1-AMU resolution) of naturally occurring ions in the troposphere with the exception of a previous measurement made in 1982 over a limited mass range in an urban environment (Eisele, 1983). Ions that were artificially produced were also studied and compared to the much longer lived natural ions.

## INTRODUCTION

Although ions are known to exist at all levels of the atmosphere, their chemistry in the ionosphere is probably the best understood. The relatively large fractional concentration of ions present at high altitudes has facilitated the identification of many ion species, despite difficulties in accessing this region of the atmosphere. In addition the lower pressures at higher altitudes limit the number and type of collisions that can occur during an ion's lifetime and therefore make the ion chemistry less complicated. Only recently have ions been mass identified in the stratosphere, where the fractional ion concentration is much lower and the ion chemistry is far more complex. The stratospheric ion chemistry is largely controlled by the neutral species, such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{CH}_3\text{CN}$  [Arnold *et al.*, 1980; Henschen *et al.*, 1981; Viggiano and Arnold, 1983; Heitmann and Arnold, 1983]. At sea level the fractional ion concentration drops to one part in  $10^{17}$ , thus there are very few ions to measure. These ions undergo about  $10^{12}$  or  $10^{13}$  collisions during their lifetime, so the ion chemistry could be primarily controlled by trace neutral species at concentrations of a part per trillion (ppt) or less. A lack of measurements and a multiplicity of possible reactions have perpetuated our lack of understanding of tropospheric ion chemistry.

The sequence of chemical reactions that alters the ion species between their creation by cosmic rays or radioactive decay and their removal by either ion-ion recombination, attachment to a particle, or some other loss mechanism may be quite complex. Categories of reactions that must be considered are two- and three-body reactions, which control the identity of the core ion, and ligand attachment or dissociation reactions, which determine what molecules may be clustered to a core ion. Although core ion and ligand attachment reactions are not actually independent of each other, it is often helpful to consider them separately.

Ion lifetimes in clear air are expected to be on the order of 100 s [Ferguson *et al.*, 1979]. However, during the first second after ionization, most of the ions in the troposphere have experienced enough collisions with neutral species whose con-

centrations are in the parts per billion (ppb) range or higher to have established very stable core ions. The endothermicity for a reaction resulting in the loss of the ion's charge to one of the more common constituents of air, such as nitrogen or oxygen, can typically be of the order of 100 kcal/mol. These stable core ions presumably have few reactive collisions during the majority of their lifetimes. The identity of the terminal core ion species could be controlled by very low concentrations of neutral species that can undergo exothermic reactions to form even more stable core ions if such molecules exist in the troposphere with concentrations around the ppt range.

Attachment and dissociation of ligand molecules such as water occur continuously in the lower troposphere, although the core ion may remain unchanged over much of the ion's lifetime. These reactions are expected to be quite temperature dependent as a result of the relatively low ligand binding energies. These reactions may result in a series of ions that have various numbers of attached ligands clustered to the same core ion. Such a series of complexed ions will be called an ion family. Ligands may also be important in determining terminal ion identities, even though they may only occur in the ppt range, if their binding is sufficiently strong. Present results (this work) suggest that, in the troposphere, molecules such as  $\text{HNO}_3$  may well fall into this category.

The present paper describes our attempt to improve the understanding of tropospheric ion chemistry by mass identifying some of the more abundant ions present. The measurements were carried out at two vastly different sites. The first was performed on the coast of the Atlantic Ocean at Sapelo Island, Georgia, and the second was performed on top of Mt. Evans in the Rocky Mountains of Colorado. These measurements were made over a period of several months under a variety of weather conditions. Due to the complexity of the chemistry, the lack of knowledge of neutral species present at or below the ppt range, and the low signal levels, only a few of the ion masses observed can, at present, be tentatively identified as a specific chemical species.

## DESCRIPTION AND OPERATION OF APPARATUS

A laboratory apparatus, previously described by Eisele [1983], capable of directly sampling and mass identifying tropospheric ions has been incorporated into a mobile laboratory. A schematic drawing of the laboratory is shown in Figure 1, and details describing the surrounding terrain at each experimental site will be given in the next section.

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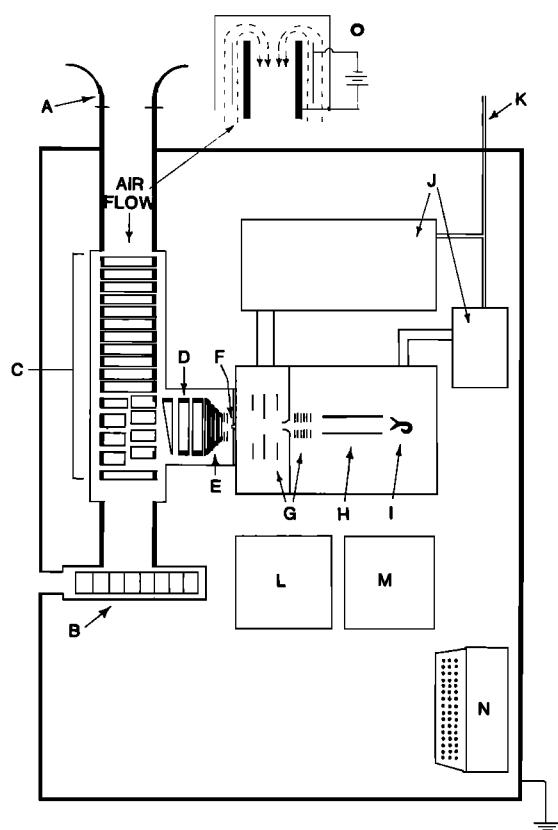


Fig. 1. General scheme of the laboratory: (A) detachable intake scoop, (B) blower, (C) flow opposed drift tube (FODT), (D) extracting rings, (E) high-pressure ion optics (HPIO) focusing rings, (F) aperture (130 to 200  $\mu$ ), (G) vacuum ion optics, (H) quadrupole mass filter, (I) electron multiplier, (J) mechanical pumps for backing of two 10" diffusion pumps, (K) mechanical pump exhaust, (L) supporting power supplies and electronics, (M) mass spectrometer control, (N) computer, (O) ion cutoff apparatus (interchangeable with the intake scoop).

