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Detection of massive negative chemiions in the exhaust plume of a jet aircraft in flight

F. Arnold, J. Curtius, B. Sierau,[1] and V. Bürger[2]

Max-Planck-Institute for Nuclear Physics, Atmospheric Physics Division, Heidelberg, Germany

R. Busen, and U. Schumann

DLR, Institut für Physik der Atmosphäre, Weßling, Germany

Abstract. Gaseous negative ions were mass spectrometrically measured in the exhaust plume of a jet aircraft in flight. Using a quadrupole mass spectrometer operated in a high-pass mode, it was found that by far most of the ions had mass numbers > 450 amu (atomic mass units) and number densities which markedly exceeded the number densities of ambient atmospheric ions. The latter were observed outside the exhaust plume and had mostly mass numbers < 200 amu. Both their large numbers and large concentrations strongly suggest that the massive ions observed inside the plume are chemiions which were produced by the jet engines. The low fuel sulfur content (22 µg/g) suggests that the massive ions consist at least partly of species other than sulfuric acid. By interaction with exhaust gases these chemiions experienced rapid chemical transformation and growth in the early exhaust plume already at plume ages < 0.4 s.

Introduction

Chemiions (CI) produced by jet engines may have important roles in exhaust plumes of jet aircraft. CI most probably promote the formation of aerosol particles and eventually even water contrails via CI-induced nucleation and coagulation (*Frenzel and Arnold*, 1994, *Yu and Turco*, 1997, *Kärcher et al.*, 1998, *Yu et al.*, 1998, *Yu and Turco*, 1998). Furthermore CI may also serve as probes for certain trace gases formed in jet engine exhaust (*Frenzel and Arnold*, 1994, *Arnold et al.*, 1998a, *Arnold et al.*, 1998b). Among these trace gases sulfuric acid is particularly interesting and important as it represents an efficient aerosol forming agent. Gaseous sulfuric acid may undergo bimolecular nucleation and condensation with water vapor. This nucleation may proceed via a homogeneous, an ion, and/or a heterogeneous (on soot) mechanism.

First CI-composition measurements in jet engine exhaust at the ground have recently been reported (*Arnold et al.*, 1998a). It was found that negative CI react with SO_3 and H_2SO_4 ultimately leading to cluster ions of the type $HSO_4^-(H_2SO_4)_m(H_2O)_n$. Such ions have been observed in the exhaust of modern large turbofan engines (JT9, CF6-80) (*Kiendler et al.*, 1999, manuscript in preparation) and in the exhaust of a small jet engine (Rolls-Royce, SNCEMA M45H Mk501, *Arnold et al.*, 1998a). Already prior to these jet engine exhaust experiments laboratory experiments in jet fuel combustion plumes revealed the most abundant negative CI-species to be $HSO_4^-(H_2SO_4)_m(H_2O)_n$ (Frenzel and Arnold, 1994). The presence of H_2SO_4 in the exhaust plume of a jet aircraft in flight has recently been measured for the first time directly by our group (*Curtius et al.*, 1998).

The present paper reports on the first mass spectrometric observations of massive negative CI in the exhaust plume of a jet aircraft in flight. It was found that these CI are far more massive and more abundant than ambient atmospheric ions observed outside the plume, and are present even for low fuel sulfur content. This supports the hypothesis that CI, not necessarily formed from sulfuric acid, grow into an aerosol mode in the exhaust plume of jet aircraft.

