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Gas Phase Interactions in the Shuttle Environment
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Abstract

A quadrupole mass spectrometer was flown on STS-4 by the Air Force Geophysics Laboratory. A retarding potential grid located in the ion source distinguished between high and low energy ionic and neutral species in the Shuttle environment. The bulk of the neutral water molecules entering the mass spectrometer appear to be thermal. In contrast, a considerable fraction of water ions, which are formed from charge transfer reactions with ambient O³, have energies greater than thermal. The high energy species are attributed to non-reactive collisions between the thermal water ions and the high energy incoming flux of ambient neutrals. The energy distributions of the ions are affected more by these interactions because of their greater collision cross sections.

Introduction

A quadrupole mass spectrometer was flown by the Ionospheric Physics Division of ARL on STS-4 in June and July of 1982. This instrument, designed by the late Dr. Rocco Narcisi and coworkers, measured the ionic and neutral constituents in the vicinity of the Shuttle. A retarding potential analyzer was used to differentiate the fraction of each incoming species with energy greater than a certain cutoff energy from the fraction with less energy. The "non-retarded" (NR) intensity of each species was recorded with -10 V on the retarding grid, whereas the "retarded" (R) intensity was recorded with +2.5 V. Thus, the cutoff energy for neutrals was 2.5 eV. For the ionic species, the cutoff energy depended on the ion source potential, and was in the range 0.5 - 1.5 eV.

The original experimental plan was to interpret the R mode intensity of each species as a measure of the ambient concentration and to attribute the difference between the NR and R mode intensities to the thermal or low energy species formed within the Shuttle environment. In a previous paper, we showed that, in the case of the ions, this plan was complicated substantially by reactive and non-reactive scattering processes that occur within the contaminant cloud surrounding the Shuttle. In the present paper, we extend the analysis of the R mode data to the neutral species in the Shuttle environment.

Figure 1 is a schematic diagram of the internal construction of the mass spectrometer. The retarding potential analyzer is labelled the energy analysis grid, and is located between the ion source and the entrance aperture to the quadrupole rods. The "non-retarded" (NR) intensity of each ionic and neutral species was recorded with -10 V on this grid. Because the grid was essentially transparent at this voltage, the NR intensity was a measure of the total flux of each species entering the spectrometer. The "retarded" (R) intensity was recorded with +2.5 V on the grid. This voltage was chosen because the motion of the Orbiter through the atmosphere gives ambient species considerable energy with respect to the Orbiter. In electron volts, this energy is approximately equal to the mass number of the species divided by three. Thus, ambient...
Results and Discussion

The mass spectrometer was not operated continuously on STS-4, but was turned on for many five to fifteen minute periods throughout the flight. The instrument collected one complete mass spectrum approximately every second during these periods. One method which has proved useful in reducing this large volume of data is to first separate out the data taken when the RCS engines were firing and then to calculate an average intensity for each ion and neutral species for each data collection period. This method shows nicely how the overall species concentrations changed during the flight.

The results of using this data reduction technique on neutral water vapor are shown in Figure 2. Averaged NR intensities are plotted as the solid line and the averaged R intensities as the dashed line. Around orbits 5, 18 and 32, there are prominent features in the NR water intensity profile where the water concentration rises about an order of magnitude above the adjacent levels. Narcisi et al. have pointed out the striking correlation between the water concentration and the temperature of the mass spectrometer. The peaks in water concentration are due to the increased surface outgassing rate at higher surface temperature.

An unexpected result is the behavior of the R mode water intensity. Throughout most of the flight, the R intensity was nearly equal to the NR intensity. However, at the same times the total water concentration increased due to the temperature changes, the R mode intensity dropped dramatically to as much as three orders of magnitude below the NR signal. In the water data, this behavior is seen most clearly at orbit 32.

The orbit averages of the neutral NR and R mode mass 17 signals are shown in Figure 3. Because the mass 17 signal is almost entirely due to OH produced from dissociative ionization of water in the ion source, it shows the same behavior as the mass 18 parent water signal. The three large peaks in the NR signal correspond to the water peaks in Figure 2. In addition, the mirror image behavior of the R mode signal is even clearer in the mass 17 data than in the parent water signal.

The final example of the orbit averaged flight histories of neutral NR and R intensities is the mass 16 data shown in Figure 4. Mass 16 ions can be produced in the ion source by ionization of the ambient atomic oxygen and also by dissociative ionization of water. Because of this, the NR and R intensity patterns due to the parent water are somewhat obscured.

We had no influence over the attitude of the Orbiter during the STS-4 flight. Hence, the data in Figures 2-4 were obtained at many different instrument angles of attack (the angle between the centerline of the sensor and the velocity vector). Therefore, we have evaluated how the intensities of the species in Figures 2-4 varied with angle of attack by sorting the data into 15° angle of attack bins and then calculating bin averages.
Figure 5: Angle of attack variation of neutral NR water signal.

Figure 7: Angle of attack variation of neutral R water signal.