Air, along with the naturally occurring ions contained within it, is sampled continuously through a 10-cm-diameter, 1.5-m-long aluminum pipe that begins with a turbulence-reducing scoop about 1 m above the laboratory. The air velocity has been measured with both a pitot tube and a heat capacity wind gauge to be approximately 2000 cm/s. The ions are slowed down, concentrated, and extracted from the main air flow by electric fields in the flow-opposed drift tube (FODT) and extraction region. The ions then enter the high-pressure ion optics region (HPIO), where they are focused to the vicinity of a sampling aperture and stripped of many clustered water molecules by pushing them through an environment of clean, dry nitrogen or argon buffer gas that fills the region between the vacuum entrance aperture and the nearest high-pressure electrode. The ions then pass through an aperture and into the two stage differentially pumped sampling system and are mass analyzed. Further details on the operation of the apparatus are given in the paper by Eisele [1983].

Ion spectra were searched by operating the mass spectrometer at high and low resolution and in the integral mode. One AMU was resolvable at high resolution for all masses up to 1000 AMU and low resolution typically varied from  $\pm 1$  AMU at low masses to about  $\pm 15$  AMU at highest masses measured. The high-resolution mode was used for ion mass identification, while the low-resolution mode offered more sen-

sitivity and was used to search for the ions present. The width of the low resolution was, in general, comparable with the separation between successive measurements and varied with mass, as shown in Figures 5b and 7. The integral mode viewed all ion masses above a preset value at very low resolution but high sensitivity. When an ion was found, tests were performed to insure that it was being correctly mass identified and that the ion was not being produced in the apparatus itself.

Mass calibration of the mass spectrometer was performed by using various freons as the buffer gas in front of the aperture. The neutral gas entering the system was therefore predominantly freon. The expanding jet of gas was ionized by 70-eV electrons from an electron gun installed inside the first chamber. A spectrum was recorded and compared with published spectra.

Argon gas was also used as a buffer gas in front of the vacuum aperture during both natural and X ray ion mass identification measurements in order to help identify cluster formation in the expanding gas jet when less expensive  $N_2$  buffer gas was used. Only a small amount of clustering was observed in the positive ammonia spectrum as shown by Figure 3 mass 82. Figure 4, however, suggests somewhat more clustering to the  $NO_3^-$  ion family in the negative spectrum at mass peaks 108 and 118 (and 90, which is not large enough to be seen during the measurement shown in Figure 4).

The possibility exists that the observed ions may be produced inside of the FODT or in the HPIO region because of the high potentials present there. For example the apparatus described previously [Eisele, 1983] occasionally suffered from ion production at a grid located at the top of the FODT whenever the grid became dirty as a result of collection of insects, hairs, or dust. A similar problem sometimes occurred with the shutter grid that was used at the entrance to the sampling tube to stop naturally occurring ions from entering the apparatus and to assist in the determination of the ions' origin. It was found that no appreciable loss in ion signal resulted from the removal of the grid at the top of the FODT, so it was removed for our field measurements. Also, a new method was developed for determining whether the ions observed were actually being produced external to the apparatus. An ion deflection device that is interchangeable with the intake scoop was made. It consists of three concentric cylinders and a cutaway view of the apparatus is shown in Figure 1. The center cylinder is held at a high positive or negative potential (900 V) with respect to the outer and the inner (sampling tube) cylinders. The fields set up between the cylinders are transverse to the direction of the air flow, and all ions with a mobility greater than  $0.24 \text{ cm}^2/\text{V}\cdot\text{s}$  (at sea level) will be swept out of the flow and neutralized. The apparatus is periodically installed on the sampling tube, and the ion count rate is measured with the mass spectrometer in the integral mode and with the central cylinder at 900 V. Then the central cylinder is grounded, allowing the ions to pass into the sampling tube, and the ion count rate is measured again. The count rate typically differed by a factor of greater than 50, unless ions were being created within the FODT region or farther into the sampling apparatus. Ion creation was not observed during the course of either field measurements, with the exception of one instance where an insect had positioned itself between a couple of the high-voltage rings and the ion count rate consequently stayed high, regardless of whether the central cylinder voltage was on or off. The ion cutoff apparatus was also used with the mass spectrometer in the single ion monitoring mode whenever a substantial peak was observed

to make certain that the ions were coming from outside the apparatus.

Measurement of the ion concentration was also performed during both experiments by the use of an ion current monitoring apparatus. The apparatus consists of two concentric conducting cylinders with the inner cylinder connected through an electrometer to ground and the outer cylinder connected to a high potential (600 V). A blower pulls air through the apparatus. The electric fields set up between the cylinders are transverse to the direction of the air flow, and all ions with a mobility greater than  $0.8 \text{ cm}^2/\text{V-s}$  (this value is a function of the design of the apparatus) attach to the central cylinder and establish a current flow in the electrometer. With a measurement of the current and the air velocity through the apparatus, the ion concentration can be determined.

In addition to studies of the naturally occurring air ions, whose lifetimes are a few hundred seconds, ions with much shorter lifetimes (about 0.1 to several seconds) were also studied. These ions were artificially produced by X ray ionization of the air directly in front of the sampling tube. A low-yield X ray tube with a copper target was operated at 15 kV and 2 mA for this purpose. It was located about 30 cm below the air/ion sampling tube entrance and irradiated air in a  $30^\circ$  half-angle cone opening skyward. The ions formed at concentrations of  $10^5$ – $10^7/\text{cm}^3$  are sampled and analyzed very soon after they are created. The observed spectrum generated by X rays would not necessarily be expected to be identical to the ambient air ion spectrum because the artificially produced ions would have less time to react with any trace neutral molecules that might be present. Thus a comparison of natural and artificial spectra can be used to help insure that the origin of the natural ions observed is far from the sampling apparatus itself.