Experimental

The ion composition measurements to be reported here were made by an aircraft-based Ion Mass Spectrometer (IOMAS) which was developed and built by our group at the Max-Planck-Institute for Nuclear Physics, Heidelberg. IOMAS is a cryogenically pumped quadrupole mass spectrometer which was operated in a high-pass-mode (HPM), very similar to the ac-mode described in the literature (c.f. *Yang and Leck*, 1982, *Ross and Leck*, 1983). In the HPM no dc voltage is applied to the quadrupole rods. The HPM measures total count rates for ions whose mass exceeds critical mass number m_c. By varying the amplitude of the ac voltage linearly with time, m_c is varied between 1 and 450 amu and a so-called "integral spectrum" (hereafter termed HPM spectrum) is obtained which gives crude information about the mass distribution of ions with masses ≤ 450 amu. For ions > 450 amu only a total count rate but no information on mass distribution is obtained. For very large ion masses the efficiency of ion detection by the Channeltron Electron Multiplier (CEM) should ultimately decrease which would lead to an underestimation of the abundance of very massive ions. The variation of the ion detector efficiency with ion mass is not exactly known for very massive ions. At least during test measurements in our lab it was possible to detect ions with masses up to at least 9000 amu. A more detailed description of IOMAS can be found in previous publications of our group (*Möhler and Arnold*, 1992, *Krieger and Arnold*, 1994). Exhaust gases and ions are transported to the IOMAS through a stainless steel tubing of 4 cm diameter using a passive flow driven by ram pressure (velocity: 38 m/s). In order to minimize losses of ions to the inner wall of the flow tube the length of the flow tube was kept as short as possible (0.95 m). HPM mass spectra are

[1]Now at Institut für Troposphärenforschung, Leipzig, Germany
[2]Now at Greenpeace Germany, Hamburg, Germany

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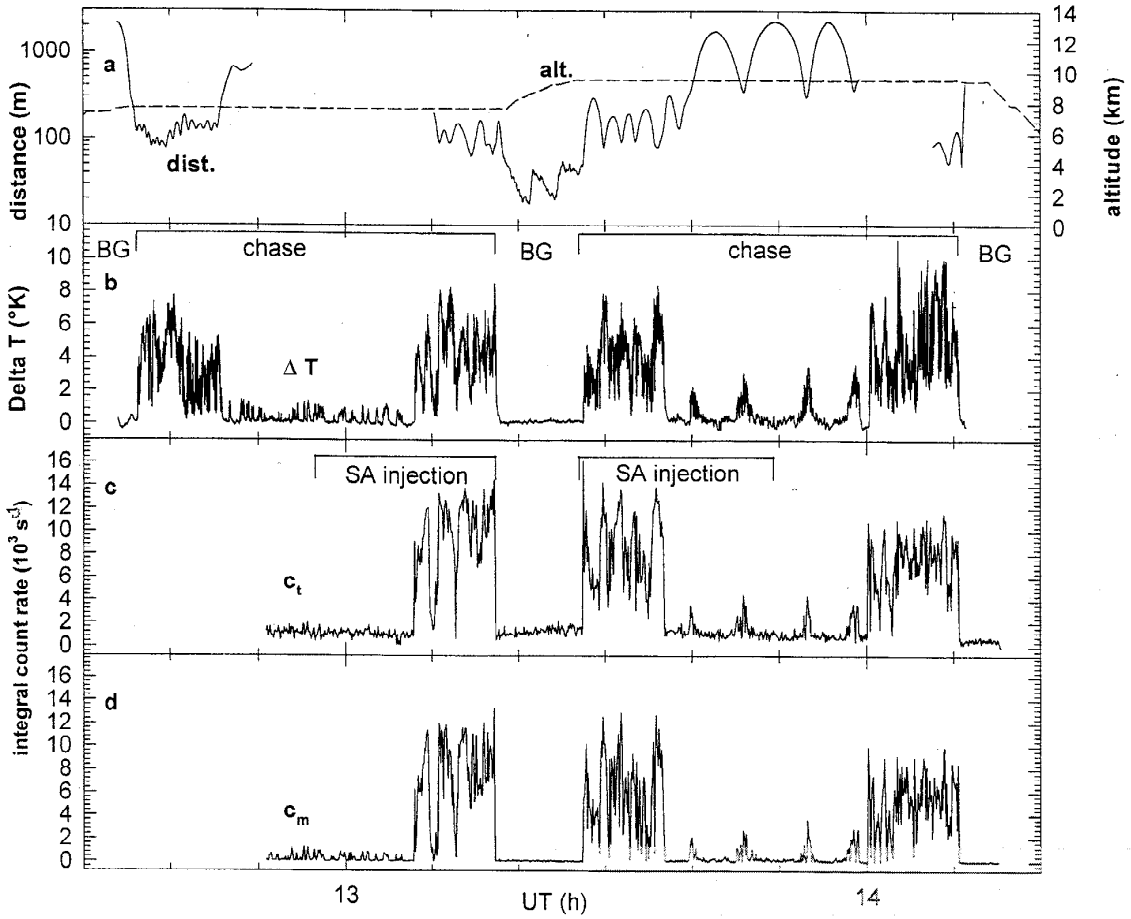