Figure 5 shows that there is virtually no variation in NR water intensity with angle of attack. Because there is very little ambient water at Shuttle altitudes, the only source of water in the Shuttle environment is outgassing of the Shuttle surfaces. The water seen by the mass spectrometer may be directed outgassing flux from the surfaces or may come from a cloud that travels with the Shuttle. The flat angle of attack curve is consistent with either explanation.

For comparison, the angle of attack variation in the atomic oxygen signal is plotted in Figure 6. In the first 45°, the intensity of the atomic oxygen falls off by approximately three orders of magnitude and then flattens out into a long tail that extends to 180°. The large signals near ram are due to ambient atomic oxygen and the smaller signals at higher attack angles are due to dissociative ionization of water.

The data in Figure 6 make it clear why the flight history of atomic oxygen in Figure 4 is so different from that of water. The orbits showing the highest intensity of atomic oxygen were taken with the instrument in ram. These large signals are due to ambient atomic oxygen. When the instrument was out of ram, the signal was much lower, and was due to dissociative ionization of water. These lower signals are more characteristic of the water behavior. This is particularly evident at orbit 32 where the mass 16 NR and R signals show the same mirror image shape as the parent water.

Figure 2 shows that the R mode water intensity was nearly equal to the NR intensity throughout most of the flight. This is reflected in Figure 7, where the angle of attack variation of the R mode water signal is plotted. The retarded water signal is as independent of angle of attack as the NR signal. The large differences between the NR and R
signals at orbits 5, 18 and 32 have been averaged out by the sorting procedure.

As mentioned above, we intended to interpret the R mode intensity as a measure of the amount of high kinetic energy species entering the mass spectrometer. The data in Figure 7 seem to indicate that the R mode of this high energy water gets into the instrument when it is pointed into wake as when it is in ram.

It is difficult to explain the apparent detection of high energy water in wake. In a previous paper, we discussed a number of mechanisms that could give rise to energetic water ions in the Shuttle environment. The most important of these is collisional scattering between the ambient species and the outgassing water ions that are formed from charge transfer reactions. Similar backscattering could contribute to a flux of high energy neutral water molecules. However, this would be a directed flux moving in the same direction as the ambient species. Because of the position of the mass spectrometer in the payload bay, these high energy water ions that would prevent this directed flux of molecules from reaching the mass spectrometer in the wake orientation. Even if they are formed in collisions, there is no way that the mass spectrometer could sample these high energy water molecules when it is in wake.

At this time, we must conclude that the apparent high energy neutral water flux detected in wake is likely due to a difference between the effective retarding potential felt by the ions and the potential applied to the retarding grid. However, the mirror image behavior of the NR and R water signals at orbits 5, 18 and 32 indicates that the instrument was not equally affected by this difference at all times during the flight. In particular, it is worth comparing orbits 30-35 to orbits 65-75. In all of these orbits, the Shuttle was in a tail-to-sun orientation with the attitude that gave an attack angle of 90° ± 20°.

Despite the common attitude, the instrument behaved very differently in the two periods. There is a three order of magnitude difference between the NR and R water signals in orbits 30-35, but less than a factor of two difference during orbits 65-75.

At an attack angle of 90°, ambient-contaminant scattering should direct very few high energy water molecules into the mass spectrometer sampling orifice. The large difference between the NR and R signals at orbits 30-35 is consistent with little high energy water, whereas the factor of two difference at orbits 65-75 is not. Hence, we conclude that the retarding potential analyzer was working properly (i.e. gave reasonable results) during orbits 30-35, but was not working properly during orbits 65-75. Similar comparisons of attitude to the rest of the data in Figures 2 and 3 suggest further that the retarding grid worked properly only during the times that the water vapor pressure and the temperature were high.

The apparent anomalous behavior of the retarding potential analyzer may be due to so-called "contact potentials." It is commonly observed in high vacuum ion and electron beam apparatus that the effective potential felt by a charged particle passing through a biased grid may be as much as several volts different from the applied voltage. Empirical laboratory experience suggests that the effect is due to adsorbed layers of gas on the grid surfaces. The effective potential of the grid depends strongly on the pressure and composition of the gas in which the grid is immersed.

The effects of adsorbed gases on the electrical properties of metal surfaces have been studied in ultra-high vacuum experiments with single crystal metal surfaces. The adsorbed gas creates an electrical double layer which changes the effective work function of the metal. The change in the work function is equal in magnitude and opposite in sign to the change in the surface potential. The magnitude and sign of this effect vary with the type of adsorbed species, the type of metal, the crystal plane of the metal and the degree of surface coverage. Nevertheless, the trend toward higher work functions with greater surface coverage. This trend generally applies to both adsorbed water and oxygen. As the work function increases, the surface potential becomes more negative, and the effective potential between the metal surface and a reference electrode is reduced.

It is difficult to apply the results of surface potential studies in the controlled environment of an ultra-high vacuum chamber to the relatively uncontrolled environment of the mass spectrometer ion source. The ion source surfaces are made of polycrystalline rather than single crystal metals. Further, the various surfaces may have different temperatures and surface coverages.