#### EXPERIMENTAL SETUP

The first of the two field measurements to be described took place at Sapelo Island, Georgia, on the coast of the Atlantic Ocean, from April 21 to May 25 of 1983. The laboratory was located at  $81^\circ 15' 54''\text{W}$  and  $31^\circ 23' 23''\text{N}$ . It was situated approximately 75 m from the coastline and was oriented so that the predominantly easterly sea breeze blew directly into the sampling scoop. The scoop was well above any of the surrounding terrain or vegetation. Electric power was supplied by a 15-kW gasoline generator, which was located 75 m to the northwest, and the exhaust from the mechanical pumps was vented about 7 m to the northwest of the lab.

Sapelo Island was relatively isolated and not open to the general public, with the only access being by boat. There was very little automobile traffic on the island. A one lane roadway, which ended about 30 m to the northwest of the laboratory, was used infrequently. The nearest major cities were Brunswick, Georgia, located about 38 km to the southwest, and Savannah, Georgia, located about 71 km to the north northwest.

The second set of measurements was carried out from July 6 to July 30, 1983. The laboratory was set up at an altitude of 4.3 km at a University of Denver research laboratory situated at the top of Mt. Evans in Colorado ( $105^\circ 38' 19''\text{W}$  and  $39^\circ 35' 13''\text{N}$ ). The lab was oriented so that the sampling scoop pointed toward the southwest, the prevalent wind direction. The peak of Mt. Evans extended about 75 m above and about 200 m to the northwest of our sampling site. All other directions were visually unobstructed. Power was supplied by a 50-kW generator, which was located about 60 m to the north

of the laboratory. The exhaust from the mechanical pumps was vented downwind of the lab. The nearest major cities were Denver, Colorado, located about 60 km to the east northwest, and Colorado Springs, Colorado, located about 110 km to the southeast. There were no major cities located to the west for hundreds of kilometers. There was some automobile traffic on the mountain, primarily in the afternoon and on weekends, but no correlation was observed between the ions observed and the traffic.

#### RESULTS AND DISCUSSION

##### *Sapelo Island*

Naturally occurring positive ions were identified at Sapelo in the 30–120 AMU range. Low-resolution measurements were extended up to mass 300, but only background levels were observed. Not much was expected above mass 250 because the count rates were low when we looked at the total signal from all ions with masses above 250 AMU by using the integral mode. The positive ion concentrations were measured with the ion current apparatus described previously and were typically found to be in the range of 300–400 ions/ $\text{cm}^3$ . No negative ion spectra of naturally occurring ions were taken because of the low signal levels and the higher background noise present when we examined the negative spectrum.

The total cumulative raw data taken at Sapelo Island are shown in Figure 2. Each data point shown in the figure represents the total number of counts accumulated in 5 min at a particular mass setting. The lower line in the figure represents the average background noise level for the entire experiment (5.5 counts in 5 min), and the upper line represents the average noise level plus two standard deviations of the noise distribution (13.5 counts in 5 min). It should be pointed out that the background noise value at any particular time was actually known more precisely than the standard deviations shown in the figures suggest. This is because the standard deviations were calculated by treating the background noise for the whole experiment as a random distribution when it actually varied slowly over the period of hours and days.

On a typical sampling day the wind was from the ocean, and it was sunny. At least one of the four masses 54, 72, 90, or 108, was consistently observed, although usually not very far above the background noise level. These peaks are 18 mass units apart and are probably related to each other as water clusters of a smaller core ion. The relative heights between any two of these peaks was constant throughout any particular day, as would be expected if the peaks were all part of the same family. In the early part of the measurements, masses 90 and 108 were observed, but after improvements in the dry nitrogen buffer gas flow the peaks were observed at the lower masses: 72, 54, and occasionally even 36. The improved gas flow led to drier gas in the HPIO region, thus shifting the family to lower water clusters.

In the positive X ray, spectra peaks were seen at mass 18, 36, 54, 72, 90, 108, and 126, many of which were also observed in the ambient air. A small peak was also seen at mass 82, and this peak is probably a nitrogen cluster of mass 54. A positive X ray spectrum is shown in Figure 3. A strong possibility for the ions seen at masses 18, 36, ..., 126 is the family of  $\text{NH}_4^+ \cdot n(\text{H}_2\text{O})$  ions.  $\text{NH}_3$  is known to exist in the troposphere with a variable concentration of 1–10 ppb primarily as a result of biological activity in the soil [Junge, 1963]. It also has a large polarizability and a large proton affinity (both greater than water) and therefore might be expected to form  $\text{NH}_4^+ \cdot$