Figure 1. Results from chase of ATTAS aircraft versus time during Falcon measurement flight of April 16, 1997. (a) Flight altitude (dashed line), and distance between the two aircraft (solid line) from GPS measurements. (b) Temperature inside the plume above ambient temperature ΔT, time intervals of chase are indicated by brackets, BG designates background periods. (c) Global maximum of ion count rate of high pass mode mass spectra c_t. Time intervals when additional sulfuric acid was injected are indicated by brackets. (d) Ion count rate at 450 atomic mass units c_m.

obtained with a sampling frequency of 0.15 Hz. The uncertainty of measured count rates for ions with different lower mass boundaries is ±30 %. In the mass range ≤ 450 amu where a variation of the ion detection efficiency can probably be neglected, ion abundances are equal to ion count rates. However for ions with masses exceeding several thousand amu, the abundance may be larger than the measured count rate (see above).

For the measurements to be reported here IOMAS was installed on board of the research aircraft Falcon while the Falcon was chasing another research aircraft ATTAS (Advanced Technology Testing Aircraft System). Both aircraft were operated by DLR (Deutsches Zentrum für Luft- und Raumfahrt) and the measuring campaign SULFUR 5 was coordinated by DLR-IPA (IPA = Institut für Physik der Atmosphäre). The DLR also provided flight data, especially the measurement of ΔT (plume temperature above ambient temperature), which was used as a marker for plume dilution (*Schumann et al.*, 1998). The measurements to be reported took place on 16 April 1997 over Germany at two altitude levels (8000 and 9500m). The engines of the ATTAS were burning fuel with a sulfur content of 22±5 µg sulfur per gram fuel, far below average fuel sulfur content values (~ 400 µg/g) (*Busen and Schumann*, 1995). A visible water contrail was present only at the upper altitude level. During two phases of the flight a liquid mixture of sulfuric acid and water was injected directly into the center of the hot exhaust jet of the ATTAS aircraft. These injections were performed to verify the operation of the VACA system for the detection of aerosol sulfuric acid described in *Curtius et al.*, 1998. Further details of the campaign can also be found in *Curtius et al.*, 1998, and *Schröder et al.*, 1998.

Results and Discussion

Total negative ion count rates c_t (global maximum of the HPM spectrum) measured by IOMAS during the flight are shown in figure 1 along with flight altitude, horizontal distance d between the two aircraft and ΔT (exhaust temperature above ambient temperature). During plume penetrations, indicated by elevated ΔT, c_t increases markedly from typically about 1,000 counts per

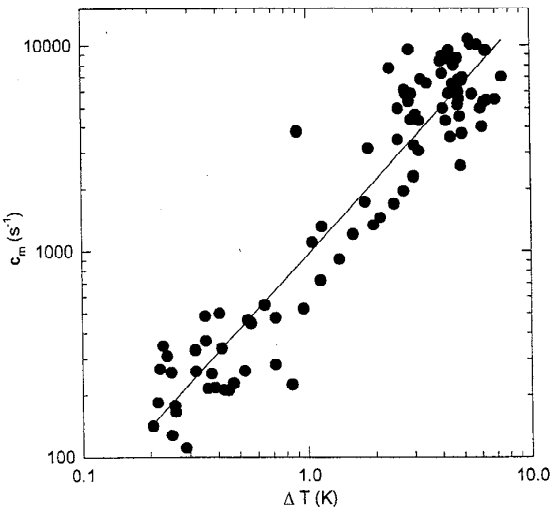

Figure 2. Scatter plot of ΔT versus c_m. Data from figure 1 averaged by 5 mass spectra, and out of plume events eliminated.