The retarding potential analyzer data appear to be valid when both the total water vapor pressure and the mass spectrometer temperature were high. The amount of a surface covered by gas phase molecules is governed by the kinetics of both adsorption and desorption. Despite the increased gas phase water vapor concentration during the periods of valid retarding grid data, the increased temperature may have warmed the grid sufficiently to decrease the surface coverage of water.

The trends described above offer a qualitatively consistent explanation of the neutral mode data. When the temperature was low, the retarding grid was covered by a large amount of water which caused the effective voltage to be considerably lower then the applied voltage. Low energy water molecules were then able to pass through the retarding grid even during the R mode measurements, leading to the near equality of the NR and R intensities. Conversely, at higher temperatures, the water was driven off the surface of the retarding grid and the effective potential rose closer to the applied potential. The low energy water molecules were stopped by the grid during the R mode measurements, and the difference between the NR and R intensities was large.

If we restrict our attention to orbits 4-8, 15-20 and 30-35, the periods when the retarding potential analyzer appears to have provided valid data, we may draw some qualitative conclusions about the gas phase interactions that occur in the Shuttle environment. During these periods, the R mode water intensity was as much as three orders of magnitude lower than the NR mode intensity; at least 99% of the water molecules entering the mass spectrometer had energy less than the effective potential on the retarding grid.

It is not possible to determine what the actual effective potential on the retarding grid. The applied voltage on the grid for all the R mode measurements was +2.5 V. With this
applied voltage, the effective voltage varied from
a value that allowed passage of most of the water
molecules to a value that stopped almost all of
them. Since the temperature changes that caused
the changes in effective voltage were rather small
(varying from 5 to 25°C), we expect that rather
small changes in the effective voltage caused the
very large changes in the NR/R water signal inten-
sity ratio. This suggests that the energy distrib-
ution of the water molecules was narrow and that
the effective voltage moved from approximately zero
to a slightly positive value. The data are con-
istent with the majority of the neutral water
being thermal.

We cannot rule out the possibility that a cer-
tain fraction of the neutral water molecules had
energy higher than thermal. The energetic com-
ponent can be detected by the mass spectrometer only
when it is in ram. Unfortunately, no neutral ram
data was taken during the three periods outlined
above.

Throughout the STS-4 flight, the mass spec-
trometer was commanded to switch between ion and
neutral mode data frequently. Accordingly, we have
both ion and neutral data from approximately the
same times in the flight. The flight histories of
orbit averaged ion intensities show that the energy
distributions of the ions are substantially dif-
ferent from those of the neutrals. As an example,
Figure 8 plots the orbit averages of NR and R mode
H2O+ intensity for orbits 0 - 40. This portion of
the flight contains the periods when the retarding
grid was working properly according to the neutral
data.

The variations in H2O+ signal intensity are
due almost entirely to angle of attack changes.
Both the ambient H2O and the contaminant H2O+ ions
have very strong angle of attack dependences when
plotted as in Figure 6-7 despite the fact that the
H2O+ ions are formed from neutral water molecules
by charge transfer reactions.

In contrast to the neutral data, the NR and R
intensities of the water ions are approximately
equal to each other at all times during orbits
0 - 40. In particular, the R intensity is within
a factor of two or three of the NR intensity for
all points between orbits 16 and 18. During this
time, the neutral data showed a two order of mag-
nitude difference between NR and R intensity. We
take this as evidence that a larger fraction of
the water ions detected by the mass spectrometer
may have had energy exceeding the effective poten-
tial of the retarding grid.

Ion-dipole and ion-induced dipole forces gen-
erally increase ion-neutral collision cross sections
by an order of magnitude over the cross sections
for comparable neutral-neutral interactions.
Because of this, the water ions in the outgassing
flow of water from the Shuttle have a much greater
chance of colliding with an incoming ambient neutral
species. These collisions are a likely source of
the high energy species detected by the mass spec-
trometer.

Conclusions

The retarding potential analyses made by the
AFGL quadrupole mass spectrometer aboard STS-4
may have been strongly affected by contact poten-
tials. The effective potential felt by the ions
appears to have been as much as several volts less
than the applied voltage. The difference between
the applied voltage and the effective potential
correlates well with the gas phase concentration of
water and with the temperature of the instrument.

Variations in the amount of the grid surface
covered by water molecules may be the cause of the
contact potentials. We propose that the retarding
potential grid gave more valid data at higher tem-
peratures. The increased surface temperature may
have driven off some of the adsorbed water, leading
to lower surface coverage and less difference
between the effective grid potential and the applied
potential. These observations may be important in
the design of future retarding potential analyzers
for use in the Shuttle environment.

Despite the variations in the effective retar-
ding grid potential, there were times during the
flight when a consistent interpretation of the data
was possible. At these times, greater than 99% of
the neutral water molecules entering the mass spect-
rometer had energies less than the effective poten-
tial on the grid. This is consistent with the
water being thermal. In contrast, the water ions
may have had a substantial energetic fraction.

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