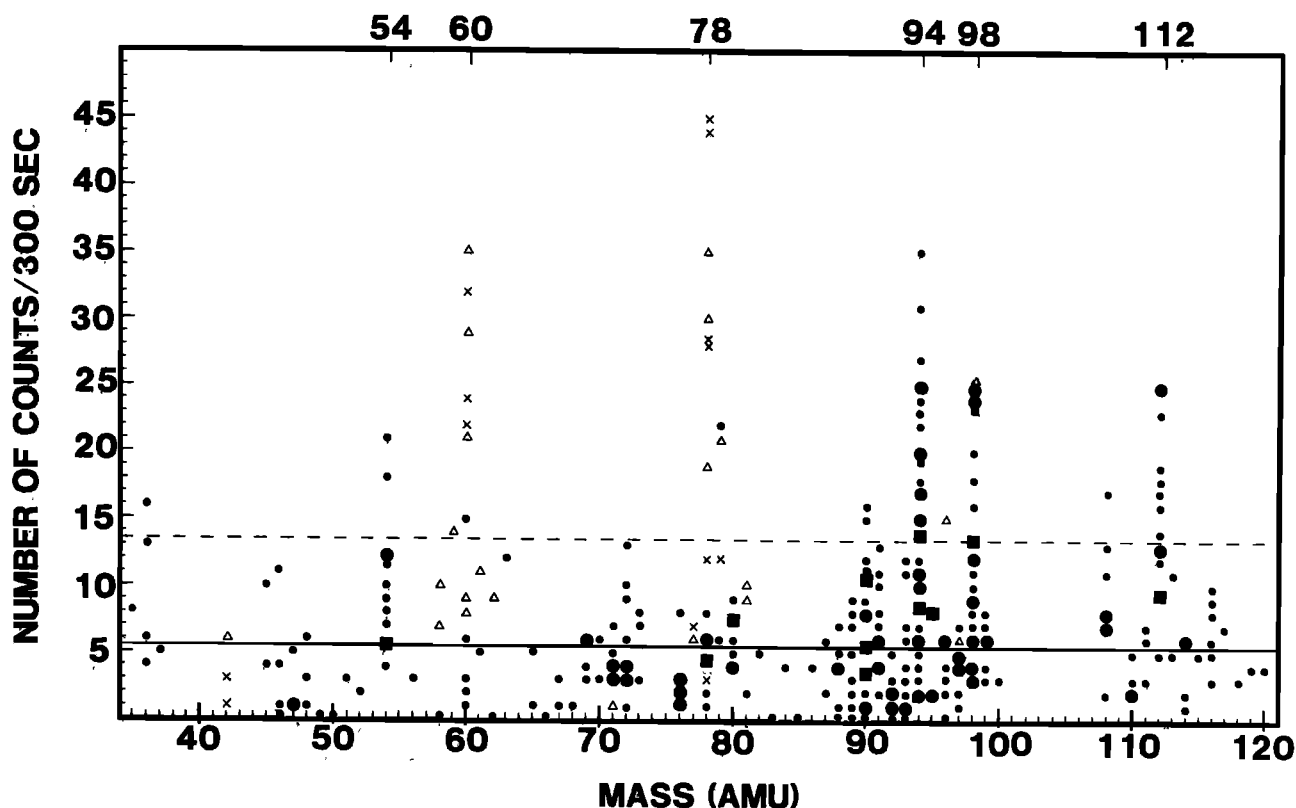
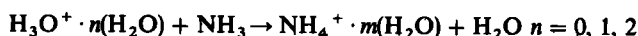


Fig. 2. Total cumulative data taken at Sapelo Island, Georgia. All measurements were taken at high resolution: (small dot) one measurement, (large dot) two measurements, (filled square) five measurements, (cross) one measurement taken on May 20, 1983, (triangle) one measurement taken on May 13, 1983.

$n(\text{H}_2\text{O})$  in the presence of  $\text{NH}_3$ . In fact the rate constant for the reaction



has been found to be very fast, and the presence of  $\text{NH}_4^+ \cdot n(\text{H}_2\text{O})$  ions in the troposphere has been previously predicted [Fehsenfeld and Ferguson, 1973]. Because  $\text{H}_3\text{O}^+ \cdot n(\text{H}_2\text{O})$  ions are only 1 AMU above the  $\text{NH}_4^+ \cdot n(\text{H}_2\text{O})$  family, it was important that the mass spectrometer was properly calibrated. The calibration procedure is described in the "Description and Operation" section. There were no ions seen at masses 19, 37, 55, etc.  $\text{NH}_4^+ \cdot n(\text{H}_2\text{O})$  ions have also been seen in air-sampling experiments at Georgia Tech in our laboratory's

drift tube mass spectrometer, where the ions were analyzed less than 0.1 s after their ionization.

A typical negative X ray spectrum is shown in Figure 4. It is believed that the peaks represent the ion family  $\text{NO}_3^- \cdot n(\text{H}_2\text{O}) \cdot m(\text{HNO}_3)$ . Peaks were seen at masses 62 ( $\text{NO}_3^-$ ), 80 ( $\text{NO}_3^- \cdot \text{H}_2\text{O}$ ), 90 ( $\text{NO}_3^- \cdot \text{N}_2$ ), 98 ( $\text{NO}_3^- \cdot 2\text{H}_2\text{O}$ ), 108 ( $\text{NO}_3^- \cdot \text{H}_2\text{O} \cdot \text{N}_2$ ), 118 ( $\text{NO}_3^- \cdot 2\text{N}_2$ ), 125 ( $\text{NO}_3^- \cdot \text{HNO}_3$ ), etc.  $\text{NO}_3^-$  is a very stable ion and has been observed in the stratosphere along with its water and nitric acid clusters. The presence of  $\text{NO}_3^-$  and its water and nitric acid clusters in the troposphere has also been predicted [Ferguson et al., 1979].

Mass peaks such as 108 could also correspond to the stable ion  $\text{NO}_3^- \cdot \text{NO}_2$ , however, the relative decrease in the mass

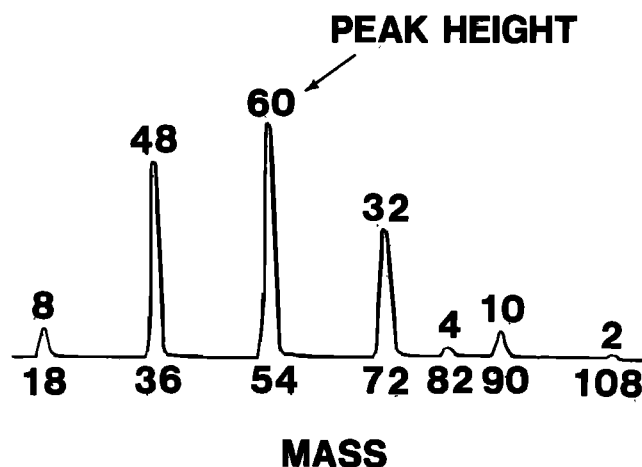


Fig. 3. Typical high-resolution positive X ray spectrum taken at Sapelo Island.