second (cps) in the background atmosphere outside the plume to up to 10,000 cps inside the plume. Since c_t should be proportional to the total negative ion concentration n_t, the measurements indicate markedly enhanced n_t inside the plume. Usually n_t is about 5,000 cm^{-3} in the background atmosphere around 10 km altitude (*Viggiano and Arnold*, 1995). Hence inside the plume n_t increases to about 50,000 cm^{-3}. However if the mean mass of the ions with masses > 450 amu would be very large (exceed a few thousand amu) the efficiency of detection by the CEM may be small and hence their concentration may markedly exceed 50,000 cm^{-3}. The shape of the HPM-spectra also changed considerably inside the plume compared to outside the plume. Outside the plume the spectrum usually decreases sharply at masses ≥ 62 amu which indicates that most ions must have masses ≤ 62 amu. By contrast inside the plume at small plume ages (< 1 s) usually no decrease occurs at all which indicates that by far most ions must have masses greater than 450 amu. Measured count rates c_m for negative ions with masses greater than 450 amu are also given in figure 1. These increase markedly in the plume from < 10 cps (dark count rate and noise level of the ion detector) to up to 10,000 cps in the plume. No significant differences in c_t, c_m, or the overall appearance of the HPM spectra was observed in regard to whether or not a contrail was visible and whether or not sulfuric acid was injected into the plume.

Figure 2 shows a scatter plot for c_m and ΔT along with a regression curve. Here only events were chosen, when the plume was clearly encountered ($\Delta T > 0.2$ K and $c_m > 100$ cps). Considering the relatively short time spans for plume penetrations and the spatial inhomogeneity of the plume the correlation of c_m and ΔT is reasonably compact ($r^2 = 0.88$). This very clearly indicates that the massive ions are closely associated with the exhaust plume.

Figure 3 shows the ratio $c_m/\Delta T$ as a function of plume age t_p which was derived from the GPS measurements of the distance between the two aircraft and aircraft speed. For small t_p (< 1.0 s) $c_m/\Delta T$ ranges between about 600 and 4500 $s^{-1} K^{-1}$ with a mean value of about 1800 $s^{-1} K^{-1}$. As t_p increases the mean $c_m/\Delta T$ decreases notably. For the entire t_p range of 0.3-12 s this decrease amounts to a factor of 5.

The increase of n_t inside the plume compared to outside the plume suggests that the observed massive ions are chemiions rather than entrained ambient ions which may have experienced growth inside the plume. When compared with previously estimated (*Arnold et al.*, 1998a) total negative chemi-ion concentrations of 10^6 - 10^8 cm^{-3} at $t_p = 1$ s our presently measured $n_t = 5 \times 10^4$ cm^{-3} is much lower. However as we have obtained only a lower mass limit for the massive ions it is at least conceivable that IOMAS may underestimate n_t due to a reduced detection efficiency of the CEM (see above). The large mass of massive ions inside the plume may be due to ion growth by clustering of gaseous sulfuric acid in the plume. Negative ion composition measurements in jet engine exhaust at the ground made by our group revealed that at least in the mass range up to 220 amu the most abundant ions are of the type $HSO_4^-(H_2SO_4)_m$ (*Arnold et al.*, 1998a). However the observed massive ions must not necessarily be made-up of sulfuric acid. The ions do not result from the injected sulfuric acid and the fuel sulfur content was low. Instead, the massive ions may have grown via clustering of other molecules or by ion attachment to neutral molecular clusters. These may have formed via homogeneous or ion nucleation. Ion attachment to soot particles cannot have led to the observed massive ions since charged soot particles (mean radius around 20nm) are by far too massive to be detectable by IOMAS.

The observed decrease of $c_m/\Delta T$ with increasing t_p may be explained by ion-removal (e.g. via ion-ion-recombination) or very extensive further ion growth. The latter may have led to extremely massive ions for which the detector efficiency might be strongly reduced. Evaporation of neutral molecules (e.g. H_2O) from the massive ions seems to be an unlikely explanation for the decreased ratio at larger plume ages since the total number of ions n_t is reduced to background values at the larger plume ages (c.f. figure 1).