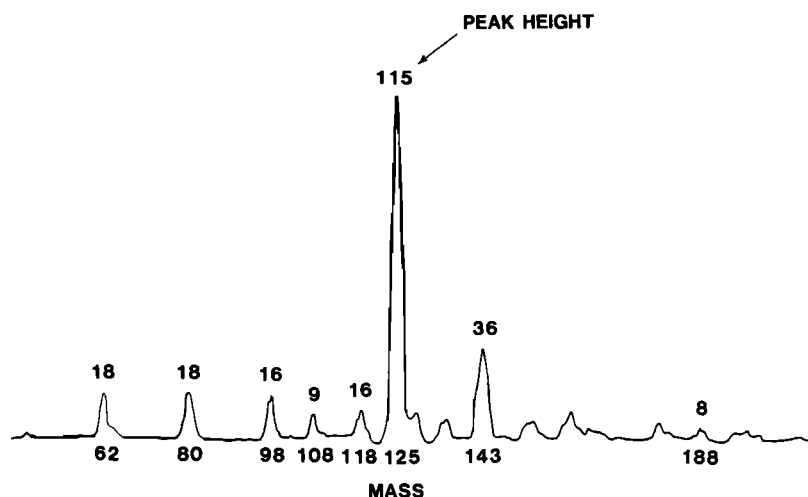


Fig. 4. Typical high-resolution negative X ray spectrum taken at Sapelo Island.

90, 108, and 118 peaks when the buffer gas was switched from  $N_2$  to Ar (in order to identify cluster formation in the sampling jet) suggests their identity as nitrogen clusters. Similarly, the mass peak at 98 might also include the ion  $NO_3^- \cdot HCl$ . It is labeled  $NO_3^- \cdot 2(H_2O)$  above because mass 80 (probably  $NO_3^- \cdot H_2O$ ) was often much more abundant than shown in Figure 4, and the presence of some  $NO_3^- \cdot 2(H_2O)$  was anticipated. Species such as  $NO_3^- \cdot HCl$  may, however, also be contributing to the observed mass peaks.

During the course of sampling of naturally occurring ions in the positive spectrum, the masses 60, 78, 80, 94, 98, and 112 were observed in addition to the  $NH_4^+ \cdot n(H_2O)$  ion family (Figure 2). The unidentified mass 94 was the most consistent ion, with the exception of the  $NH_4^+ \cdot n(H_2O)$  family. It showed up higher than the background on many days and, like the  $NH_4^+$  family, was observed in a variety of weather conditions from rainy to clear and was also observed regardless of whether the wind blew from the land or the ocean. Mass 112 was also observed, and the ratio between it and mass 94 was fairly constant, indicating that mass 112 is probably a water cluster of mass 94. Measurements at mass 76 (18 AMU below 94) were made several times while 94 was present, but no mass 76 ions were seen. X ray spectra taken on days when 94 was seen from the ambient air showed only the  $NH_4^+ \cdot n(H_2O)$  family of ions. There was no evidence of mass 94. The difference between the naturally occurring spectra and the X ray spectra indicate that the formation of mass 94 is being controlled by processes occurring in the atmosphere with times requiring much more than 1 s. These processes may be reactions with molecules in the ppt range or slightly lower.

The masses 60 and 78 were observed to be extremely variable. On two days they showed up very high, while on most other days they did not show up at all, as shown in Figure 2. Whenever mass 60 or 78 appeared, they appeared together, implying that mass 78 could be a water cluster of mass 60. Mass 42 (18 AMU below 60) was also measured several times while 60 was high, but because of low signal levels, its presence could not be definitely ascertained. No observed changes in the weather conditions accounted for the varying count rate of these ions, since the temperature, humidity, wind, and weather conditions were similar on days when they were observed and on days when they were not. On the days when masses 60 and 78 were observed the individual mass count rates were high when the measurements were started in the morning but

gradually died away in the midafternoon. No evidence of masses 60 and 78 was seen in the X ray spectra taken on these days.

Another ion that showed up on several days was the mass 80 and its probable water cluster at mass 98. Mass 62 (18 AMU below 80) was measured, but it was not clear whether this mass was present. On the day that masses 80 and 98 were highest, they were seen from the beginning of the measurements in the morning until around noon. On this particular day the ions at masses 60 and 78 were seen concurrently. However, masses 80 and 98 were also observed on several days when 60 and 78 were not. Again, these masses were not seen in any X ray spectra taken.

Unfortunately, no correlation between the appearance of the ions 60 and 80 and the temperature, humidity, wind, or weather conditions could be established because of the short time the experiment was carried out and the infrequency of the appearance of these ions. Ions 60, 80, and 94 and the  $NH_4^+ \cdot n(H_2O)$  family did, however, appear to be independent of each other. On some days they would all appear together, while on other days, only one or two of these peaks would show up.

#### Mount Evans

At Mt. Evans the positive spectrum was studied from mass 16 to over mass 700 at high and/or low resolution. The spectrum was much easier to study at Mt. Evans than it was at Sapelo Island because of the higher concentration of ions present at an altitude of 4.3 km, presumably because of increased cosmic ray ionization. Positive ion concentrations at Mt. Evans averaged around  $2000/cm^3$ . Also, since the pressure was much lower, the sampling aperture of the vacuum analysis system could be opened to a larger ( $180\text{-}\mu$ ) diameter, allowing more ions to enter the system. There was enough signal so that we were also successful in looking at the negative ion spectrum.

Due to the low atmospheric pressure of approximately 450 torr at an altitude of 4.3 km, the fields in the FODT and the HPIO were reduced to keep the ratio  $E/N$  (electric field strength/gas number density) at the same value as in the Sapelo Island experiment. This was done to guard against electrical discharges in the apparatus and to insure that the operation of the apparatus was consistent with the previous Sapelo Island experiments.

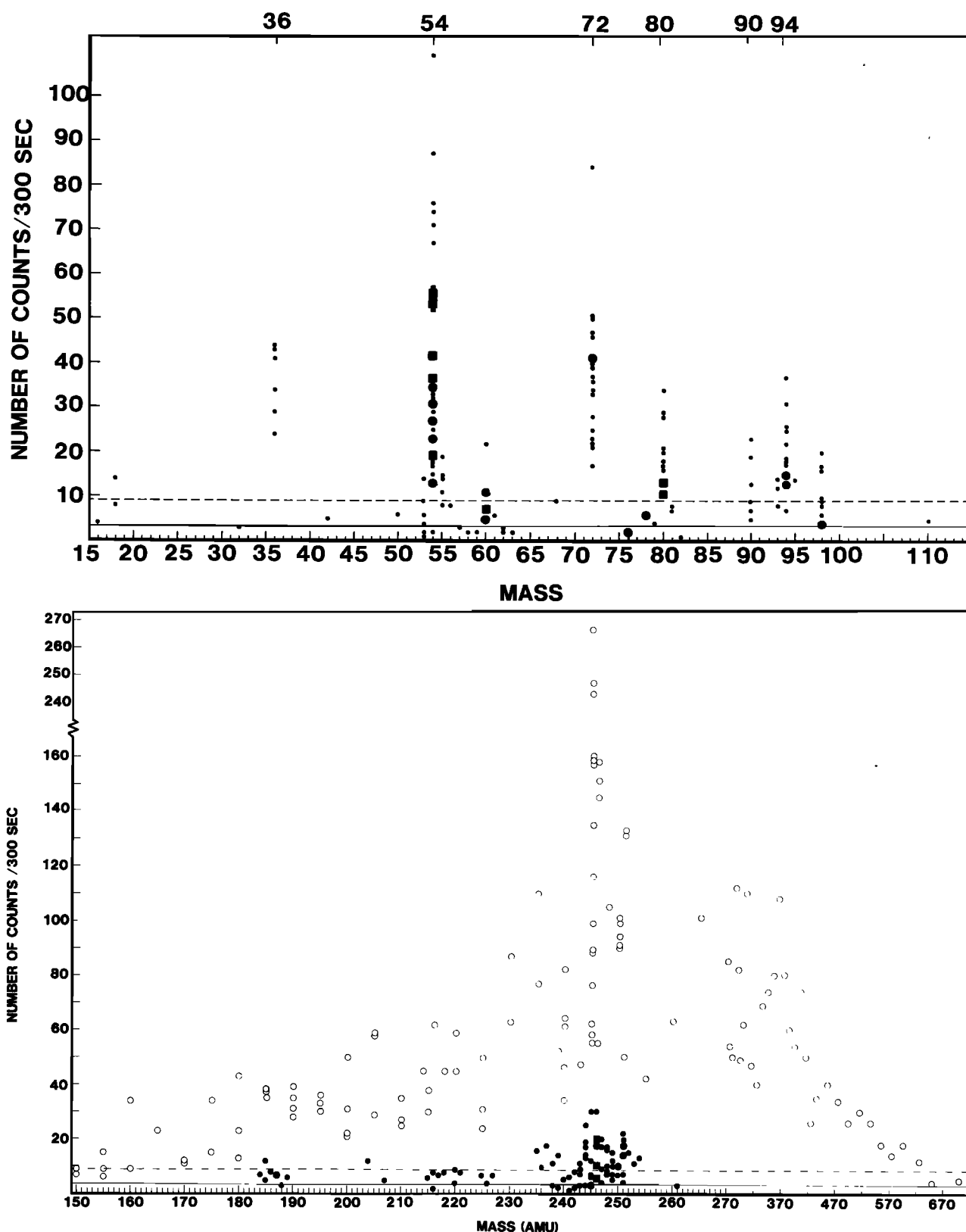


Fig. 5. (a) Cumulative data taken at Mt. Evans for the mass range 15–115 AMU. Measurements taken at high resolution: (small dot) one measurement, (large dot) two measurements, (filled square) five measurements. (b) Cumulative data taken at Mt. Evans for the mass range 150–670. Note the change of scale on the horizontal axis: (filled circle) one measurement at high resolution, (open circle) one measurement at a low resolution.

The cumulative raw data taken in the single ion monitoring mode for the positive spectrum is shown in Figure 5 (a, b). As with the Sapelo data, each point represents the total number of counts accumulated in a 5-min period, and the lines in the

figures represent the average value of the background noise (3.5 counts in 5 min) and the average value plus two standard deviations (9.0 counts in 5 min). In addition to the higher concentration of ions we were also fortunate enough to have

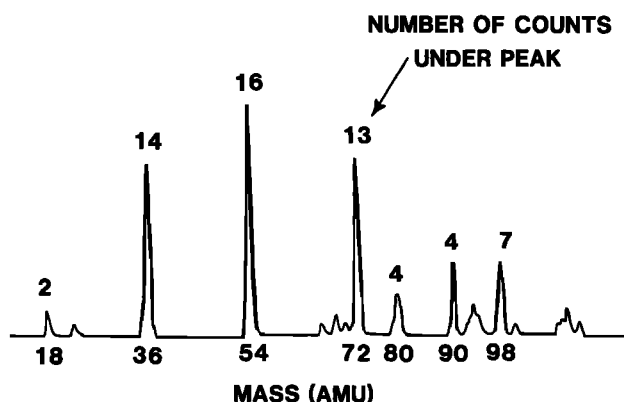


Fig. 6. Positive high-resolution spectra taken at Mt. Evans in the scanning mode for the mass range 10–110 AMU.

less background noise than at Sapelo Island. This was because in the middle of the measurements a new electron multiplier was installed in the analysis region, and its noise characteristics were superior to the previous one (about two background counts in 5 min).