As far as ion removal is concerned plausible processes are ion-ion-recombination and ion attachment to soot and other aerosol particles. From the observed decrease with t_p of the ratio $c_m/\Delta T$ an approximate ion lifetime of 10s at $t_p \approx 1$ s is inferred. If ion-ion recombination is the ion removal process responsible the ion

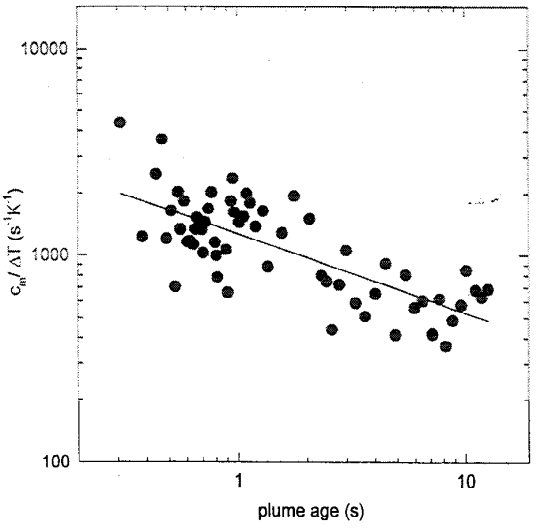

Figure 3. Ratio of $c_m/\Delta T$ plotted versus plume age t_p derived from differential GPS measurements. Only in plume events considered, and averaged over five mass spectra.

lifetime would be $t_r = (\alpha n)^{-1}$ which would lead to $\alpha n \approx 0.1\ s^{-1}$ or $n \approx 5 \times 10^4\ cm^{-3}$ (for a plausible maximum possible ion-ion recombination coefficient $\alpha = 2 \times 10^{-6}\ cm^3 s^{-1}$, see *Arnold et al.*, 1998b).

Summary and Conclusions

Measurements of negative chemiions in the exhaust plume of a jet aircraft in flight were made by an ion mass spectrometer installed aboard a second aircraft which was chasing the plume-producing aircraft. Inside the plume ions were found to be far more abundant and far more massive than ambient atmospheric ions observed outside the plume. This indicates the ions inside the plume must have been chemiions emitted by the jet engines. The measured count rate c_m for massive ions observed inside the plume decreases steeply with increasing plume age. Importantly also the ratio $c_m/\Delta T$ markedly decreases with increasing plume age. This indicates that that besides ion dilution by plume dilution an efficient ion removal process must be operative which can most likely be identified as ion-ion recombination. If so, the observed decrease would indicate a mean total negative ion concentration of about $5 \times 10^4\ cm^{-3}$ for a plume age of about one second. This observation of large concentrations of massive ions in the exhaust plume in flight supports strongly the theory of chemi ions growing into an aerosol mode in the exhaust plume of jet aircraft (*Yu and Turco*, 1997). Ion nucleation seems to be indispensable to explain the observed quantities of small volatile aerosol particles with diameters > 5 nm and > 14 nm (*Schröder et al.*, 1998, *Kärcher et al.*, 1998, *Yu et al.*, 1998).

Further experiments measuring massive ions with a substantially increased mass range should be carried out in the future.

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F. Arnold, and J. Curtius, Atmospheric Physics Division, Max-Planck-Institute for Nuclear Physics (MPI-K), P.O. Box 103980, D-69029 Heidelberg, Germany. f.arnold@mpi-hd.mpg.de, j.curtius@mpi-hd.mpg.de

V. Bürger, Greenpeace Germany, Hamburg, Große Elbstr. 39, 22767 Hamburg, Germany, veit.buerger@greenpeace.de

B. Sierau, Institut für Troposphärenforschung (ift), Permoserstr. 15, 04303 Leipzig, Germany, sierau@tropos.de

R. Busen, and U. Schumann, Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Physik der Atmosphäre, Oberpfaffenhofen, D-82234 Weßling, Germany, reinhold.busen@dlr.de, ulrich.schumann@dlr.de

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