During the sampling, the wind was generally from the southwest or the west, and it was usually cool, rarely getting about 15°C. It was almost always sunny in the morning, but clouds usually built up around midafternoon, and many times there was rain, sleet, or hail before 4 P.M.

In the positive spectrum, masses were scanned from mass 15 to mass 700 at high and/or low resolutions. Ions were seen at masses 18, 36, 54, 60, 72, 80, 90, 94, and 98, (Figure 5a) plus surprisingly, a wide range of masses between 200 and 600 AMU was also found (Figure 5b). The ions above mass 200 appeared to be almost a continuum, and so, although the signal levels were extremely high at low resolutions, when the resolution was increased, the count rates dropped considerably, although they were still above the background noise level.

Many ions were observed above mass 230 at high resolution. However, because of the large number of ions and a limited time available at the sampling site, we could not afford to study these ions in as much detail as we would have liked. Hence we concentrated our efforts on ions below 150 AMU.

Just as at Sapelo Island, the family that we believe to be  $\text{NH}_4^+ \cdot n(\text{H}_2\text{O})$  was seen at masses 18, 36, 54, 72, and 90. However, the count rate of these ions at Mt. Evans was usually much higher than any other peak observed, and the family was consistently seen almost every day. Ions were also seen at masses 80 and 98. Mass 98 was probably a water cluster ion of 80, as they always appeared together. On several days when these masses were seen, their count rates were almost as high as the count rate for mass 54, the highest peak of the  $\text{NH}_4^+ \cdot n(\text{H}_2\text{O})$  family. Mass 60, which was prominent on several occasions at Sapelo Island, was seen on only one occasion (and then in low abundance), and it was not clear whether mass 78 was there or not. Also, mass 94, which was observed fairly consistently at Sapelo Island, was more variable at Mt. Evans. It was usually above the background noise level but was high on only one or two days. As with the Sapelo Island measurements we could not find any correlation between the appearance of the observed ions and the wind direction, weather, temperature, or relative humidity.

At the high signal levels present at Mt. Evans we were also able to obtain several spectra with the mass spectrometer operating in the scanning mode. In these measurements the

background noise had to be very low, and the spectra had to be taken over a period of several hours. One of the best spectra taken is shown in Figure 6.

X ray spectra were frequently taken over the course of the measurements, and the results were similar to those at Sapelo Island. The only peaks to show up were those caused by the  $\text{NH}_4^+ \cdot n(\text{H}_2\text{O})$  family. There was, however, evidence of the conglomeration of higher masses (200 to 600 AMU) discussed previously, since the count ranges of almost all masses above mass 150 were slightly higher than the background noise. There was no evidence of masses 60, 80, or 94 in the X ray spectra.

At Mt. Evans the first measurements of the ions in the negative spectrum were also undertaken. In the negative spectrum the background noise is about a factor of 10 larger than it is in the positive spectrum, and so no spectra were taken in the scanning mode. All data was taken with the mass spectrometer in the single ion monitoring mode. The spectrum was studied from masses 30 to 150 at high and/or low resolutions. A few masses above 150 were also measured.

The accumulated data for the negative spectrum is shown in Figure 7. As before the lower line represents the average value of the noise and the upper line is the average noise plus two standard deviations. Peaks were seen at masses 62 and 125, with a slight signal present at mass 80. We believe these peaks to be  $\text{NO}_3^-$  at mass 62,  $\text{NO}_3^- \cdot \text{H}_2\text{O}$  at mass 80, and  $\text{NO}_3^- \cdot \text{HNO}_3$  at mass 125. As stated previously,  $\text{NO}_3^-$  is a very stable ion that has been seen in the stratosphere along with its water and nitric acid clusters, and it would not be unreasonable to expect that it would be present in the troposphere also. Mass 188, where  $\text{NO}_3^-$  clustered with two nitric acid molecules would show up, was measured but was not clearly observed.

The negative X ray spectra taken at Mt. Evans were similar to the ambient negative ion spectra. The ratio of  $\text{NO}_3^- \cdot \text{HNO}_3$  ions to  $\text{NO}_3^-$  ions was similar whether we were looking at the X ray spectra or the natural ion spectra. This does not necessarily mean that reactions are taking place in the sampling tube or the apparatus. If the spectra were different, then we could argue that the apparatus itself was not producing these ions, but if the spectra were similar, we could be observing ions that rapidly approach equilibrium with one another. That is, equilibrium between  $\text{NO}_3^-$  and  $\text{NO}_3^- \cdot \text{HNO}_3$  ions may be established in a shorter time than it takes for the ions to enter the vacuum apparatus. Also, there is no reason to expect that the apparatus is adding  $\text{HNO}_3$  to the sampled air, since measured  $\text{HNO}_3$  concentrations during the

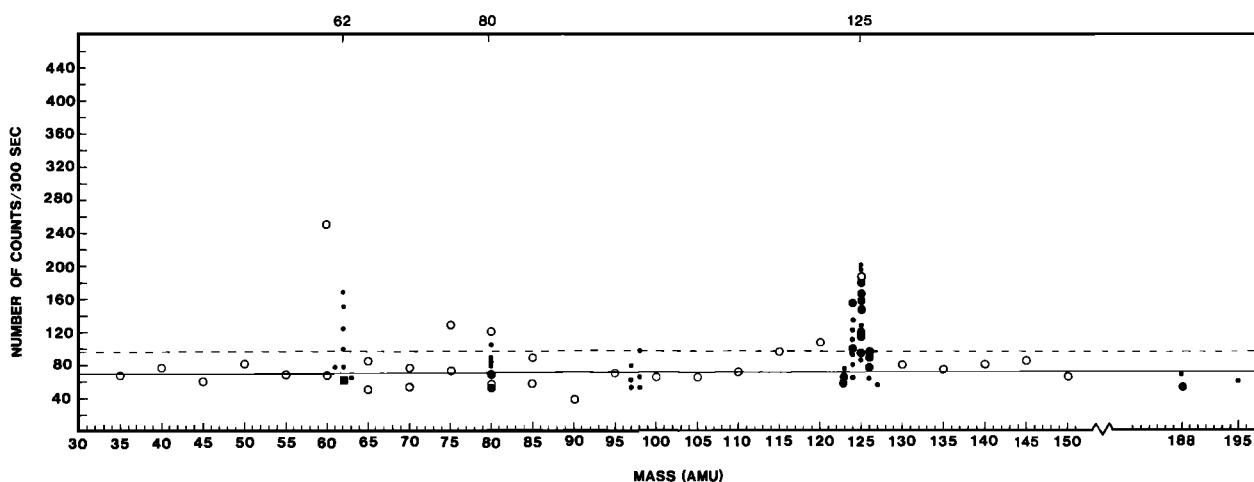


Fig. 7. Negative spectrum data taken at Mt. Evans (small dot) one measurement at high resolution, (large dot) two measurements at high resolution, (open circle) one measurement at low resolution.

summer at nearby Niwot Ridge are in the range of 100 to 900 ppt [Huebert *et al.*, 1982], which are sufficient to account for the observed ions.

#### SUMMARY AND CONCLUSIONS

Table 1 presents a summary of the naturally occurring ion families seen at Sapelo Island and the positive and negative ion families seen at Mt. Evans. The identification of the  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_3^- \cdot \text{HNO}_3$  families were discussed previously in this article. No chemical identities are, however, suggested for mass 60, 80, or 94.

A positive ion at mass 42 (of which 60 could be a water cluster) has been observed in the lower stratosphere and tentatively identified as  $\text{H}^+ \cdot \text{CH}_3\text{CN}$  [Arnold *et al.*, 1978; Henschen and Arnold, 1981; Bohringer and Arnold, 1981; Smith *et al.*, 1981; Schlager *et al.*, 1983]. Our observations of mass 60, however, showed it to be extremely variable from day to day and even during a single day. Also, these variations of at least an order of magnitude for mass 60 did not correspond to any observable change in the weather. Since tropospheric  $\text{CH}_3\text{CN}$  is expected to be a stable and long-lived species (having at least a sufficiently long life to reach the stratosphere), at the relatively high concentration of a ppbv [Becker and Ionescu, 1982] it does not appear to be a likely parent neutral for the ion observed at mass 60, unless our measurements were near an unknown  $\text{CH}_3\text{CN}$  source.

In addition the neutral parent of the mass 60 ion is prob-

ably present at very low concentrations, since 60 was not observed in the X ray spectrum.

We have considered possibilities such as  $\text{NH}_4^+ \cdot \text{H}_2\text{CO}_3$  for mass 80, but if such ions were in an equilibrium with  $\text{CO}_2$  or other gases at relatively high concentrations, they would have showed up in the positive X ray spectra because of the abundance of  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  in the troposphere.

The results of our X ray measurements as well as previous studies [Ferguson *et al.*, 1979] suggest that most tropospheric ions either are or have evolved from  $\text{NH}_4^+ \cdot n(\text{H}_2\text{O})$ . We might also expect that some small fraction of the NaCl carried by ocean breezes could be in a free gaseous state and more abundant at Sapelo Island than at Mt. Evans. Thus a possible identity for mass 94 is  $\text{Na}^+ \cdot \text{HCl} \cdot \text{NH}_4\text{OH}$  or an isomer of it in which  $\text{H}_2\text{O}$  is sufficiently strongly bound so that 76 will not appear in the spectrum. Collisional dissociation of the observed ions is planned during future measurements to aid in their identification.

In addition to being used to identify ion species in the atmosphere the apparatus may also be used as an extremely sensitive detector of trace neutral constituents that have a sufficiently high electron or proton affinity or sufficiently low ionization potential. For example the measurement of the  $\text{NH}_4^+ \cdot n(\text{H}_2\text{O})$  ion family in the atmosphere could be used as an analytical method for the detection of  $\text{NH}_3$ . Other candidates for such analysis are nitric acid molecules and the precursor molecules to the positive ions at mass 60, 80, and 94.

TABLE 1. Ions Mass Identified and Their Probable Chemical Identities

Maximum Counts/300 s for Most Abundant Family/Member			
Ion Families Seen	Sapelo Island, Background = 5.5	Mt. Evans, Background = 3.5	Probable Identification
Positive Ions			
18, 36, 54, 72, 90, 108	21 (mass 54)	110 (mass 54)	NH <sub>4</sub> <sup>+</sup> · n(H <sub>2</sub> O)
60, 78	45 (mass 78)	22 (mass 60)	unknown
80, 98, 116	25 (mass 98)	35 (mass 80)	unknown
94, 112	35 (mass 94)	38 (mass 94)	unknown
Background = 65			
Negative Ions			
62, 80		165 (mass 62)	NO <sub>3</sub> <sup>-</sup> · n(H <sub>2</sub> O)
125		360 (mass 125)	NO <sub>3</sub> <sup>-</sup> · (HNO <sub>3</sub> )



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